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## **Supporting Information**

# Novel Sky Blue Heteroleptic Iridium(III) Complexes with Finely-Optimized Emission Spectra for Highly Efficient Organic Light-Emitting Diodes

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#### **1. Experimental Section**

1.1 General Information. The reagents and solvents purchased from commercial suppliers, such as Adamas-beta, and Energy Chemical were used without further purification. Glassware, syringes, magnetic stirring bars, and needles were dried in a convection oven for over 4h. All organic synthesis proceeded in a dry nitrogen atmosphere. <sup>1</sup>H NMR spectra were measured by a Bruker AVANCE 500 MHz spectrometer operating at 500.1 MHz, where tetramethylsilane(TMS) was used as internal standard. Mass spectra were obtained using an ITQ 1100 (Thermo Fisher) mass spectrometer. Elemental analyses were performed on a Vario Micro (Elementary) analyzer. A Shimadzu UV-2550 spectrophotometer and a Shimadzu 5301PC fluorescence spectrophotometer were used to measure the steady-state absorption and emission spectra, respectively. Phosphorescence quantum yields were quantified by an Edinburgh FLS920 spectrometer combined with a calibrated integrating sphere. TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetric) measurements were performed on TA Q500 thermogravimeter and NETZSCH DSC204 instrument at a heating rate of 10 °C min<sup>-1</sup> under nitrogen, respectively.

**1.2 Electrochemical measurements.** Cyclic voltammetry were performed on Bio-Logic electrochemical work station, using a platinum (Pt) electrode as the working electrode, a Pt wire as the auxiliary electrode and an  $Ag/Ag^+$ electrode as the reference electrode. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple was used as the reference of voltammograms. Dry  $CH_2Cl_2/THF$  solutions dissolving  $n-Bu_4NPF_6$  with a concentration of 0.1 M were used as the supporting electrolyte for the measurement of oxidation/reduction behavior of both phosphors. The HOMO/LUMO levels of Ir1 and Ir2 were calculated from the onset of the oxidation/reduction potential in the cyclic voltammetry (CV) curves.

$$E_{HOMO} = -|E_{[onset, ox vs. Fc^+/Fc]} + 4.8|(eV)|$$

$$E_{LUMO} = -|E_{[onset, re vs. Fc^{+}/Fc]} + 4.8|$$
 (eV)

**1.3 Device Fabrication and Characterization.** Patterned indium tin oxide (ITO)-coated glass substrates ( $20\Omega$ /square) were cleaned in a turn of using detergent solution in an ultrasonic bath, then deionized water, ethanol, acetone and isopropanol. All organics were purified by vacuum sublimation ahead of vacuum deposition process to fabricate OLEDs, in which the evaporation rate of organics, LiF and Al is 1.0 Å s<sup>-1</sup>, 0.2 Å s<sup>-1</sup> and 10 Å s<sup>-1</sup>, respectively, at a pressure of ca.  $3.5 \times 10^{-4}$  Pa. The overlapping active area of devices was  $2 \times 2.5$  mm<sup>2</sup>. EL spectra and L-J-V values were measured by a OLED test system combining a computer-controlled Keithley model 2400 voltage-current source and a Spectrascan PR-655 spectrophotometer in ambient conditions and under room temperature.

**1.4 Theoretical calculations.** All the calculations were performed on the platform of the Gaussian 09 package.<sup>S1</sup> We optimized the geometries of the molecules by using the B3LYP/6-31G basis set for the ligands, then the relativistic effective core potential of Los Alamos and Double-basis sets (LANL2DZ)<sup>S2</sup> were used for Ir (as implemented

in Gaussian 03 package<sup>\$3</sup>). In order to estimate the energy levels, density functional theory (DFT)<sup>\$4</sup> calculations were also performed. And the orbital electron density distributions as well as triplet transition energies were based on the structures optimized in their ground states.

#### 1.5 Synthesis.



Scheme S1. Synthesis of Ir1 and Ir2.

As shown in Scheme S1, the cyclometalating ligands, dfpypy and Medfpypy were synthesized according to classic Suzuki coupling.<sup>S5</sup> IrCl<sub>3</sub>·3H2O was reacted with excess of the synthesized ligands to produce the corresponding  $\mu$ -chloro-bridged dimers [(dfpypy)<sub>2</sub>-Ir( $\mu$ -Cl)]<sub>2</sub> and [(Medfpypy)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub>.<sup>S6</sup>

Synthesis of (Medfpypy)<sub>2</sub>IrPy (Ir1). A hexane solution of BuLi (0.20 mL x 2.5 M) and pyrrole (67 mg, 0.5 mmol) in 10 mL hexane was stirred about 1 h at room temperature, N,N-diisopropylcarbodiimide (DIC, 63 mg, 0.5 mmol) was dropped into and stirred for another 1h. 25 mL hexane solution of  $[(Medfpypy)_2Ir-(\mu-Cl)]_2$  (318 mg, 0.25 mmol) was added dropwise to above mixture solution of pyrrole, DIC and BuLi. Then, this reaction solution was refluxed for 8h and gradually cooled to room temperature. The crude product was obtained by recrystallization from methanol to give a yellow-green solid. Vacuum sublimation was performed to change crude product to pure

(Medfpypy)<sub>2</sub>IrPy (Ir1) (206 mg, 52% yield). ESI-MS: m/z 794.51 (M<sup>+</sup>) (calcd: 795.20). Anal. Calcd for C<sub>33</sub>H<sub>32</sub>F<sub>4</sub>IrN<sub>7</sub>: C, 49.81; H, 4.02; N, 12.30. Found: C, 49.79; H, 4.03; N,12.29. <sup>1</sup>H NMR (500 MHz, DMSO-d6)  $\delta$  9.06 (d, J = 5.9 Hz, 1H), 8.11 (s, 1H), 7.54 (d, J = 6.4 Hz, 1H), 7.06 (d, J = 2.1 Hz, 1H), 6.24 (d, J = 2.1 Hz, 1H), 5.64 (s, 1H), 2.66 (s, 2H), 2.63 – 2.40 (m, 11H), 0.66 (d, J = 6.4 Hz, 2H), -0.15 (d, J = 6.3 Hz, 2H).

**Synthesis of (dfpypy)**<sub>2</sub>**IrPy (Ir2)**. According to the same procedure for Ir1, (dfpypy)<sub>2</sub>IrPy (Ir2) was synthesized as a yellow-green powder. (Ir2) (211 mg, 55% yield). ESI-MS: m/z 767.28 (M<sup>+</sup>) (calcd: 767.20). Anal. Calcd for C<sub>31</sub>H<sub>28</sub>F<sub>4</sub>IrN<sub>7</sub>: C, 48.50; H, 3.65; N, 12.78. Found: C, 48.53; H, 3.67; N,12.76. 1H NMR (500 MHz, DMSO-d6) <sup> $\delta$ </sup> 8.66 (d, J = 4.8 Hz, 1H), 8.39 – 7.95 (m, 4H), 7.62 – 7.33 (m, 2H), 7.21 (d, J = 4.4 Hz, 1H), 6.61 (d, J = 3.5 Hz, 1H), 6.04 – 5.68 (m, 4H), 5.46 (s, 1H), 4.47 (s, 1H), 4.03 (s, 1H), 1.26 (dd, J = 13.8, 6.3 Hz, 6H), 0.87 (d, J = 6.3 Hz, 4H), 0.18 (s, 3H).

### 4. Supplementary Figures



Figure S1. Cyclic voltammograms (CV) of complexes Ir1 and Ir2 recorded in  $CH_2Cl_2$  for oxidation and in THF for reduction



Figure S2. Thermal analyses of Ir1 and Ir2: TGA thermograms (top) and DSC thermograms (bottom).



Figure S3. Luminance-current density curves of four devices.



Figure S4. Chemical formulae of all the materials used in device preparation.



Figure S5. NMR spectrum of Ir1 (top) and Ir2 (bottom) in DMSO-d6.



**Figure S6.** Angle-dependent PL spectra of the doping films employing Ir1 (a) and Ir2 (b) doped in PPF.



**Figure S7.** The PL curves of the doping films employing Ir1 (a) and Ir2 (b) doped in PPF for the quantum yield measurement by an integrating sphere.

#### 5. S-Reference

- S1 M. J. Frisch, et al, Gaussian 09, Revision D.01, Gaussian Inc, WallingfordCT, 2013.
- S2 P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299-310.
- S3 S. Lee, S. O. Kim, H. Shin, H. J. Yun, K. Yang, S. K. Kwon, J. J. Kim, Y. H. Kim, J. Am. Chem. Soc. 2013, 135, 1432–4328.
- S4 M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, J. Chem. Phys. 1998, 108, 4439-4449.
- S5 S. J. Lee, K. M. Park, K. Yang, Y. Kang, Inorg. Chem. 2009, 48, 1030–1037.
- S6 (a) H. Oh, K. M. Park, H. Hwang, S. Oh, J. H. Lee, J. S. Lu, S. Wang, Y. Kang, Organometallics. 2013, 32, 6427–6436; (b) H. Xu, Y. Yue, L. Qu, Y. Hao, H. Wang, L. Chen, B. Xu, Dyes and Pigments. 2013, 99, 67–73; (c) H. J. Park, J. N. Kim, H. J. Yoo, K. R. Wee, S. O. Kang, D. W. Cho, U. C. Yoon, J. Org. Chem. 2013, 78, 8054–8064.