

## Supporting Information

### **A Phosphorescent Material with High and Balanced Carriers Mobility for Efficient OLEDs**

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**Synthesis:** Materials obtained from commercial suppliers were used without further purification. Anhydrous hexane was distilled with sodium benzophenone ketyl under nitrogen atmosphere, degassed by the freeze-pump-thaw method. All glass wares, syringes, magnetic stirring bars and needles were dried in a convection oven at least 4 hours. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were developed and the spots were seen under UV light at 254 and 365 nm. Silica column chromatography was done with silica gel 60 G (particle size 5~40  $\mu\text{m}$ , Merck Co.).  $^1\text{H}$  NMR spectrum was recorded on a Bruker AVANVE 300 MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer.

$[(\text{Fppy})_2\text{Ir}(\mu\text{-Cl})]_2$  and  $[(\text{bzq})_2\text{Ir}(\mu\text{-Cl})]_2$  were synthesized according to a modified version of the Nonoyama procedure, by refluxing  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (7 mmol, 2.5 g) with 2.5 equiv of the ligands (3.3 g of 2,4-difluorophenylpyridine or 3.1 g of benzoquinoline) in a 3:1 mixture of 2-methoxyethanol and water for 6-7 h. The reaction mixture was cooled to room temperature, and more water was added to precipitate the product. The resulting mixture was subsequently filtered through a Buchner funnel and then washed with hexane and ethyl ether several times to provide the crude product.  $[(\text{Fppy})_2\text{Ir}(\mu\text{-Cl})]_2$ : 75% yield.  $[(\text{bzq})_2\text{Ir}(\mu\text{-Cl})]_2$ , 82% yield.<sup>S1</sup>

$(\text{Fppy})_2\text{Ir}(\text{dipba})$  and  $(\text{bzq})_2\text{Ir}(\text{dipba})$ . In a 50 mL flask, a hexane solution of n-BuLi (0.15 mL x 2.6 M) was added to 1-bromobenzene (65 mg, 0.4 mmol) in hexane (10 mL) under argon. The reaction mixture was stirred at room temperature for 1 hour, and was then added dropwise to *N,N'*-diisopropylcarbodiimide (50 mg, 0.4 mmol). The colorless solution was stirred rapidly for 30 min, and then added

dropwise to [(Fppy)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (0.2 mmol, 240 mg) (or [(bzq)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub>, 230 mg) in hexane solvent (15 mL). After being stirred at 80°C for 8 hours, the reaction mixture was cooled to room temperature. The solvent was evaporated under vacuum, and the product was washed with hot Et<sub>2</sub>O (20 mL) three times, giving rise to (Fppy)<sub>2</sub>Ir(dipba) (64%) and (bzq)<sub>2</sub>Ir(dipba), (68%), respectively.

**(Fppy)<sub>2</sub>Ir(dipba):** MS: *m/z* 776 (M<sup>+</sup>). Anal. Calcd for C<sub>35</sub>H<sub>31</sub>F<sub>4</sub>IrN<sub>4</sub>: C, 54.18; H, 4.03; N, 7.22 Found: C, 54.36; H, 5.09; N, 7.22. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.32 (d, *J* = 5.70, 2H), 8.29 (d, *J* = 8.4 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 2H), 7.45-7.37 (m, 3H), 7.30-7.25 (m, 2H), 7.23-7.20 (m, 2H), 6.33-6.25 (m, 2H), 5.74 (d, *J* = 8.4 Hz, 2H), 3.27-3.14 (m, 2H), 0.67 (d, *J* = 6.3 Hz, 6H), -0.09 (d, *J* = 6.3 Hz, 6H).

**(bzq)<sub>2</sub>Ir(dipba):** MS: *m/z* 753 (M<sup>+</sup>). Anal. Calcd for C<sub>39</sub>H<sub>35</sub>IrN<sub>4</sub>: C, 62.29; H, 4.69; N, 7.45. Found: C, 62.12; H, 4.78; N, 7.55. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.63 (d, *J* = 5.10, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.62 (t, *J* = 7.2, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.44-7.33 (m, 5H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 2H), 6.38 (d, *J* = 7.2 Hz, 2H), 3.23-3.16 (m, 2H), 0.65 (d, *J* = 6.0 Hz, 6H), -0.47 (d, *J* = 6.0 Hz, 6H).

**Fabrication of the OLEDs and EL Measurements:** The general architecture of the complex multilayer diodes used in this study is as follows: The ITO (indium-tin oxide) coated glass substrates (20Ω/square) were first cleaned in ethanol, acetone, and soap ultrasonic bathes. All organics were purified by gradient sublimation and thermally evaporated at a rate of 1.0 Å S<sup>-1</sup> at a base pressure of around 3.5 × 10<sup>-4</sup> Pa. A LiF layer (0.5 nm) was deposited at a rate of 0.2 Å S<sup>-1</sup>. The finishing Al electrode (cathode) was deposited at a rate of 10 Å S<sup>-1</sup> in another chamber. The active area of the diode segments was 2 × 3 mm<sup>2</sup>. EL spectra and brightness-current density-voltage characteristics of the devices were measured by combining a Spectrascan PR-650 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient condition at room temperature.

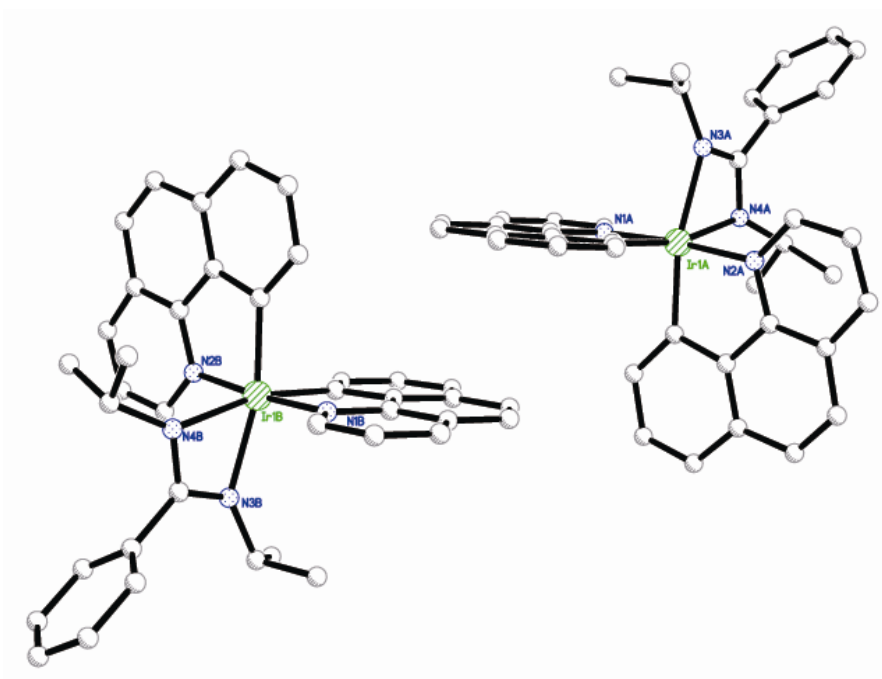
**Absorption, PL and Electrochemical Measurements:** Absorption spectrum was obtained using a Shimadzu UV-2550 UV-vis spectrometer. PL spectra were recorded by a Perkin-Elmer LS-55 fluorescence spectrometer with a Xe arc lamp excitation source. All solvents were degassed via three freeze-pump-thaw cycles. Emission lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under right-angle sample geometry. A 379 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 20 MHz) was used to excite the samples. The PL emission was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). The time constant of the instrument response function (IRF) is about 220 ps.

Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using Pt working electrode, platinum wire as auxiliary electrode, and a porous glass wick Ag/Ag<sup>+</sup> as reference electrode, standardized against ferrocene/ferrocenium couple, scan rate 100 mV S<sup>-1</sup>. The electrochemical behaviors of the corresponding compounds were studied by cyclic voltammetry using ferrocene as an internal standard. Due to the limitation<sup>S2</sup> in measuring reduction potentials in the range of -2.7 V to -3.5 V in CH<sub>2</sub>Cl<sub>2</sub>, we obtained only the oxidation potentials for (Fppy)<sub>2</sub>Ir(dipba) and (bzq)<sub>2</sub>Ir(dipba), and no reduction wave was detected within the electrochemical window of dichloromethane. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of both complexes were calculated from the cyclic voltammetry (CV) data together with the absorption spectrum.

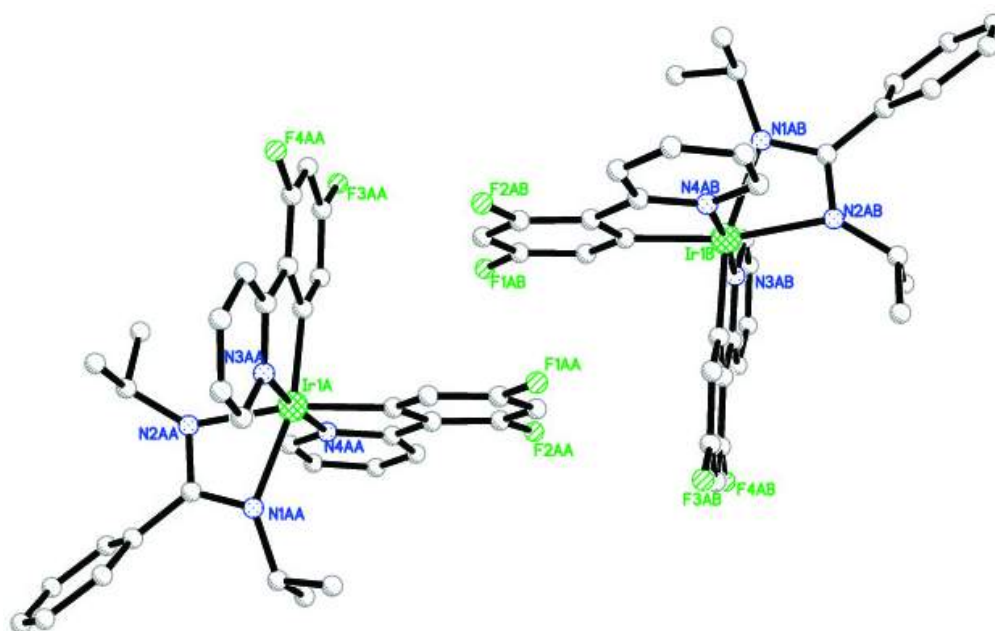
The time-of-flight (TOF) technique involves generation of carriers near one electrode with a short pulse of light and observation of the current displaced in the external circuit by the motion of the carriers through the sample. The sample for TOF measurement has been prepared on the glass substrate covered with indium tin oxide (ITO) layer with the structure of [(ITO)/(Fppy)<sub>2</sub>Ir(dipba) (1 μm)/Al]. An intense short duration (5-6 ns) light pulse from a frequency-tripled (355 nm) Nd:YAG laser was incident at one side of the sample to generate photocarriers. The sample was mounted in a vacuum and measurement was made at the electric field of 6.0 × 10<sup>-5</sup> V cm<sup>-1</sup> under room temperature (293 K).

**Single-Crystal XRD Data of Crystals:** Single crystals suitable for X-ray structural analysis were obtained by vacuum sublimation. Diffraction data were collected on a Rigaku R-Axis Rapid diffractometer (Mo Kα radiation, graphite monochromator) in the  $\psi$  rotation scan mode. The structure determination was performed by direct methods using SHELXTL 5.01v and refinements with full-matrix least squares on  $F^2$ .

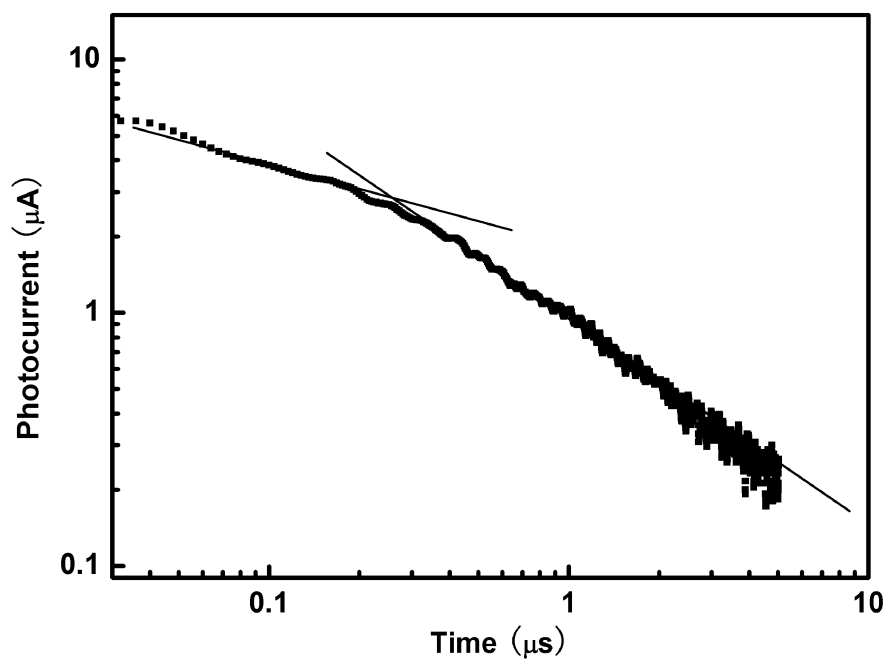
The crystal packing diagrams of (bzq)<sub>2</sub>Ir(dipba) and (Fppy)<sub>2</sub>Ir(dipba) were given in **S-Fig. 1** and **2**, and the corresponding CCDC reference number are 714888 and 775310, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



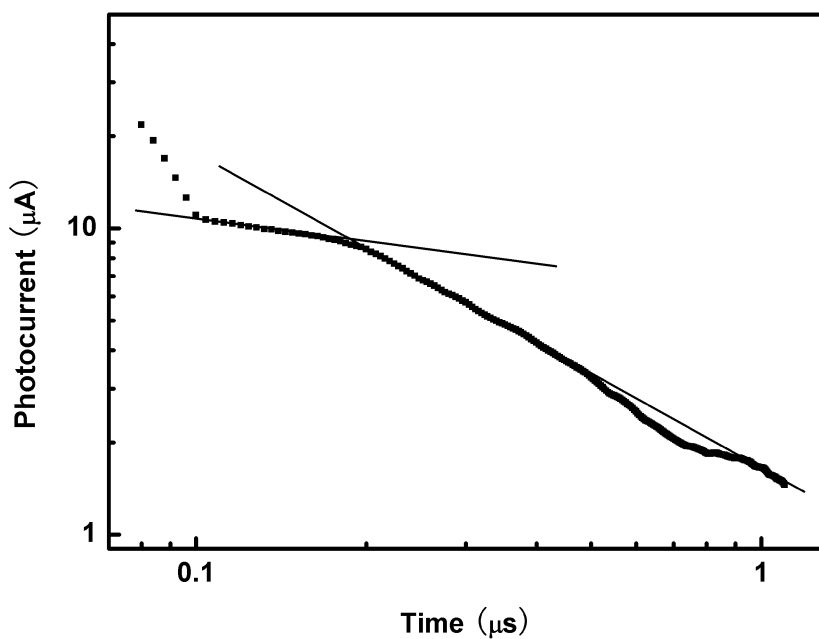
S-Fig. 1 Crystal packing diagram of (bzq)<sub>2</sub>Ir(dipba).



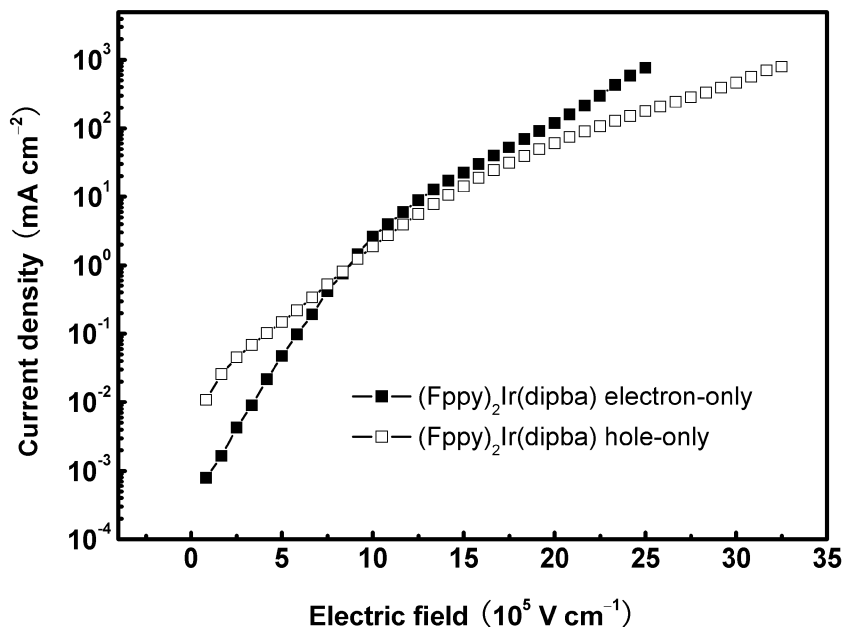
S-Fig. 2 Crystal packing diagram of (Fppy)<sub>2</sub>Ir(dipba).



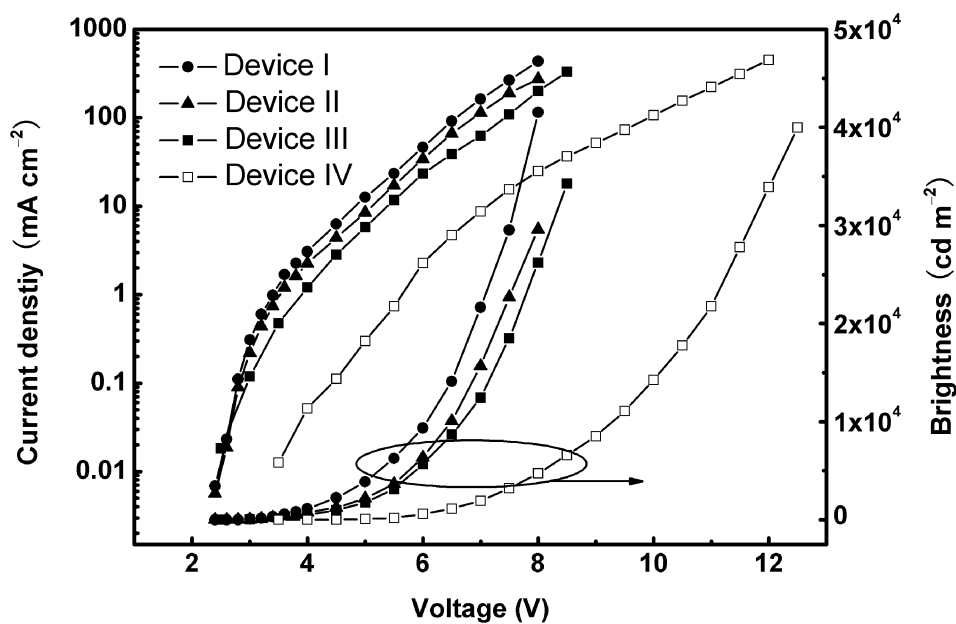
**S-Fig. 3** Log of the photocurrent vs the log of time in a time-of-flight measurement of hole mobility in a  $1\ \mu\text{m}$   $(\text{Fppy})_2\text{Ir}(\text{dipba})$  film at ambient temperature and an electric field of  $6.0 \times 10^5\ \text{V cm}^{-1}$ .



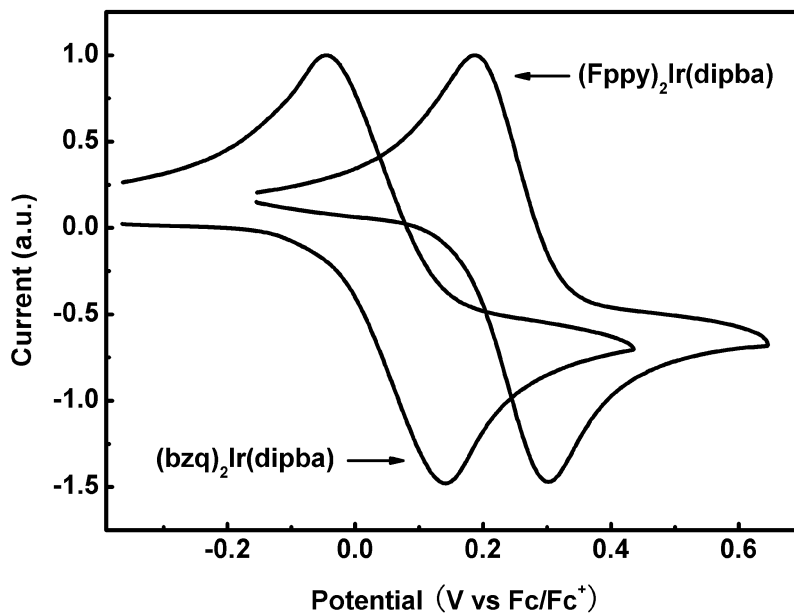
**S-Fig. 4** Log of the photocurrent vs the log of time in a time-of-flight measurement of electron mobility in a 1  $\mu\text{m}$  (Fppy)<sub>2</sub>Ir(dipba) film at ambient temperature and an electric field of  $6.0 \times 10^5 \text{ V cm}^{-1}$ .



**S-Fig. 5** Current density-electric field characteristics of (Fppy)<sub>2</sub>Ir(dipba) in single-carrier devices with the following configurations: [Al/active molecular layer/Al] (electron-only device) and [ITO/active molecular layer/Au] (hole-only device).



**S-Fig. 6** Brightness-voltage curves and current density-voltage curves of device I-IV.



**S-Fig. 7** Cyclic voltammograms of (Fppy)<sub>2</sub>Ir(dipba) and (bzq)<sub>2</sub>Ir(dipba).

**S-reference:**

- S1 M. Nonoyama, *Bull. Chem. Soc. Jpn.* 1974, **47**, 767.  
S2 S. G. Jung, Y. J. Kang, H. S. Kim, Y. H. Kim, C. L. Lee, J. J. Kim, S. K. Lee, S. K. Kwon, *Eur. J. Inorg. Chem.* 2004, **17**, 3415.