Supplementary Information

A thermally activated delayed blue fluorescence emitter with reversible externally tunable emission

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General Information

The ¹H and ¹³C NMR spectra were recorded using Varian mercury 400 spectrometer. The HRMS were measured using MAT-95XL HRMS. The decomposition temperature was determined by TGA using TG/DTA Seiko SSC-5200 instrument and glass transition temperature was determined by DSC under nitrogen atmosphere on a DSC-Q10 instrument. UV-visible absorption spectra were measured using a Hitachi U-3300 spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Hitachi F-7000 spectrophotometer. Transient PL measurement of the materials in solution were obtained using 355 nm pulsed laser (Nd:YAG laser, INDI-40-10, Spectra-Physics) as the excitation source and the sample was excited by the optical fiber (77532, Newport Corp). A highpass filter (GG-400-25.4, Lamda) at 410 nm in front of the photodiode (DET10A/M, Thorlabs) was used to prevent the scattering of 355-nm laser. The electronic signal was recorded by an oscilloscope (WaveSurfer 24MXs-B, LeCroy). The absolute PL quantum efficiency of the doped films were determined using an integrating sphere under N₂ atmosphere. The electrochemical properties of these benzoylpyridine derivatives were measured by CH Instruments 600A electrochemical analyzer. The oxidation measurements were measured using a glassy carbon electrode as the working electrode, an Ag/Ag⁺ (0.01 M AgNO₃) as the reference electrode and Pt

wire as the counter electrode, respectively in dichloromethane. The HOMO energy level were determined from the onset of the oxidation potential using the equation $-(4.8 \text{ eV} + E_{ox} \text{ (vs Fc}_{ox}))$.

DFT Calculation

The optimization of molecular geometry and electronic properties were carried out by the Gaussian 03 program with density functional theory (DFT) and time-dependent DFT (TDDFT) calculations in which the Becke's three parameter functional combined with Lee, Yang, and Parr's correlation functional (B3LYP) hybrid exchange-correlation functional with the 6-31G* basic set were used.¹ The molecular orbitals were visualized using Gaussview 4.1 software.

OLEDs Fabrication and Measurement

Organic materials used in device fabrication were usually purified by sublimation. Device were fabricated by vacuum deposition onto pre-coated ITO glass with sheet resistance of 25 Ω /square at a pressure lower than 10⁻⁶ Torr. Organic materials were deposited at the rate of 0.5~1.2 Å s⁻¹. LiF and Al were deposited at the rate of 0.1 Å s⁻¹, 3-10 Å s⁻¹, respectively. Rest of the procedures are similar to the reported method.²

Synthesis procedure

Synthesis of (3,5-dibromophenyl)(pyridin-4-yl)methanone (*mDBBP*): In a flame dried threeneck flask under nitrogen atmosphere 1,3,5-tribromobenzene (5 g, 16.1 mmol) was dissolved in 160 mL of diethyl ether, and the solution was cooled to -78 °C. A solution of *n*-BuLi (2.5 M in hexane, 6.4 mL, 16.1 mmol) was added slowly so that the temperature did not rise above -76°C. The reaction mixture was stirred for 30 min at -78 °C, and a solution of 4-cyanopyridine (1.7 g, 16.1 mmol) in diethyl ether (20 mL) was added slowly. The mixture was stirred at -78 °C for 1 h and slowly allowed to warm to -25 °C, then 2 N HCl (50 mL) was added and the mixture was stirred for 20 min at room temperature. The mixture was made basic by the addition of 1 N NaOH. The product was recrystallized from methanol to obtain pure *m*DBBP in 78% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.85 (s, 2 H), 7.91 (st, *J* = 1.6 Hz, 1 H), 7.82 (sd, *J* = 1.6 Hz, 2 H), 7.55 (d, *J* = 4.8 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 192.23 (-CO-), 150.43, 143.05, 138.71, 138.65, 131.49, 123.51, 122.72; HRMS (EI, m/z): [M⁺] cal for C₁₂H₇Br₂NO 338.8894, found 338.8885.

Synthesis of *m*DCBP:

To a dried seal tube dibromo compound (*m*DBBP) (2.5 g, 7.33 mmol), carbazole (3.06 g, 18.33 mmol), Cu (0.93 g, 14.66 mmol), K₂CO₃ (5.06 g, 36.65 mmol) and 1,2-dichlorobenzene (20 mL) were added. The reaction tube was evacuated and purged with nitrogen gas three times under stirring followed by heating at 180 °C for 2 days. The reaction mixture was filtered through Celite and washed with ethyl acetate (30 mL). The solvent was evaporated under reduced pressure followed by column chromatography purification using EtOAc/*n*-hexane (1:3) as eluent afforded *m*DCBP in 57% yield. yellow solid; m.p. 219 °C: ¹H NMR (400 MHz, CDCl₃): δ 8.85-8.83 (m, 2 H), 8.14 (d, *J* = 8.0 Hz, 4 H), 8.13-8.11 (m, 3 H), 7.72-7.71 (m, 2 H), 7.54 (d, *J* = 8.0 Hz, 4 H), 7.47-7.43 (m, 4 H), 7.35-7.31 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 193.47 (-CO-), 150.67, 143.23, 140.13, 140.05, 139.24, 129.49, 126.51, 126.39, 123.81, 122.66, 120.87, 120.64, 109.29; HRMS (FAB⁺) cal for C₃₆H₂₃N₃O 513.1841, found 513.1840.



Fig. S1 HOMO, HOMO-1 and LUMO, LUMO+1 of mDCBP



Fig. S2 The absorption (Abs.) of *m*DCBP in various solvents (10^{-5} M) at room temperature.



Fig. S3 Oxidization wave of *m*DCBP in 10^{-3} M DCM solution. The electrode potentials were measured versus Ag/Ag⁺ electrode.



Fig S4. a) The temperature dependent transient PL characteristics, b) Prompt and delayed PL spectra of codoped film (mDCBP: DPEPO) and measured using 355 nm pulsed laser at 300 K. The delayed PL spectrum was collected with 10 µs delay time.



Fig. S5 Thermogravimetric thermogram of *m*DCBP.



Fig. S6 Differential scanning calorimetry (DSC) of mDCBP



Fig. S7 Powder-XRD patterns of *m*DCBP



Fig. S8 Structures of the materials used in devices (left) and device architecture (right).



Fig. S9 a) Current density and luminance vs driving voltage of device A-D, and b) Power efficiency vs luminance of device A-D.



Fig. S10 The EL spectra of device under different voltages a) device A, b) device B, c) device C and d) device D.