# Supporting information

# Near-infrared cyclometalated iridium(III) complexes with bipolar feature for efficient OLEDs in solution-process

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### Syntheses

Synthesis of methyl 3-(6-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)phenoxy)hexyloxy)picolinate (**compound 3**)

А mixture of 2-(4-(6-bromohexyloxy)phenyl)-5-(4-tert-butylphenyl)-1,3,4oxadiazole (1) (2.20 g, 4.80 mmol), methyl 3-hydroxypicolinate (2) (367 mg, 2.40 mmol), cesium carbonate (7.82 g, 24.00 mmol) and potassium iodide (48 mg, 0.29 mmol) in dry DMF (75 mL) was heated and stirred at 80 °C under nitrogen atmosphere for 24 h. After cooled to RT, the mixture was poured into distilled water (50 mL) and extracted with DCM ( $3 \times 30$  mL). The combined organic layer was dried over MgSO<sub>4</sub> for 2 h and filtered. The filtrate was concentrated by rotary evaporator under reduced pressure. The residue was purified by silica gel column chromatography using DCM/EA (10/1, V/V) as eluent to gain light yellow solid (1.08 g, 85 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 8.29 (d, J = 4.4 Hz, 1H), 8.09-8.06 (m, 4H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.44-7.36 (m, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 4.19-4.01 (m, 4H),3.99(s, 3H) 1.93-1.88 (m, 4H), 1.63 (s, 4H), 1.40(s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$ (ppm): 164.3, 164.3, 164.1, 161.8, 155.8, 155.1, 140.8, 128.6, 127.0, 126.6, 126.0, 121.2, 121.0, 116.2, 114.9, 68.9, 68.1, 68.0, 52.5, 35.0, 31.1, 29.1, 29.0, 28.8, 25.8, 25.6, 25.6, 25.5. MALDI-TOF MS (m/z) for C<sub>31</sub>H<sub>35</sub>N<sub>3</sub>O<sub>5</sub>, Calcd: 529.257; found, 529.219.

Synthesis of 3-(6-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)phenoxy)hexyloxy)picolinic acid (**compound 4 pic-OXD**)

А mixture of methyl 3-(6-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2vl)phenoxy)hexyloxy)picolinate (500 mg, 0.94 mmol), NaOH (5%, 10 mL), ethanol (10 mL) and THF (10 mL) was heated and stirred at 70°C under nitrogen atmosphere for 4 h. After cooled to RT, the mixture was poured into distilled water (50 mL) and HCl solution (2 M) was added (pH = 2). The resulting precipitate was filtered off, washed with water and ethanol to present white powder (267 mg, 55 %).<sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3), \delta(\text{ppm}): 8.22 \text{ (d, } J = 4.4 \text{ Hz}, 1\text{H}), 8.07 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{H}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{Hz}, 4\text{Hz}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{Hz}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{Hz}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{Hz}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}, 4\text{Hz}), 7.57 \text{ (d, } J = 8.6 \text{ Hz}), 7.57 \text{ (d, } J =$ J = 8.6 Hz, 3H), 7.49 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 8.9 Hz, 2H), 4.19 (t, J = 6.4 Hz, 2H), 4.09 (t, J = 6.3 Hz, 2H), 2.01-1.97 (m, 2H), 1.96-1.87 (m, 2H), 1.68-1.61 (m, 5H), 1.39 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ(ppm): 164.3, 164.2, 161.8, 156.8, 156.5, 155.1, 139.2, 129.2, 128.6, 126.6, 126.0, 122.7, 121.2, 116.2, 116.1, 114.9, 69.3, 67.9, 35.08, 31.1, 29.7, 28.9, 28.7, 25.6, 25.5. MALDI-TOF MS (m/z) for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>5</sub>, Calcd: 515.242; found, 516.188.

#### Characterization, device fabrication and measurement

#### Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 10 °C min<sup>-1</sup> on a Perkin-Elmer TGA 7. The

UV/Vis absorption and photoluminescent spectra are measured with a Varian Cray 50 absorption spectrometer and Perkin-Elmer LS50B luminescence spectrometer, respectively. The equation of  $\Phi_s = \Phi_r(\eta_s^2 A_r I_s/\eta_r^2 A_s I_r)$  is used to calculate the fluorescence quantum yield ( $\Phi$ ) using a reference of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> in N<sub>2</sub> atmosphere, where the subscript *s* and *r* represent the sample and reference,  $\eta$  is a refractive index of the solvent, *A* is an absorbance at the given excitation wavelength and *I* is an integrated area of the emission band [1]. Cyclic voltammetry (CV) was performed on a CHI 600E electrochemical work station with a scan rate of 100 mV·S<sup>-1</sup> at room temperature under argon, in which a Pt disk, Pt plate, and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode in n-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) acetonitrile solution, respectively. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured under the same conditions.

#### **Device fabrication and measurement**

The structure of device is ITO/PEDOT:PSS (40 nm)/m-MTDATA:x wt% Ir complexes (40 nm)/TmPyPB(30 nm)/Liq (1 nm)/Al(100 nm) (Device I) and ITO/ PEDOT:PSS (40 nm)/ poly-TPD (30 nm)/ PVK:OXD-7 (70:30): x wt% Ir complexes (45 nm)/TmPyPB (50 nm)/ Liq (1 nm)/ Al (100 nm) (Device II). In Device I, the ITO coated substrate was firstly cleaned respectively with acetone and ethanol in an ultrasonic bath. After treated with UV-ozone for 20 min, the substrate was coated with a layer of PEDOT:PSS for hole injection which was annealed at 120 °C for 10 min. m-MTDATA serves as host as their good hole-electron transporting properties and x wt% represents the doping ratio into m-MTDATA. The emitting layer dissolved

in chlorobenzene was then spin-coated onto the PEDOT:PSS layer. After backing the emitting layer at 50 °C for 10 min, the sample was loaded into a vacuum chamber. The electron transporting layer (TmPyPB), the electron injecting layer (Liq) and Al cathode were consecutively evaporated in the vacuum chamber. The device was sealed with curable UV resin in N<sub>2</sub>-filled glove-box. The EL properties of the devices were measured in ambient air after encapsulation. A PR735 SpectraScan Spectroradiometer (Photo Research) combined with a Keithley 2400 SourceMeter unit was controlled with a customized software to simultaneously determine the current-voltage-luminous intensity characteristics and the EL spectra. In Device II, the poly-TPD act as hole-injection layer (HIL) and hole-transporting layer (HTL), PVK: OXD-7 serves as host and x wt% represents the doping ratio into PVK: OXD-7. The blend of PVK: OXD-7 and phosphors in chlorobenzene solution was spin coated on top of the poly-TPD.

## **Reference:**

Jian L, Djurovich PI, Alleyne BD, Yousufuddin M, Ho NN, Thomas JC, Peters JC, Rand B, Thompson ME. Synthetic control of excited-state properties in cyclometalated Ir(III) complexes using ancillary ligands. Inorg Chem 2005; 44: 1713-26.

## **Captions of Figures**

Figure S1 TGA curve of the iridium(III) complex under a stream of nitrogen at a scanning rate of 10 °C·min<sup>-1</sup>.

Figure S2 Cyclic voltammogram of the iridium(III) complex.

**Figure S3** Device structures and chemical structures of the relevant materials used in OLEDs.

Figure S4 The EL spectrum of m-MTDATA.

**Figure S5** <sup>1</sup>H NMR, <sup>13</sup>C NMR and MALDI-TOF MS of the (CH<sub>3</sub>OTPA-BTz-Iq)<sub>2</sub>Ir(pic-OXD).

Figure S1







## Figure S3









Figure S4



Figure S5

<sup>1</sup>H NMR of (CH<sub>3</sub>OTPA-BTz-Iq)<sub>2</sub>Ir(pic-OXD)



<sup>13</sup>C NMR of (CH<sub>3</sub>OTPA-BTz-Iq)<sub>2</sub>Ir(pic-OXD)



MALDI-TOF MS of (CH<sub>3</sub>OTPA-BTz-Iq)<sub>2</sub>Ir(pic-OXD)

