

## ***Supporting Information***

### 1. Materials, measurements, device fabrication and measurements

#### 1. 1. Materials

Benzene-d<sub>6</sub> (Aldrich, 99.6 atom % D) and pyridine-d<sub>5</sub> (Norell, 99.5 atom % D) were purchased from Cambridge Isotopes and dried over activated molecular sieves. Benzene and pyridine was obtained from SCRC. Benzene was purified by distillation from sodium/benzophenone ketyl. And pyridine were distilled over CaH<sub>2</sub> and stored with molecular sieves. Ir(ppy)<sub>3</sub> was synthesized by the procedures commonly found in literature.<sup>[1]</sup> All solvents used in the reaction were purified by routine procedures. Other reagents were used as received from commercial sources, unless otherwise stated.

#### 1. 2. Measurements

The <sup>1</sup>H NMR spectra were collected from a Bruker 400 MHz spectrometer. The absorption spectra were carried out with a Perkin–Elmer Lambda-35 UV-vis spectrometer. FT-IR spectra were measured on a Nicolet 60SXR infrared spectrophotometer. The photoluminescence (PL) spectra were obtained by a Hitachi F-4500 fluorescence spectrophotometer. The PL emission quantum yields (PLQYs) in degassed (by a freeze-pump-thaw technique) dichloromethane solution were determined using quinine in 1.0 N H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.54$  at 365 nm) as a reference<sup>[2]</sup> at room temperature with the absorption to be adjusted under 0.1. To obtain the quantum-yield data as precisely as possible, the PL had to be measured in a single machine run to compare the integrated emission areas. The difference between the

refractive index of the solvent and that of the standard should also be counted. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Perkin–Elmer MAS-5800 instrument with a heating/cooling rate of 10 °C min<sup>-1</sup> and a nitrogen flow rate of 90 ml min<sup>-1</sup>. Cyclic voltammetry (CV) was performed on a CHI 600 C instrument in anhydrous dichloromethane solution containing 0.1M (Bu)<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte at a scan rate of 50 mVs<sup>-1</sup> using ferrocene (Fc) as the internal standard. The working electrode was glass carbon and the reference electrode was Ag/Ag<sup>+</sup>. The phosphorescence intensity decay was measured FLSP920 combined fluorescence lifetime and steady state spectrometer.

The X-ray diffraction data were collected at room temperature with graphite monochromatic Mo K $\alpha$  radiation ( $k = 0.71073 \text{ \AA}$ ) on a Bruker Apex II X-ray diffractometer. Structures were solved by direct methods and were refined by full-matrix least squares on F2 using SHELXL 97 program package. The non-hydrogen atoms were refined anisotropically. Quantum mechanic calculations were carried out with Gaussian 09 program package in this study. Density functional theory (DFT) was used with the popular B3LYP functional in terms of noncovalent interactions at reasonable calculation cost. 6-31G(d,p) was selected for C, D, and N atoms.

### 1. 3. Device Fabrication

The devices were fabricated by conventional vacuum deposition of the organic layers and cathode onto an ITO-coated glass substrate below a pressure of  $5 \times 10^{-6}$  Torr. Al was used as the cathode. The ITO was cleaned by UV-ozone treatment at 150 °C. The

entire organic layers and the Al cathode were deposited without exposure to the atmosphere. The deposition rates for the organic materials, LiF, and Al were typically 0.1, 0.025, and 0.5 nm s<sup>-1</sup>, respectively. Prior to the fabrication, the ITO substrate was carefully cleaned and subjected to O<sub>3</sub> bleaching.

#### 1. 4. Device Measurement

The devices were carried with a Hewlett–Packard 4140 B source measure unit and a PR-650 luminance color meter. The color meter was placed on the bottom of the test device to measure the front luminance. The fluorescence spectra were recorded using a Jasco FP-75 spectrophotometer. For the lifetime measurements, the devices were encapsulated with glass lids under a N<sub>2</sub> atmosphere. The voltage rise and luminance degradation were recorded simultaneously every hour.

#### 2. Synthesis

##### 2.1. Bromobenzene-D<sub>5</sub> (**1**)

The synthesis of bromobenzene-D<sub>5</sub><sup>[3]</sup>: 64.88 g (0.81 mol) liquid bromine was added dropwise to a three-neck flask containing 40.42 g (0.48 mol) benzene-D<sub>6</sub> and 1.20 g (0.0214 mol) iron shavings. Then the mixture was heated to keep faint boiling for about 4 h. After cooling to room temperature, water was added to quench the reaction, the iron shavings was filtered off and washed with water for 3 times. The filtrate was transferred into a 500 mL separating funnel and extracted using 60 mL NaOH solution and 100 mL water orderly, the organic phase was distilled twice – first at 145~170 °C followed by redistillation at 156~158 °C to yield the product (45.0 g, 0.278 mol, yield 57.7%).

## 2.2. 2-phenylpyridine-D<sub>9</sub> (**2**)

2-phenylpyridine-D<sub>9</sub> was prepared by a modification of the literature procedure <sup>[4]</sup>. The mixture of 40.5 g (0.250 mol) anhydrous bromobenzene-D<sub>5</sub> and 50 mL anhydrous ether was added gradually to a three-neck flask containing 3.5 g (0.5 mol) Li and 100 mL anhydrous ether. And then the reaction mixture was refluxed for 1.5 h. The mixture of 50 mL anhydrous toluene and 41.8 g (0.50 mol) pyridine-D<sub>5</sub> was then added dropwise. The mixture was then stirred for about 50 min at room temperature and refluxed for another 4 h. The reaction mixture was poured cautiously into ice-water, and then acidified with concentrated hydrochloric acid, which was transferred to 500 mL separating funnel and extracted with 100 mL water, the aqueous solution was saturated with sodium hydroxide and extracted with ether. The organic phase was concentrated to give oil crude product, then purified by distillation under reduced pressure twice – first at 90~110 °C followed by redistillation at 100~102 °C to yield the desired compound (20.2 g, 0.123 mol, 54.9%): ESI-MS (m/z): 164.3, [M]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, DMSO) δ [ppm]: very weak signals, the deuterium content rate was determined to be more than 99 % in average using CH<sub>2</sub>Br<sub>2</sub> as an external standard. <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ [ppm]: 155.94, 148.95-149.46, 138.53-138.61, 136.42-136.75, 128.02-128.79, 125.91-126.36, 121.77-122.23, 119.57-120.02.

## 2.3. Synthesis of [(2-phenylpyridine-D<sub>8</sub>)<sub>2</sub>IrCl]<sub>2</sub> (**3**) <sup>[5]</sup>

0.8 g IrCl<sub>3</sub> and 0.777 g 2-phenylpyridine-D<sub>9</sub> were heated at 110 °C in a mixture of 40 mL 2-ethoxyethanol and 5 mL water for overnight under nitrogen. After being

cooled to room temperature, water was added to quench the reaction, and the resulting precipitate was filtered off, washed with methanol then Et<sub>2</sub>O and finally dried to afford green powder with yield 57.3% (1.05 g).

#### 2.4. The Synthesis of Ir(ppy)<sub>3</sub>-D<sub>24</sub> (**4**)<sup>[1]</sup>

The mixture of 0.5 g [(2-phenylpyridine-D<sub>8</sub>)<sub>2</sub>IrCl]<sub>2</sub>, 0.145 g 2-phenylpyridine-D<sub>9</sub>, 0.52 g K<sub>2</sub>CO<sub>3</sub> and 10 mL glycerol was gradually heated to 200 °C under nitrogen atmosphere for 24 h. After the mixture was cooled to room temperature, water was added to quench the reaction, and the resulted precipitate was filtered off, washed with methanol then Et<sub>2</sub>O and finally dried to afford crude product. The desired product was purified by an aluminum oxide column chromatography with dichloromethane/petroleum ether (2:1, v/v) as an eluent. Then it was further purified by train sublimation twice to yield the desired compound as yellow crystals (0.38 g, 68.8%): ESI-MS (m/z): 679.3, [M]<sup>+</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ [ppm]: no signals. So the deuterium content rate was determined to be ~100% in average using CH<sub>2</sub>Br<sub>2</sub> as an external standard. The deuterated complex is purer than the ligand because train sublimation was used to purify it and train sublimation has a close relationship with molecular mass. <sup>13</sup>C NMR (100 MHz, DMSO) δ [ppm]: 118.81, 119.43, 122.34, 124.02, 128.48, 136.33, 136.66, 143.77, 146.76, 160.55, 165.55; Anal. Calcd. for C<sub>33</sub>H<sub>27</sub>N<sub>3</sub>Ir: C 58.38, D 7.12, N 6.19. found: C 57.90, H 6.84, N 5.86.

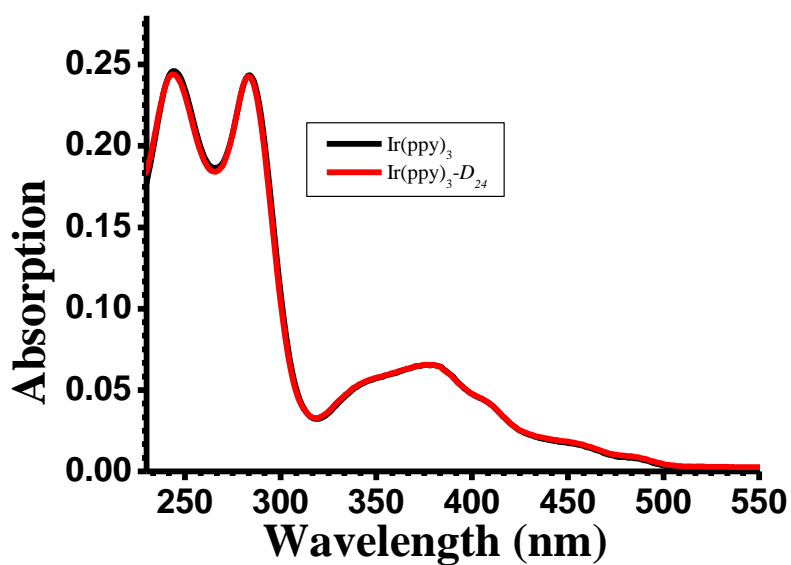


Figure 1, Absorption spectra of the compounds in CH<sub>2</sub>Cl<sub>2</sub>

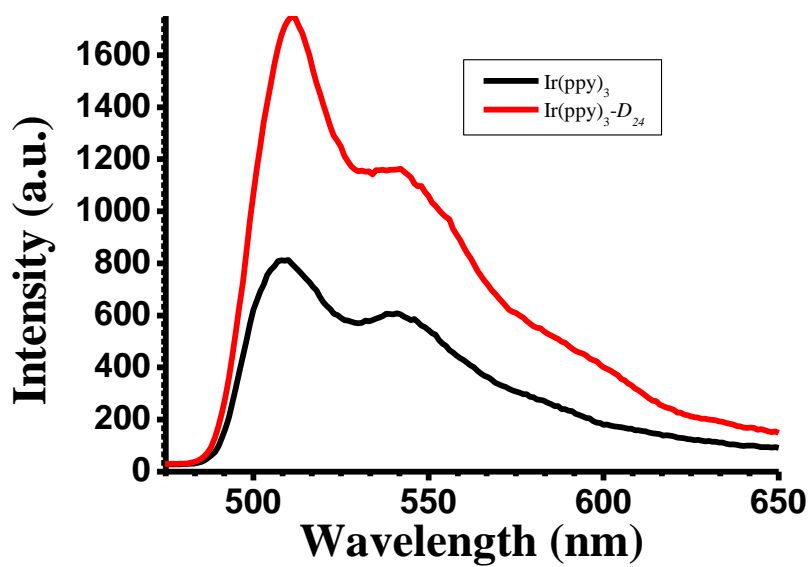


Figure 2, Emission spectra of the compounds in CH<sub>2</sub>Cl<sub>2</sub> at 77 K, excited by 365 nm.

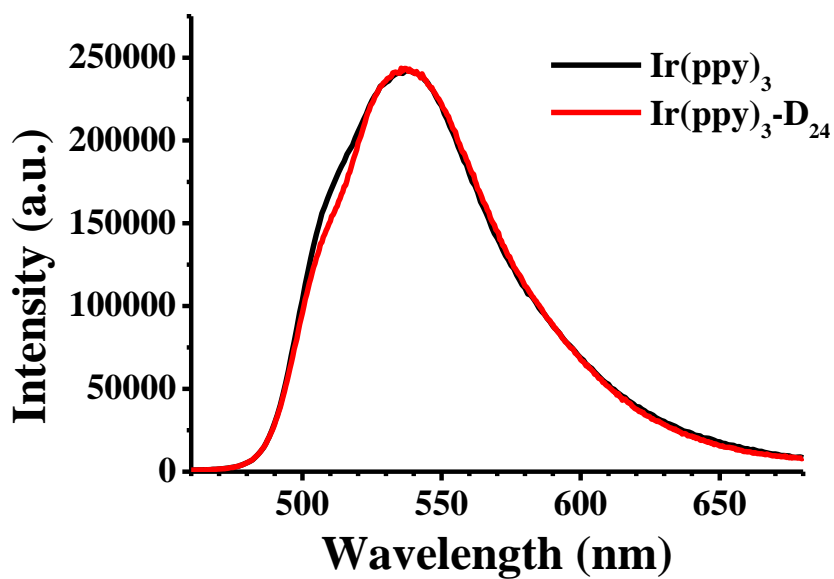


Figure 3, PL spectra of the 6% (wt) Ir complex:CBP thin film.

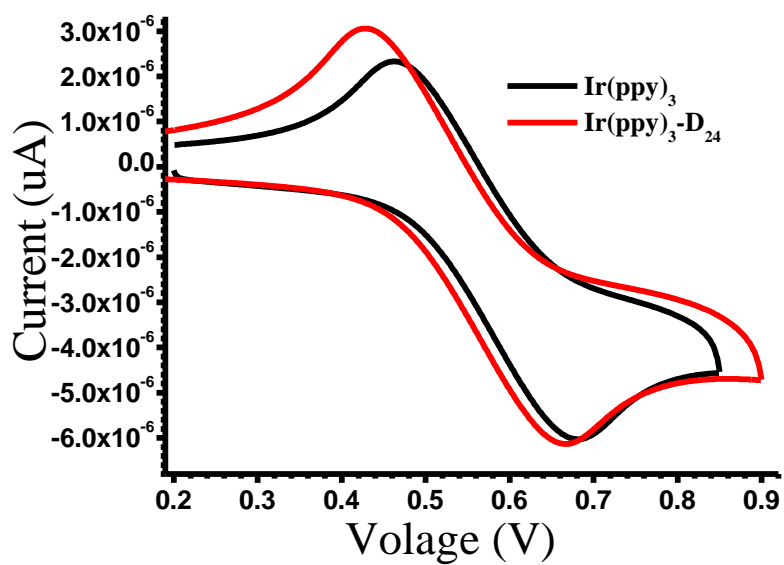


Figure 4, Cyclic voltammograms of the complexes.

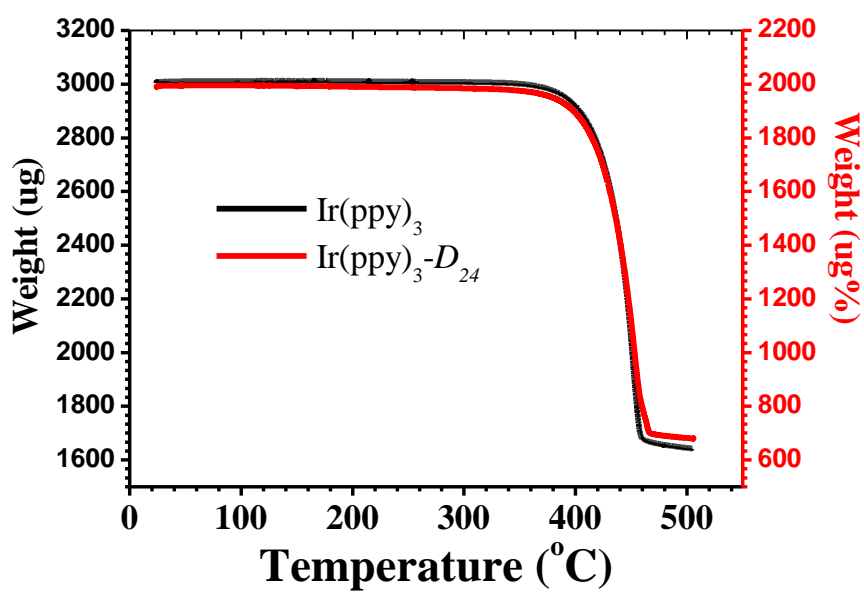


Figure 5, DTA cures of the complexes

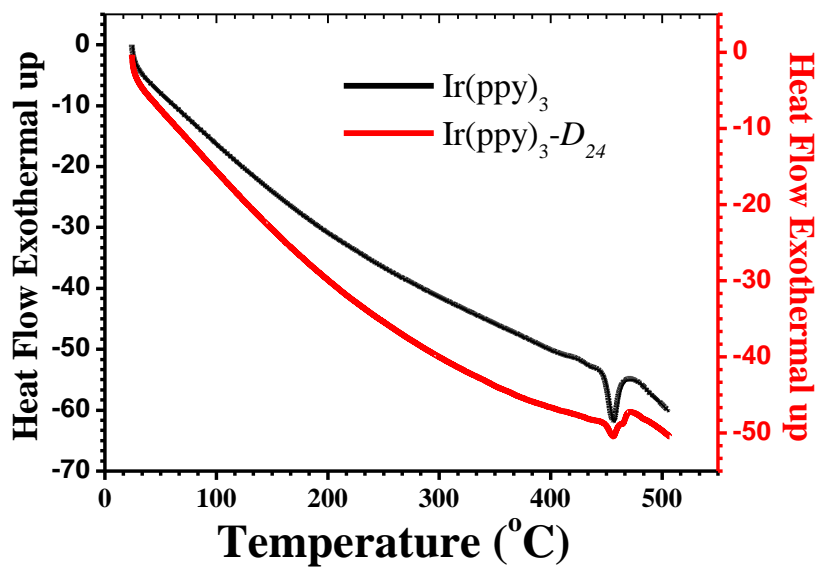


Figure 6, DSC curves of the complexes.



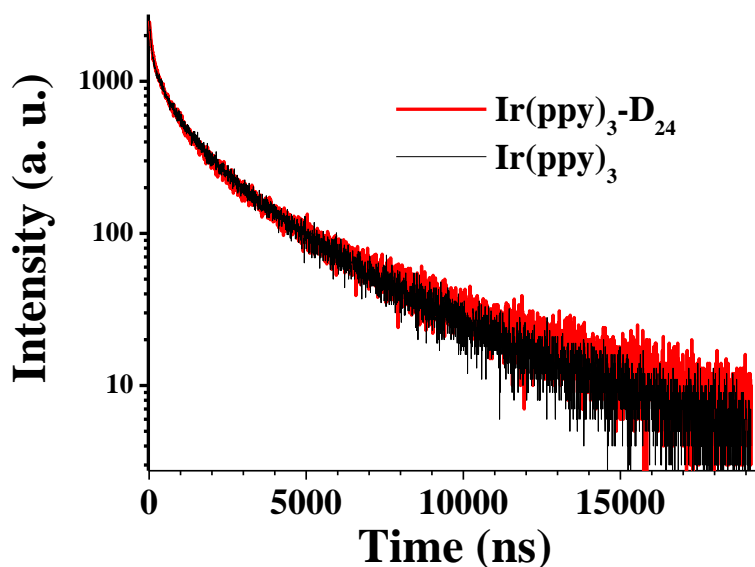


Figure 7, Phosphorescence intensity decay curves of the complexes as solid powder.

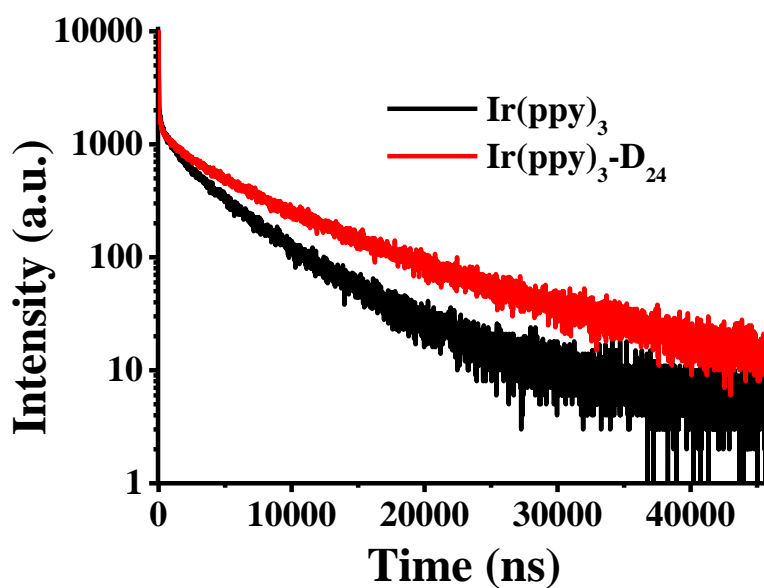


Figure 8, Phosphorescence intensity decay curves of the complexes in  $\text{CH}_2\text{Cl}_2$  at 77K.

## References

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