Supplementary material for:

Significant differences in photophysical and photovoltaic properties of flexible chain terminated homoleptic tris-Ir(III) complexes

Duoquan You,[a#] Tianjian Yang,[a#] Aihua Zhou,[a#] Siyuan Li,[b] Kaiqi Lv,[a] Huili Ma,[a] Hongliang Zhong [b] and Youtian Tao*[a]

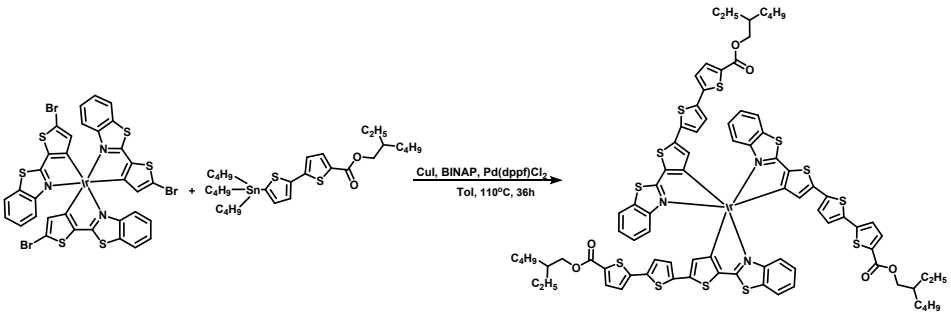
[a.] *Key Lab for Flexible Electronics and Institute of Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211816, China*

[b.] *School of Chemistry and Chemical Engineering, Shanghai Key Lab of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, P. R. China*

E-mail: iamyttao@njtech.edu.cn (Y. Tao)

# These authors contributed equally to this work

Synthesis of ATBz3Ir



Scheme S1. Synthetic routes for ATBz3Ir.

Fabrication of OSC devices

OSCs with conventional structure of ITO/PEDOT:PSS/active layer/PDINN/Ag were 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 40 seconds and baked at 150°C for 15 min in air to give a film thickness around 30 nm. After that, the ATBz3Ir:Y6 blend solution was dissolved in CF in a glove box at a weight ratio of 1:1, and the total solution concentration was 20 mg/mL and dissolved at 50 °C for 1 hour.

After cooling to room temperature, spin-coating on the PEDOT:PSS at 2000 rpm. For PM6:Y6, the blend solution was dissolved in CF in a glove box with D:A of 1:1.2 and total solution concentration of 18 mg/mL, then dissolved at 50 °C for 1 hour. After cooling to room temperature, add a 0.5% volume of 1-CN to the solution. The prepared solution was then coated on PEDOT:PSS at 3000 rpm, and placed on a hot table of 90 °C for thermal annealing for 10 minutes. For ternary devices, the optimal PM6:third component:Y6 ratio is 0.95:0.05:1.2, total concentration of 20 mg/mL, CF solvent with 0.5%vol 1-CN additive. The cathode buffer layers of PDINN were spin-coated at 3500 rpm for 60 seconds. Finally, Ag with thickness of 100 nm were evaporated under vacuum (≈10^{-5} Pa) as the back electrode. As for the hole-only and electron-only devices for SCLC measurements, the device structure of ITO/PEDOT:PSS/active layer/Au were used to measure the hole mobility and the electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/Al. And the processing details of blend films were same with the fabricating conditions of OSCs. Hole and electron mobility were measured using the space charge limited current (SCLC) method based on Mott-Gurney equation.[1,2]

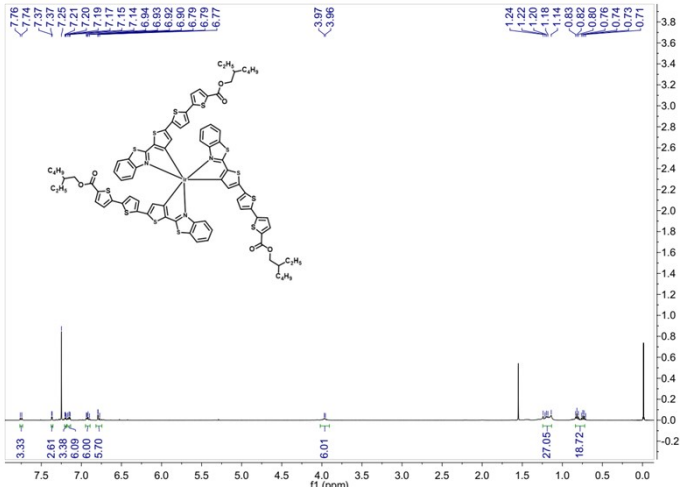


Fig. S1. ^{1}H NMR spectrum of ATBz3Ir.

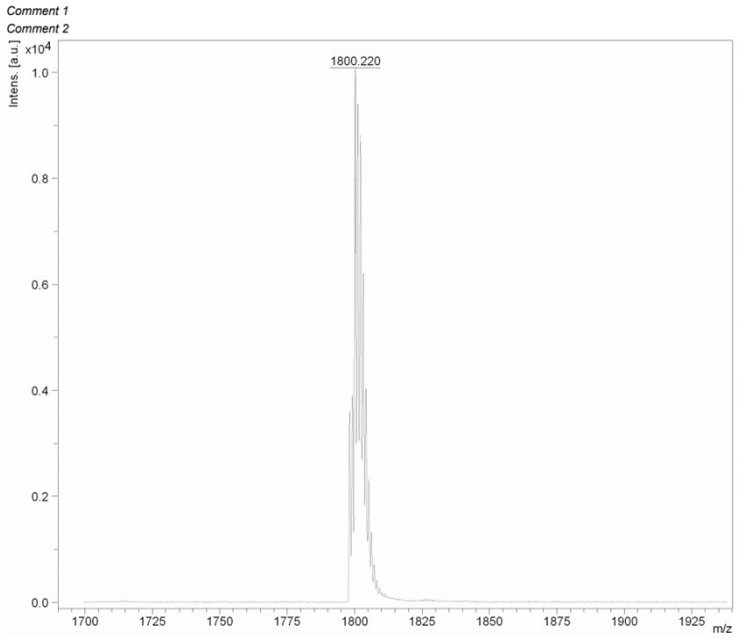


Fig. S2. MALDI-TOF mass spectrum of ATBz3Ir.

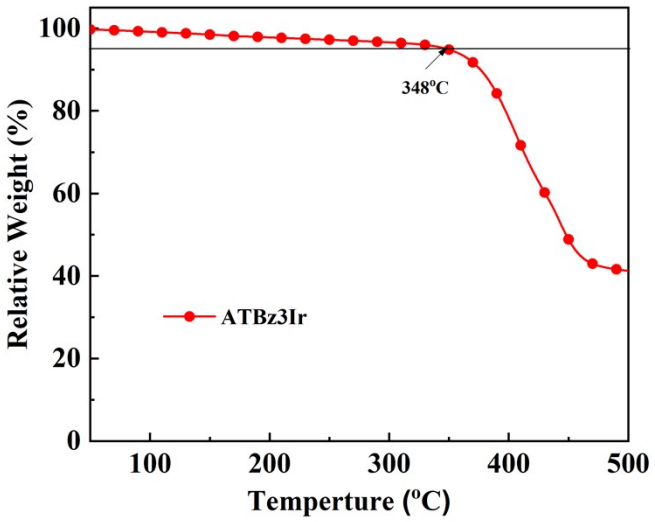


Fig. S3. TGA curves for compounds of (a) ATBz3Ir.

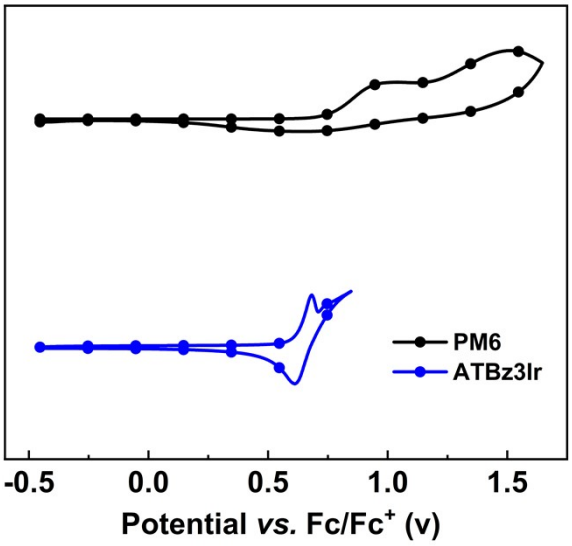


Fig. S4 Oxidation curves of PM6 and ATBz3Ir from CV characterizations.

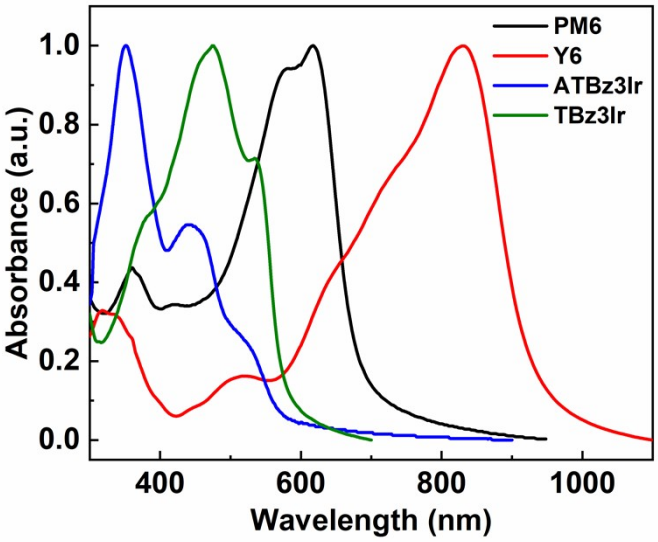


Fig. S5 Normalized UV-Vis absorption spectra of PM6, Y6, ATBz3Ir and TBz3Ir in neat films.

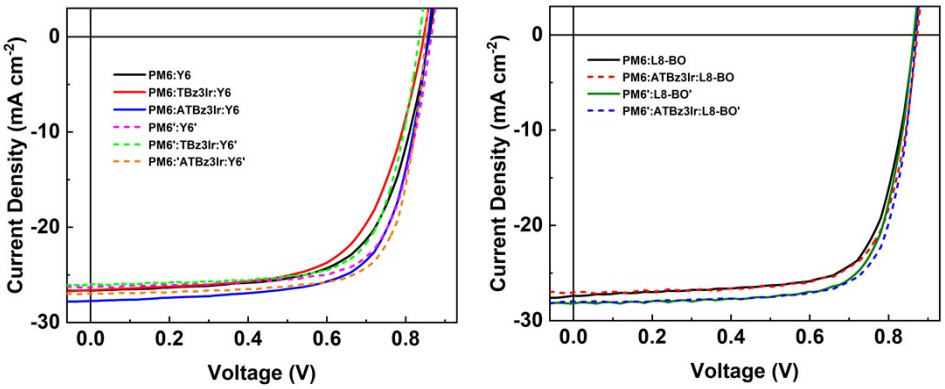


Fig. S6 *J-V* curves of binary and ternary devices based on the corresponding blended films from different batches of active layer materials.

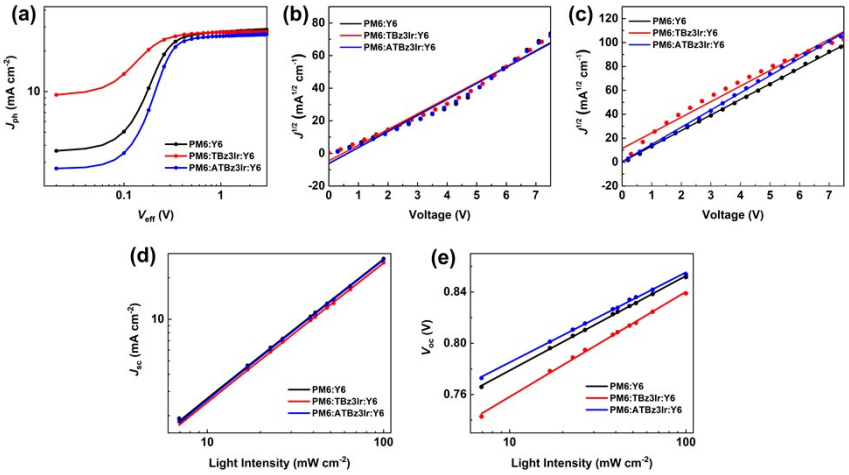


Fig. S7 (a) J_{ph} *vs.* V_{eff} curves, *J-V* curves fitted by SCLC method for (b) hole-only and (c) electron-only devices, (d) J_{SC} and (e) V_{OC} *vs.* light intensity on charge dynamics based on corresponding blend films.

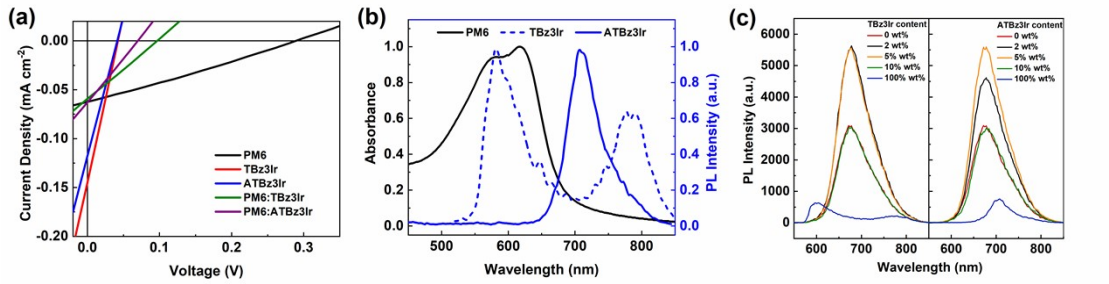


Fig. S8 (a) *J-V* curves of devices with PM6, ATBz3Ir and PM6:ATBz3Ir (1:1) as active layers. (b) UV-Vis absorption spectra of PM6 neat film and PL spectra of ATBz3Ir neat film. (c) PL spectra of PM6, PM6:ATBz3Ir (0.95:0.05) and ATBz3Ir in film state,

PM6:ATBz3Ir blends showed increased intensity for PM6 emission when with 5 wt% of ATBz3Ir, while the emission characteristics for ATBz3Ir disappeared, this inferred potential energy transfer from ATBz3Ir to PM6.

Table S1 Photovoltaic parameters of ternary OSCs based on different ratio of ATBz3Ir

PM6:ATBz3Ir:Y6	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF	PCE [%]	PCE [%]
0.98:0.02:1.2	0.86	27.27	0.67	15.68	15.41
0.95:0.05:1.2	0.86	27.75	0.70	16.50	16.37
0.92:0.08:1.2	0.86	27.12	0.69	16.02	15.89
0.9:0.1:1.2	0.85	27.42	0.68	15.74	15.57
0.85:0.15:1.2	0.86	26.10	0.68	15.06	14.97
0.8:0.2:1.2	0.86	26.22	0.66	14.96	14.75
0.7:0.3:1.2	0.86	24.61	0.66	14.04	13.96

Table S2. Photovoltaic parameters of devices based on L8-BO as acceptors.

Active Layer	V_{oc} [V]	J_{sc} [mA/cm^2]	FF	PCE [%]	PCE^{ave} [%]
PM6:L8-BO	0.87	27.39	0.72	17.13	17.02
PM6:ATBz3Ir:L8-BO	0.87	28.21	0.74	18.07	17.95
PM6':L8-BO'	0.87	27.03	0.73	17.25	17.10
PM6':ATBz3Ir:L8-BO'	0.87	27.98	0.75	18.37	18.22

Table S3 Key parameters from characterizations of carrier dynamic

Active Layer	$P_{(E,T)}$ [%]	α	n	μ_h [cm^2 V^{-1} s^{-1}]	μ_e [cm^2 V^{-1} s^{-1}]
PM6:Y6	94.6	0.995	1.25	3.84×10^{-4}	6.57×10^{-4}
PM6:TBz3Ir:Y6	91.5	0.993	1.38	3.59×10^{-4}	6.59×10^{-4}
PM6:ATBz3Ir:Y6	96.5	0.997	1.19	3.76×10^{-4}	8.03×10^{-4}

Table S4. Detailed parameters for contact angle measurements.

	θ_{water} [°]	θ_{oil} [°]	surface energies [mJ m^{-2}]
PM6	101.9	59.5	28.46
TBz3Ir	97.2	25.8	44.70
ATBz3Ir	96.5	27.9	43.95

Y6	94.7	39.9	39.03

Reference

1 P. W. M. Blom, J. M. Jong, M. G. Munster, *Phys. Rev*.,1997, **B 55**, R656–R659.

2 G. G. Malliaras, J. R. Salem, P. J. Brock, C. Scott, *Phys. Rev*., 1998**, B 58**, R13411–R13414