Cyclometalating organic ligand with Iridium center toward dramatically improved photovoltaic performance in organic solar cells

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Characterization

General measurements and characterization

^{1}H NMR spectra were recorded on a Bruker DMX-500 spectrometer in deuterochloroform using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard. Mass spectra were recorded using a Bruker Autoflex matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF). Elemental analysis (EA) of C, H, N, and S were performed on a Vario EL III micro analyzer. Absorption spectra: Ultraviolet-visible (UV-Vis) absorption spectra of dilute solution ($1*10^{-5}$ M) in chlorobenzene and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer, and photoluminescence (PL) spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer. PL of TBzIr in solution and film was excited at 440 nm, TBz at 400 and 380 nm, respectively. The transient lifetime was carried out using Edinburgh FLS-980 Instruments in chlorobenzene of N_2 degassed solution and thin film state. PL decay for TBzIr was excited at 470 nm and taken at 800 nm, TBz-S excited at 400 nm, taken at 510 nm, TBz-F excited at 375 nm, taken at 550 nm. Thermal analysis: Thermal gravimetric analysis (TGA) was undertaken with a METTLER TOLEDO TGA2 instrument. The thermal stability of the samples was determined by measuring their weight loss at a heating rate of 10^oC min^{-1} from 25 to 500^oC using 3 mg sample under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit within the temperature range of 50 to 300^oC, heating at a rate of 10^oC min^{-1} under N_2 atmosphere. Absorption spectra: Ultraviolet-visible (UV-Vis) absorption spectra of solution in chlorobenzene and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. Cyclic voltametry (CV): The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate ($n\text{-}Bu_4NPF_6$) at a potential scan rate of 100 mV s^{-1}. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The polymer sample was coated on the platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc^+/Fc) as internal standard as recommended by IUPAC (the vacuum energy level: -4.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of $E_{HOMO} = -(E_{onset}(ox) + 4.8)$ eV, and LUMO energy levels were deduced from the optical band gap (E_g) values and HOMO levels. Photoluminescence quenching measurement: Photoluminescence (PL) spectra were carried out using Hitachi F-4600 fluorescence spectrophotometer. The samples were prepared in the same condition with device fabricating. Atomic force microscopy (AFM): Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.

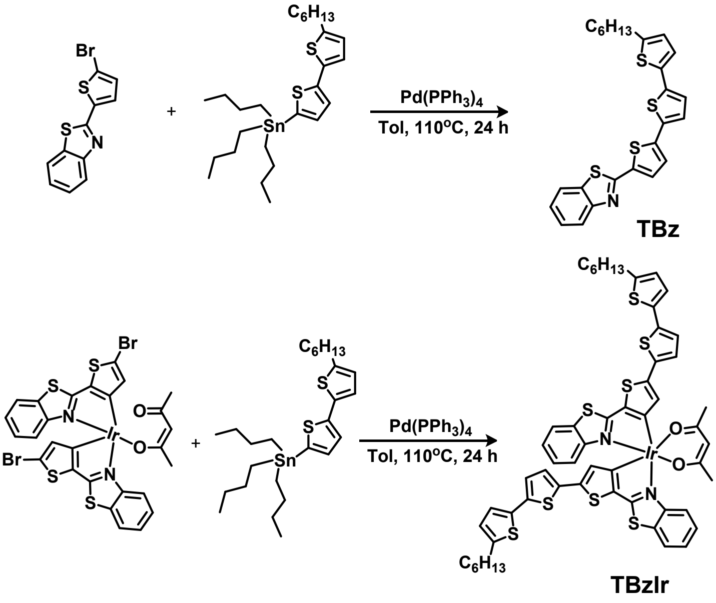
Materials and synthetic procedures

Materials:

All solvents were purchased from Sigma Aldrich Co., Energy Chemical Co., Alfa Aesar without further purification. Tributyl(5'-hexyl-[2,2'-bithiophen]-5-yl)stannane were purchased from Suna Tech. The Ir complex was synthesized according to reported literatures. The general synthetic route towards Bis(2-(5''-hexyl-[2,2':5',2''-terthiophen]-5-yl)benzo[*d*]thiazole)iridium(III)(acetylacetonate) (TBzIr), TBz is outlined in Scheme 1 with detailed synthetic procedures given by TBzIr.

Synthesis of TBzIr: Bis [2-(5-bromothiophen-2-yl)benzo[*d*]thiazole]iridium(III)(acetylacetonate) $(BrBz)_2Iracac$ (300 mg, 0.34 mmol), tributyl(5′-hexyl-[2,2′-bithiophen]-5-yl)stannane (403 mg, 0.75 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol) were stirred in anhydrous toluene(15 mL) at 110°C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was extracted with CH_2Cl_2:PE(2:1), washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (eluent: dichloromethane) and washed with MeOH to yield the title compound as red solid TBzIr (215 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.38 (dt, *J* = 21.3, 7.0 Hz, 4H), 6.94 (d, *J* = 3.8 Hz, 2H), 6.88 (t, *J* = 3.1 Hz, 4H), 6.62 (d, *J* = 3.5 Hz, 2H), 6.25 (s, 2H), 5.18 (s, 1H), 2.75 (t, *J* = 7.6 Hz, 4H), 1.82 (s, 6H), 1.70-1.60 (m, 4H), 1.40-1.24 (m, 13H), 0.88 (t, *J* = 6.8 Hz, 6H). MALDI-TOF (m/z): M^+ calculated at 1220.13, found at 1219.44; Anal. Calcd for $C_{61}H_{51}IrN_2O_2S_{10}$: C 54.11, H 4.21, N 2.29, S 21.01%; found: C 54.39, H 4.26, N 2.20, S 20.74%.

Synthesis of TBz: 2-(5-bromothiophen-2-yl)benzo[*d*]thiazole (100 mg, 0.34 mmol), tributyl(5′-hexyl-[2,2′-bithiophen]-5-yl)stannane (200 mg, 0.37 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.010 mmol) were stirred in anhydrous toluene(10 mL) at 110°C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the precipitate was extracted with CH_2Cl_2, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (eluent: dichloromethane) and washed with MeOH to yield the title compound as yellow solid TBz (127 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.02 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 3.8 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 10.3, 3.8 Hz, 2H), 7.02 (dd, *J* = 7.9, 3.6 Hz, 2H), 6.70 (d, *J* = 3.2 Hz, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 1.77-1.67 (m, 2H), 1.50-1.36 (m, 4H), 0.92 (t, *J* = 6.5 Hz, 3H). MALDI-TOF (m/z): M^+ calculated at 465.07, found at 464.66; Anal. Calcd for $C_{25}H_{23}NS_4$: C 64.47, H 4.98, N 3.01, S 27.54%; found: C 64.85, H 4.2, N 2.88, S 28.01%.



Scheme S1. Synthetic routes of TBz and TBzIr.

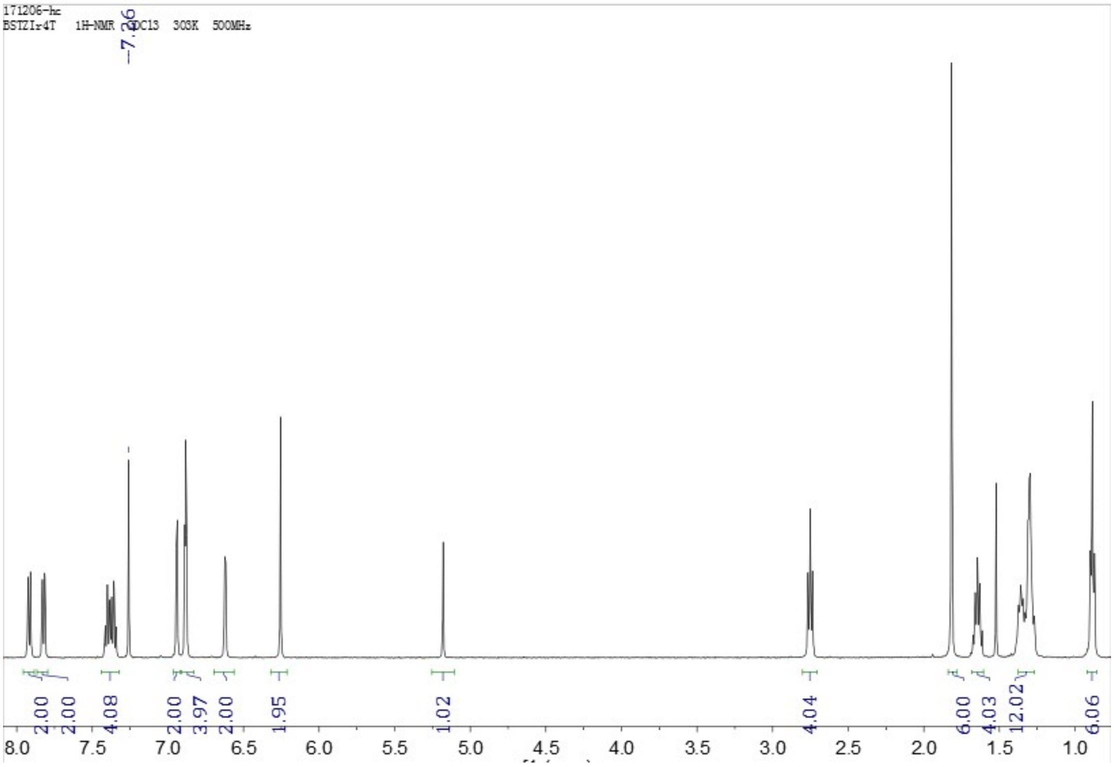


Figure S1. a) ¹H NMR Spectra: TbzIr,

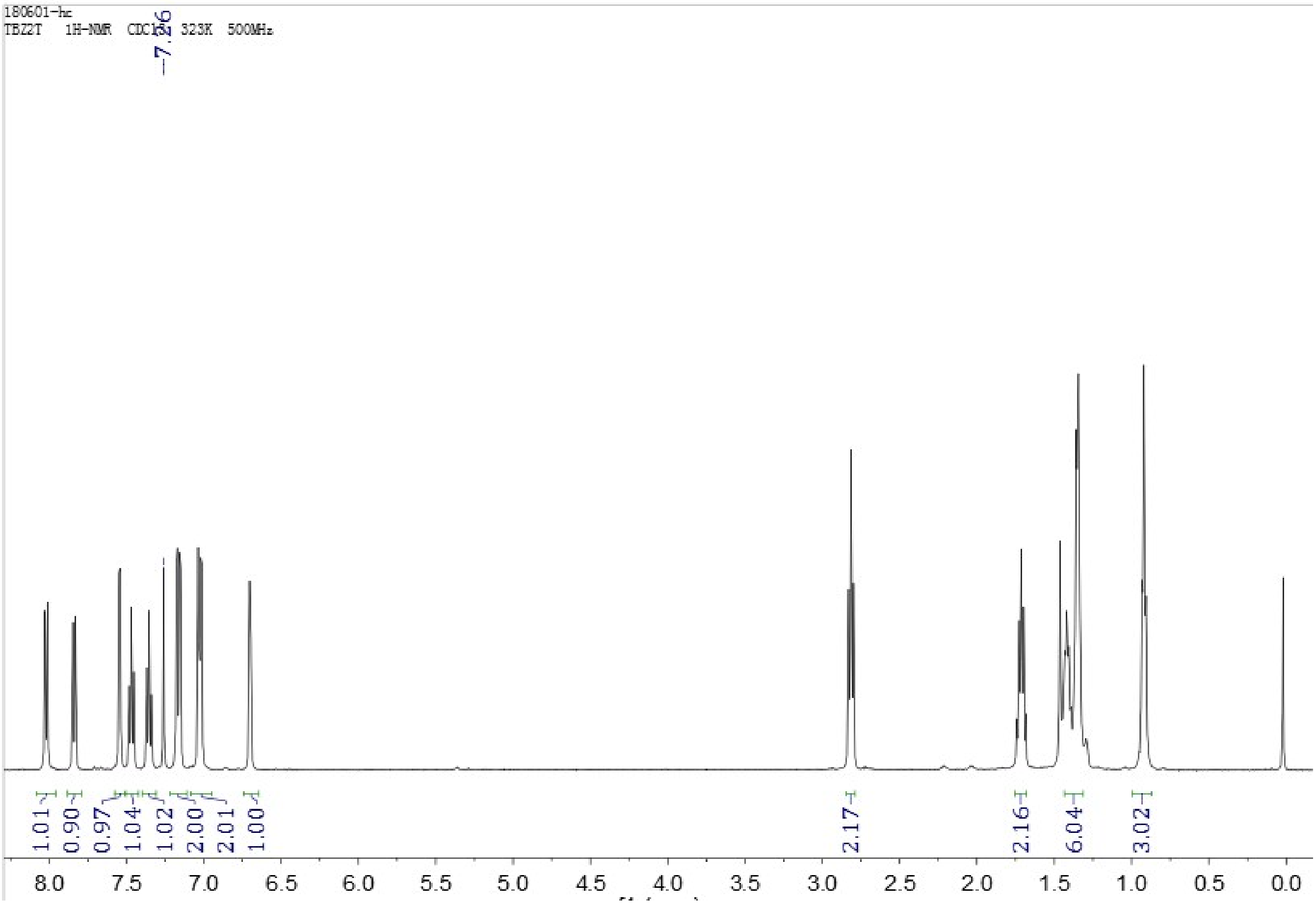
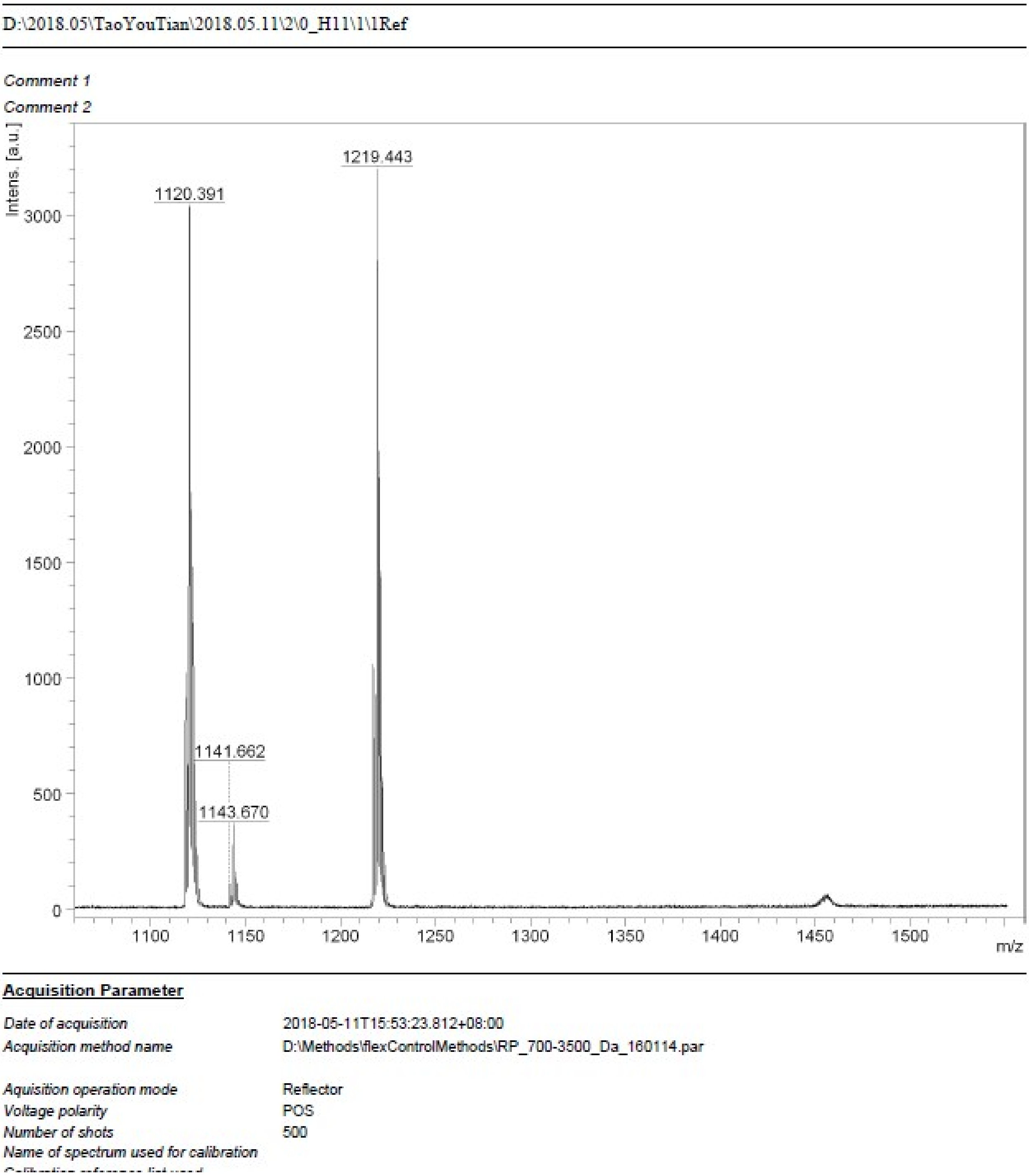


Figure S1. b) ¹H NMR Spectra: TBz.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Comment 1

Comment 2

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Name of spectrum used for calibration	

Figure S2. The mass spectrometry of TBzIr.

Thermal properties

The thermal stability investigated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were shown in Figure S3. The thermal properties of the two were determined by TGA under N_2 flow.

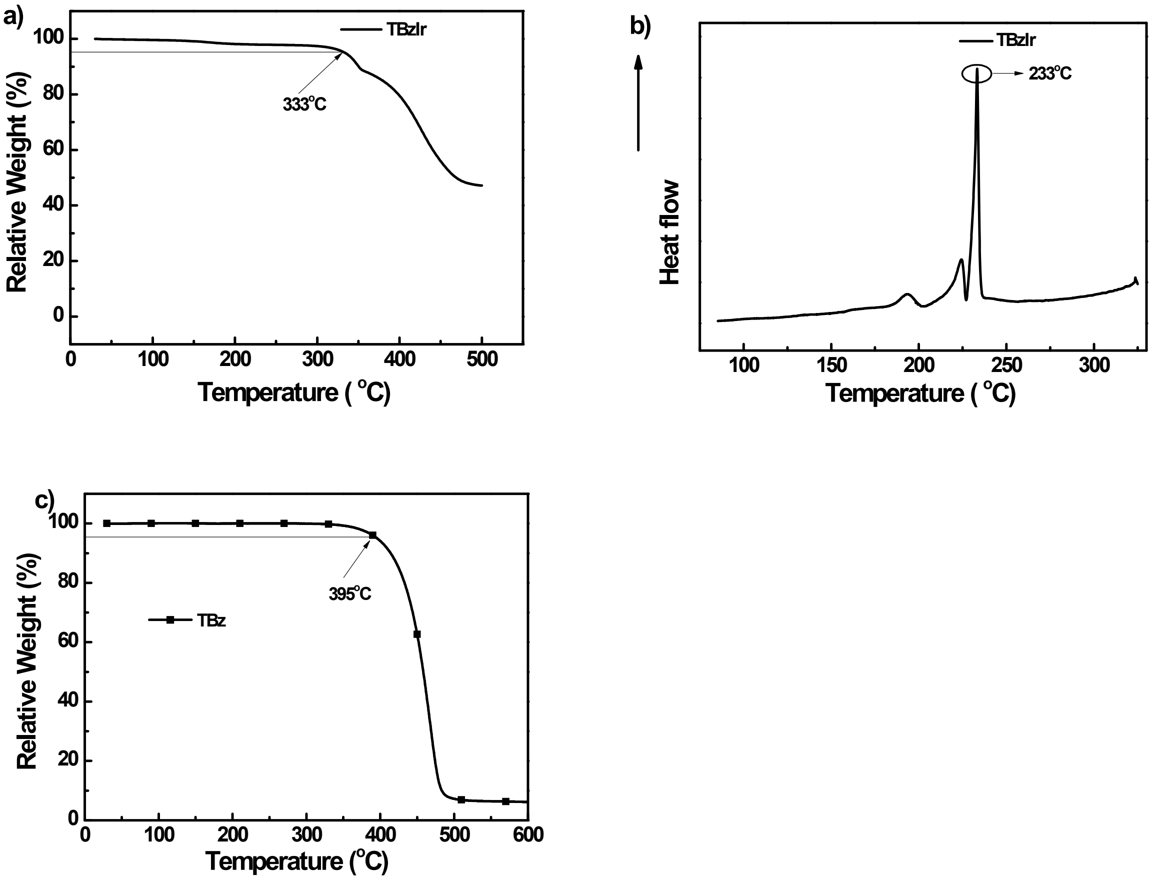

Figure S3. a) TGA and b) DSC curves for Compound TbzIr, and c) TGA curves for Compound TBz.

Absorption spectra

Ultraviolet-visible (UV-Vis) absorption spectra of dilute solution ($1*10^{-5}$ M) in chlorobenzene and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer.

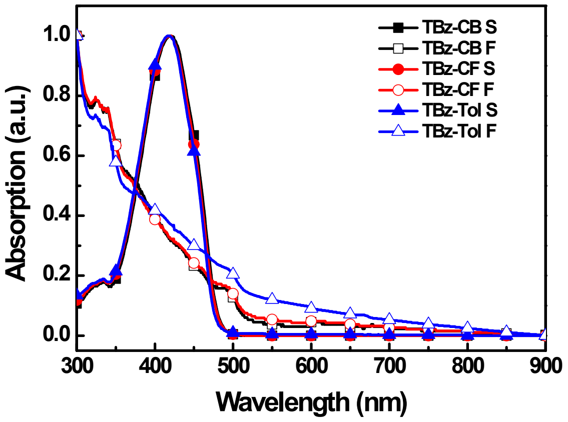

Figure S4. Normalized UV-Vis absorption spectra in various solution (S, 1*10-5 M) and the corresponding spin-coated film (F).

Cyclic voltammetry

The electrochemical properties for TBzIr and TBz were conducted by cyclic voltammetry (CV) measurements using ferrocene as the internal standard.

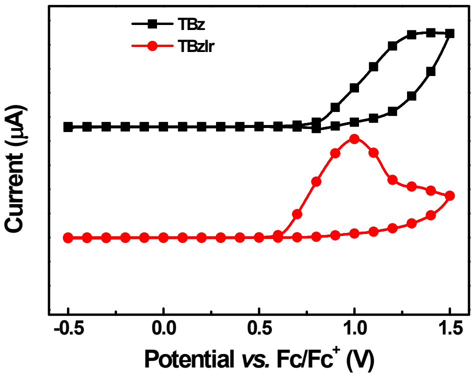

Figure S5**.** Cyclic voltammograms of TBzIr and TBz in CH_3CN for oxidation scan (*vs*. Fc/Fc^+), HOMO values were included.

Table S1. Physical properties of compound TBzIr and TB

Compound	λ_{abs}^{a} [nm]	λ_{abs}^{b} [nm]	λ_{PL}^{a} [nm]	λ_{PL}^{b} [nm]	E_g^{c} [eV]	τ^{b} (ns)	τ_1^{b} (ns)/(%)	τ_2^{b} (ns)/(%)	τ_3^{b} (ns)/(%)	HOMO/LUMO^{d} [eV]	T_d^{e} [°C]
TBzIr	457,531	474,545	510,570,815	508,590,832	2.09	139.0	9.2/15	59.4/51	315.4/34	-5.42/-3.33	333
TBz	416	273,319	505	560	2.36	0.96	0.38/36	1.3/64	-	-5.61/-3.25	395

a Measured in CB solution at room temperature. b Measured in film state at room temperature. c Optical bandgap (Eg) calculated from the absorption edge of film state UV-Vis spectra. d HOMO measured from CV, LUMO calculated from the difference between HOMO and Eg. e Decomposition temperature at 5% weight loss

OSC devices fabrication and measurement

Indium tin oxide (ITO) glass substrates were cleaned successively with detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 10 minutes each, followed by drying at 120°C for 30 minutes and treatment with UV-ozone for 25 minutes. PEDOT:PSS (Baytron P Al 4083) was then spin-coated on the ITO glass substrates at 5000 rpm for 40 seconds and baked at 125°C for 30 minutes to give a thickness of 40 nm. The active layer was spin-coated on top of the PEDOT:PSS layer using a solution of TBzIr (10 mg/mL) and $PC_{71}BM$ (10 mg/mL) in CB. After that, methanol solution of PDINO at a concentration of 1.0 mg mL^{-1} was deposited upon the active layer at 3000 rpm to afford a PDINO cathode buffer layer with thickness of *ca.* 10 nm. An aluminum (approx. 100 nm) layer was subsequently evaporated onto the surface of the PDINO layer under vacuum (approx. 8×10^{-5} Pa to form the negative electrode. The active area of the device was detecting as 5 mm^2 with NIKON LV100ND optical microscope. The current density-voltage (*J-V*) characteristics of the PSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a Newport Oriel 91150V reference cell. The PCE results in the manuscript were obtained using more than 15 individual devices fabricated under the same conditions. The external quantum efficiency (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Table S2. Photovoltaic performance of the OSCs based on TBzIr:$PC_{71}BM$ and TBz:$PC_{71}BM$.

Donor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max}/PCE_{avr}[a] (%)
TBzIr[b]	0.91±0.01 (0.92)	8.84±0.07 (8.91)	45±2 (47)	3.81/3.66

TBzIr[c]	0.92±0.00 (0.92)	6.05±0.30 (6.35)	34±0 (34)	2.00/1.92
TBz[c]	0.044 ±0.01 (0.045)	0.11±0.02 (0.13)	32±0.3 (32.3)	0.002/0.0017

[a] The maximum PCE and average values obtained from over 10 devices. [b] Cathode interface material based on PDINO. [c] Cathode interface material based on Ca.

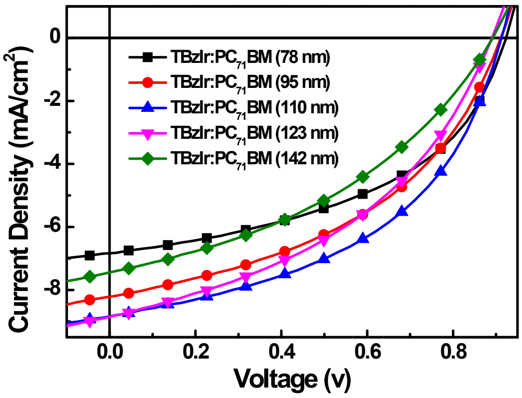

Figure S6. *J-V* curves of the optimal binary devices.

Table S2. Photovoltaic performance of the PSCs based on TBzIr:PC$_{71}$BM (1:1, w/w) with different thickness under the illumination of AM 1.5 G (100 mW cm^2).

Thickness	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE$_{max}$/PCE$_{avr}$^{a} (%)
78 nm	0.91±0.01 (0.92)	6.83±0.32 (7.15)	46±1 (47)	3.10 / 2.91
95 nm	0.89±0.03 (0.92)	8.45±0.66 (9.11)	44±2 (46)	3.54 / 3.33
110 nm	0.91±0.01 (0.92)	8.84±0.07 (8.91)	45±2 (47)	3.81 / 3.66
123 nm	0.88±0.01 (0.89)	8.38±0.42 (8.80)	41±1 (42)	3.28 / 3.08
142 nm	0.86±0.03 (0.89)	7.42±0.42 (7.84)	37±1 (38)	2.62 / 2.46

[a] The maximum PCE and average values obtained from over 10 devices.

Hole/electron-only devices fabrication and hole/electron mobility measurement

Hole mobility and electron mobility were measured using the space charge limited current (SCLC) method. The hole-only device structure for the pristine films of TBzIr and TBz is ITO/PEDOT:PSS/TBzIr or TBz/Au. The hole-only and electron-only device structures for the two blends of TBzIr:PC$_{71}$BM and TBz:PC$_{71}$BM are ITO/PEDOT:PSS/Active layer/Au and ITO/ZnO/Active layer/PDINO/Al, respectively. The hole and electron mobilitiy were calculated by Mott–Gurney equation.[1,2]The thickness of active layers and buffer layers was measured with stylus profiler (KLA Tencor P-7).

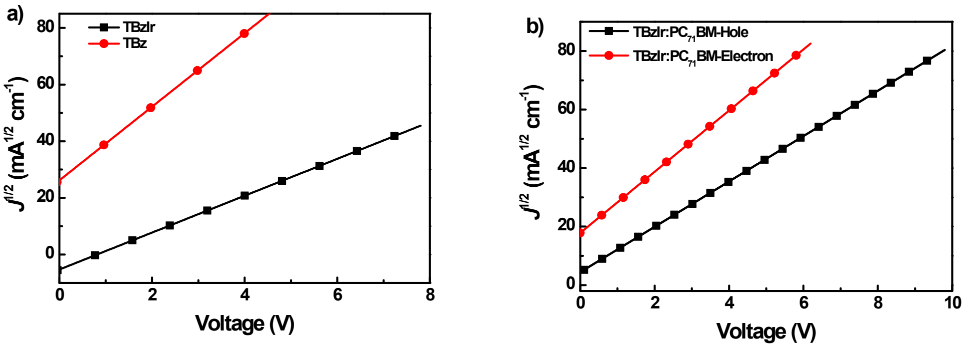

Figure S7. a) $J^{1/2}$-V plots of hole-only devices for the relevant pure compounds, b) Hole-only and Electron-only devices for the relevant compounds.

Photoluminescence

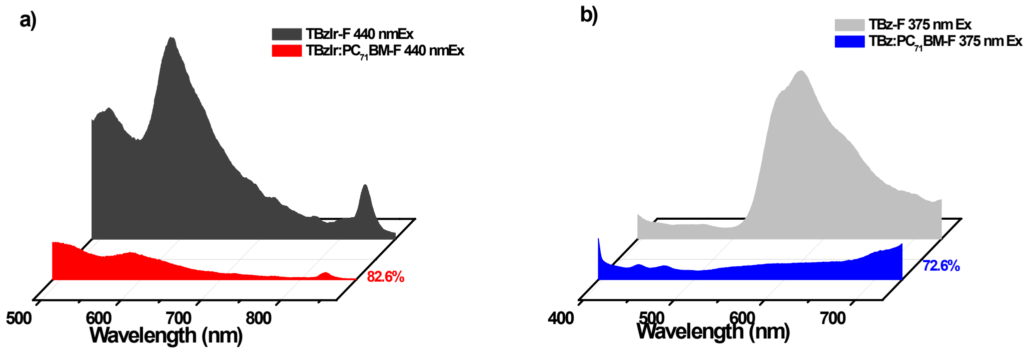

Figure S8. a) the PL spectra of TBzIr and the related blend films (excited at 440 nm), b) the PL spectra of TBz blend films (excited at 375 nm).

Atomic force microscopy

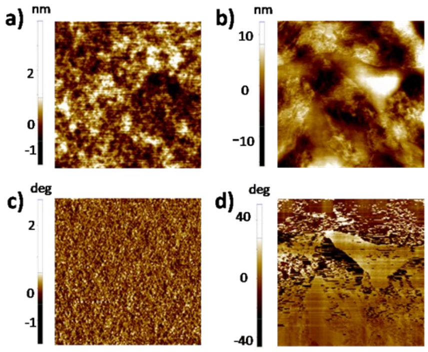

Figure S9. AFM height (a, b) and phase (c, d) images (3*3 μm) for active layers of TBzIr:PC$_{71}$BM (a, c) and TBz:PC$_{71}$BM (b, d) bended films

References

1. P. W. M. Blom, J. M. Jong, M. G. Munster, *Phys. Rev. B*, 1997, **55**, 656-659.
2. G. G. Malliaras, J. R. Salem, P. J. Brock, C. Scott, *Phys. Rev. B.*, 1998, **58**, 13411-13414.