

## Supporting information

### Highly electron deficient pyrido[3',2':4,5]furo[2,3-b]pyridine as the core 5 structure of triplet host material for high efficiency green phosphorescent organic light-emitting diodes

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#### 15 **Experimental Section**

##### **General information**

5-Chloro-2-methoxyphenyl boronic acid and other important reagents were purchased from Aldrich and TCI Chem. All reactions were carried out under N<sub>2</sub> atmosphere.

The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) were recorded on Avance 500 (Bruker). The  
20 attenuated total reflection (ATR) fourier transform-infrared (FT-IR) spectra for all the samples were  
obtained using a Nicolet 380 FT-IR spectrometer. The mass spectra were recorded using a JEOL,  
JMS-600W spectrometer in fast atom bombardment mode. Elemental analysis of the materials was  
carried out using Flash2000 (Thermofisher). The differential scanning calorimetric (DSC)  
measurements were performed on a Mettler DSC822e under nitrogen at a heating rate of 10 °C/min.  
25 The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (HITACHI,  
F-7000) and the ultraviolet-visible (UV-Vis) spectra were obtained by means of a UV-Vis

spectrophotometer (Shimadzu, UV-2501PC). Low temperature PL measurement was carried out using Perkin Elmer LS55 fluorescence spectrometer in liquid nitrogen. Delay time was 1 ms. Transient PL measurement of CzPFP and CzPFP:Ir(ppy)<sub>3</sub> was carried out by exciting the film using Q-switched 30 pulsed ND YAG laser with a wavelength of 355 nm. Photomultiplier tube was used as a detector. The highest occupied molecular orbital and lowest unoccupied molecular orbital of compounds was measured with a cyclic voltammetry.

## Synthesis

### 35 5-Chloro-2'-methoxy-3,3'-bipyridin-2-amine

(2-Methoxypyridin-3-yl)boronic acid (2.4 g, 15.5 mmol), 5-chloro-3-iodopyridin-2-amine (4.0 g, 15.5 mmol), potassium carbonate (6.45 g, 46.7 mmol), 100 mL of toluene and 50 mL of distilled water were added to a 2-neck flask, and then the solution was bubbled with N<sub>2</sub> for 30 min.

Tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.47 mmol) was added to the solution and the 40 resulting solution was refluxed for 24h under N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature, extracted with ethyl acetate and distilled water. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to give the crude product, which was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate gradient mixture as an eluent, providing 2.8 g of 5-chloro-2'-methoxy-3,3'-bipyridin-2-amine.

45 Yield 75%. MS (FAB) *m/z* 236 [(M+H)<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.98 (s, 3H), 4.50 (s, 2H), 7.01 (t, 1H, J = 4.2 Hz), 7.34 (s, 1H), 7.56 (d, 1H, J = 4.5 Hz), 8.06 (s, 1H), 8.24 (d, 1H, J = 3.5 Hz).

### 3-Chloropyrido[3',2':4,5]furo[2,3-*b*]pyridine

5-Chloro-2'-methoxy-3,3'-bipyridin-2-amine (2.7 g, 11.5 mmol) in tetrahydrofuran (20 mL) and glacial 50 acetic acid (40 ml) was stirred at -10 °C and *tert*-butyl nitrite (4.6 g, 34.4 mmol) was added via syringe over a period of 10 min. After stirring for 1 h at -10 °C, the reaction mixture was stirred at 0 °C over a

period of 12h. The reaction mixture was warmed to room temperature, diluted with 100 mL of water.

Solid material was filtered and isolated by silica gel column chromatography (ethyl acetate/*n*-hexane), providing 1.3 g of pure 3-chloropyrido[3',2':4,5]furo[2,3-*b*]pyridine.

55 Yield 55%. MS (FAB)  $m/z$  205 [(M+H)<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.43 (t, 1H, J = 4.3 Hz), 8.26 ~ 8.28 (m, 2H), 8.48 (s, 1H), 8.57 (d, 1H, J = 2.0 Hz).

### 3-(3-(Carbazole-9-yl)phenyl)pyrido[3',2':4,5]furo[2,3-*b*]pyridine (CzPFP)

A mixture of 3-chloropyrido[3',2':4,5]furo[2,3-*b*]pyridine (1.2 g, 5.87 mmol), 3-(9*H*-carbazol-9-yl)phenylboronic acid (2.0 g, 7.03 mmol), potassium phosphate tribasic (3.8 g, 17.6 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 0.36 g, 0.88 mmol), and tris(dibenzylideneacetone)dipalladium (0.16 g, 18 mmol) in toluene (120 ml) and distilled water (12 ml) was refluxed under N<sub>2</sub> for 36 h. The solution was cooled down to room temperature, diluted with 50 mL water and extracted with ethyl acetate. The organic extracts were dried over anhydrous 65 magnesium sulfate, filtered, and evaporated to yield a brown solid. The crude material was purified by column chromatography on silica gel using dichloromethane/*n*-hexane as an eluent. Additional purification by sublimation (230 °C. at 10<sup>-5</sup> mm Hg) resulted in 1.5 g of pure white compound. Yield 62%. mp 217 °C. Tg 97 °C, FT-IR 3053.0, 1593.4, 1450.4, 1388.7, 1334.5, 1228.9, 1185.4, 1112.3, 872.7, 794.6, 748.3, 696.5, 663.4 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.29 (t, 2H, J = 5.0 Hz), 70 7.37 (t, 1H, J = 4.3 Hz), 7.41 (t, 2H, J = 5.0 Hz), 7.46 (d, 2H, J = 4.2 Hz), 7.63 (d, 1H, J = 5.2 Hz), 7.72 ~ 7.76 (m, 2H), 7.84 (s, 1H), 8.14 (d, 2H, J = 3.8 Hz), 8.27 (d, 1H, J = 4.5 Hz), 8.45 (s, 1H), 8.51 (d, 1H, J = 3.2 Hz), 8.77 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 109.6, 115.5, 115.7, 120.0, 120.2, 120.4, 123.5, 125.9, 126.1, 126.3, 126.6, 128.8, 130.6, 130.8, 132.8, 138.7, 139.6, 140.8, 146.4, 147.9, 161.4, 162.2. MS (FAB)  $m/z$  412 [(M+H)<sup>+</sup>]. Anal. Calcd for C<sub>29</sub>H<sub>18</sub>N<sub>2</sub>O: C, 81.73%; H, 4.16%; N, 10.21% O, 75 3.89%. Found : C, 81.79%; H, 4.11%; N, 10.27% O, 3.87%.

## Device fabrication and measurements

The device structure of green PHOLED was indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 60 nm)/4,4'-cyclohexylidenebis[*N,N*-80 bis(4-methylphenyl)aniline] (TAPC, 20 nm)/1,3-bis(*N*-carbazolyl)benzene (mCP, 10 nm)/CzPFP:tris(2-phenylpyridine) iridium ( $\text{Ir}(\text{ppy})_3$ ) (25 nm, 3%) /diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 30 nm)/LiF (1 nm)/Al (200 nm). Hole only device with a device structure of ITO (50 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/CzPFP (25 nm)/Al (200 nm) and electron only device with a device structure of ITO (50 nm)/Ca (5 nm)/CzPFP (25 85 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm) were fabricated to compare hole and electron density of the device. All devices were prepared by vacuum thermal evaporation except the PEDOT:PSS layer which was deposited by spin coating process. The device performances of the blue and green PHOLEDs were evaluated using Keithley 2400 source measurement unit and CS1000 spectroradiometer.

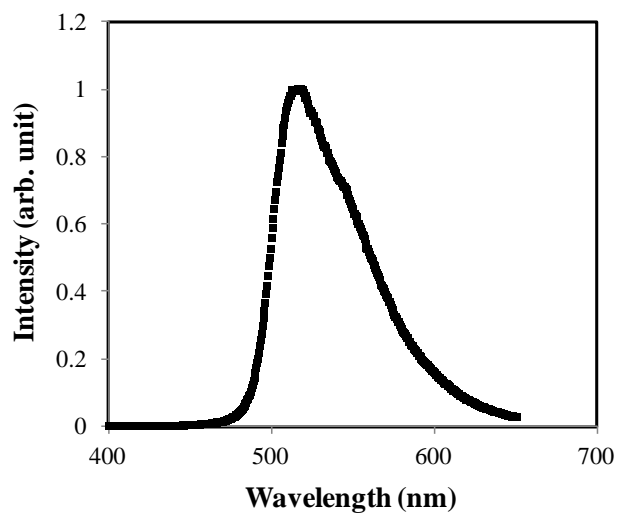


Figure S1. PL emission spectrum of Ir(ppy)<sub>3</sub> doped CzPFP film.

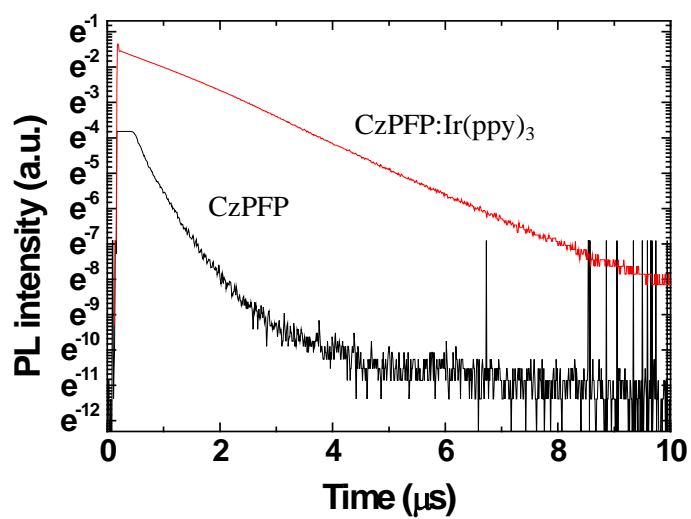


Figure S2. Transient PL spectra of CzPFP and CzPFP:Ir(ppy)<sub>3</sub>.

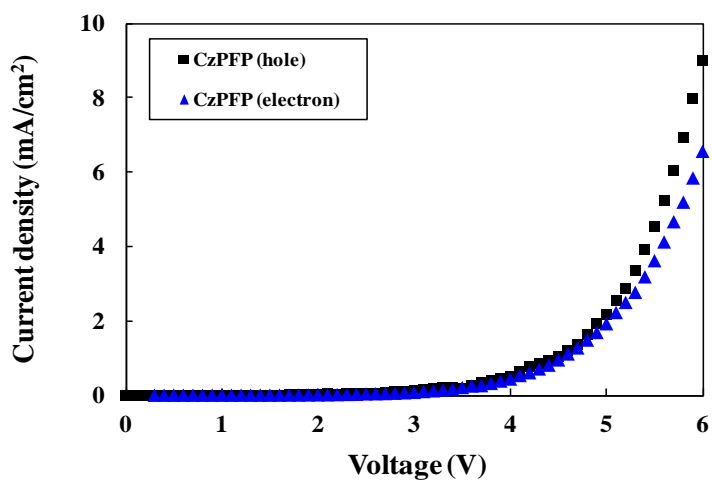


Figure S3. Current density-voltage curves of hole only and electron only devices of CzPFP.