

## Supporting Information

### 5 Synthesis of 2-Bromo-5-(trimethylsilyl)pyridine (a)

A solution of 2,5-dibromopyridine (5 g, 21.11 mmol) in dry ether (200 mL) was cooled to -78 °C addition of n-BuLi (7.02 g, 25.39 mmol, 2.5 M in hexane) over 10 min resulted in pale yellow solution. After stirring for 1 h, chlorotrimethylsilane (TMSCl) was added to the solution (3.74 g, 29.55 mmol). The solution was allowed to warm to room temperature overnight. Water (100 mL) was added to the diethyl ether. The organic layer was separated and dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. The crude material was purified by vacuum distillation. Yield (3.5 g, 76%). T<sub>b</sub> = 79-80 °C (1.5 mmHg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.35 (s, 1H), 7.61 (d, 1H), 7.42 (d, 1H), 0.32 (s, 9H) ppm.

### Synthesis of 2-Bromo-4-(trimethylsilyl)pyridine (d)

A solution of 2,4-dibromopyridine (5 g, 21.11 mmol) in dry ether (200 mL) was cooled to -78 °C addition of n-BuLi (7.02 g, 25.39 mmol, 2.5 M in hexane) over 10 min resulted in pale yellow solution. After stirring for 1 h at this temperature, chlorotrimethylsilane (TMSCl) was added to the solution (3.74 g, 29.55 mmol). The solution was allowed to warm to room temperature overnight. Water (100 mL) was added to the diethyl ether. The organic layer was separated and dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. The crude material was purified by vacuum distillation. Yield (3.5 g, 75%). T<sub>b</sub> = 81-84 °C (1.5 mmHg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.31 (d, 1H), 7.55 (s, 1H), 7.33 (d, 1H), 0.31 (s, 9H) ppm.

### Synthesis of 2-(2-(4-difluorophenyl)-5-(trimethylsilyl)pyridine (b)

2-Bromo-5-(trimethylsilyl)pyridine (5.0 g, 21.7 mmol), 2,4-difluorophenylboronic acid (5.06 g, 26.1 mmol), and Pd(pfp)<sub>3</sub> were dissolved on tetrahydrofuran (THF) (130 mL). A solution of 2 M K<sub>2</sub>CO<sub>3</sub> (15 mL) was added, and the mixture was refluxed with stirring for 24 h in an atmosphere of N<sub>2</sub>. After being cooled, the mixture was poured into aqueous HCl and extracted with methylene chloride. The organic layer was dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give dark yellow oil. The crude product was purified by chromatography on silica gel (EtOAc / hexane, 1 / 10, v / v) to obtain yellowish oil. Yield (4.0 g, 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.79 (s, 1H), 8.03 (q, 1H), 7.86 (d, 1H), 7.73 (d, 1H), 6.93 (m, 2H), 0.37 (s, 9H) ppm.

### Synthesis of 2-(2-(4-difluorophenyl)-4-(trimethylsilyl)pyridine (e)

The procedure is the same as that for preparation of 2-(2-(4-difluorophenyl)-5-(trimethylsilyl)pyridine. Yield (4.4 g, 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.67 (d, 1H), 7.96 (q, 1H), 7.84 (s, 1H), 7.35 (d, 1H), 6.98 (t, 1H), 6.56 (t, 1H), 0.30 (s, 9H) ppm.

### Synthesis of 2-(3-(perfluoropropyl)-1H-1, 2, 4-triazole-5-yl)pyridine (fptp) (c)

A mixture of ethyl pentafluoropanoate and hydrazine

55 monohydrate was dissolved on tetrahydrofuran (THF) (100 mL). And the mixture was refluxed with stirring for 1 h in atmosphere of N<sub>2</sub>. After cooled, the acetamidine hydrochloride and NaOH were added mixture, and then the mixture was refluxed with stirring for 3 h. Cooled to room temperature, THF was removed and then dissolved in ethyl acetate. The organic phase was dried over MgSO<sub>4</sub>. Solvent was then removed and the residue was purified by column chromatography on silica gel (Hexane / ethyl acetate, 2 / 1, v / v) to obtain white solid. Yield (25%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.82 (d, 1H), 8.35 (d, 1H), 7.99 (t, 1H), 7.56 (m, 1H) ppm.

### Synthesis of (F<sub>2</sub>-m-trimethylsilyl)<sub>2</sub>Ir(μ-Cl)Ir(F<sub>2</sub>-m-trimethylsilyl)<sub>2</sub>

The mixture of 2-(2-(4-difluorophenyl)-5-(trimethylsilyl)pyridine (0.97 g, 2.2 mmol), IrCl<sub>3</sub> 3H<sub>2</sub>O (0.5 g, 1 mmol) in a mixed solvent of 2-ethoxyethanol (15 mL) and water (5 mL) was stirred under N<sub>2</sub> at 120 °C for 24 h. Cooled to room temperature, the precipitate was collected by filtration and washed with water and then dried in vacuum to give a cyclometalated Ir(III)-chloro-bridged dimer.

### Instrument

<sup>1</sup>H NMR spectra were recorded using a Bruker Avance-300 MHz FT-NMR spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as internal standard. FT-IR spectra were recorded using a Bruker IFS66 spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instruments 2050 thermogravimetric analyzer. Differential scanning calorimeter (DSC) was conducted under nitrogen using a TA instrument DSC Q10. The both samples were heated at a rate of 10 °C/min. Absorption spectra of dyes were measured in dichloromethane solution (~10<sup>-5</sup> M) by UV-visible spectrophotometer (Varian Cary 5000). The absolute PL efficiency of each dopants was measured with an integrating sphere (Labsphere 6" diameter) method developed by de Mello et al.<sup>4</sup> A He:Cd laser was used as the excitation source and a monochromator attached with a photomultiplier tube as detector system. All the systems were calibrated by using a standard tungsten-halogen lamp and a deuterium lamp. The samples for the measurement were prepared by co-deposition on quartz substrates with N,N'-dicabazoyl-3,5-benzene as host material. The doping concentration of the film was 6wt% and the thickness was 50 nm. To avoid a degradation of the materials during measurement, the samples were kept in inert environment by blowing nitrogen gas into the integrating sphere. The PL spectra were measured by the same set up as the absolute PL efficiency measurement except not using an integrating sphere. Transient PL experiments of dyes were performed with a Nd:YAG laser (10 Hz, 9 ns pulse) and a photomultiplier tube with a monochromator. The samples were prepared by the same method for the absolute PL efficiency measurement and kept in a vacuum chamber maintained at pressure under 10<sup>-3</sup> torr during measurement to avoid degradation.

### Fabrication of OLEDs

The patterned ITO glasses were cleaned with acetone and isopropyl alcohol and treated with UV- ozone to further clean organics and to increase the work function of ITO. All organic layers and cathode were successively evaporated by the thermal evaporator onto the cleaned ITO without breaking vacuum (< 5 ×

$10^{-7}$  torr). After deposition, the devices were encapsulated with glass cans in nitrogen environment. The current density-voltage-luminance (J-V-L) characteristics of the devices were measured by a spectro radiometer (Photo Research Co., PR- 650) linked to a source meter (Keithley 2400).