

Supplementary Information

Multifunctional phosphine oxide/diphenylamine hybrid compound as high performance deep-blue fluorescent emitter and green phosphorescent host

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EXPERIMENTAL SECTION

General Procedures. NMR spectra were determined on a Bruker Advance-400 spectrometer with chemical shifts reported as ppm. Mass spectrum data were obtained with a Finnigan 4021C GC-MS spectrometer. Elemental analysis (C, H, N) was carried out with an Elementar Vario ELIII element analyzer. Absorption and photoluminescence spectra were recorded with a Hitachi UV-vis spectrophotometer U-3010 and a Hitachi fluorescence spectrometer F-4500, respectively. Film state quantum fluorescence yield was measured by the integrating sphere method with an Edinburgh Instruments FLS920 spectrometer. TGA and DSC measurements were performed on a TA instrument TGA2050 and TA instrument DSC2910, respectively, with a heating rate of 10 °C min⁻¹ under the nitrogen atmosphere. Cyclic voltammetry was performed on a CHI660E electrochemical analyzer with 0.1 M Bu₄NPF₆ as a supporting electrolyte, saturated calomel electrode (SCE) as a reference electrode, Pt disk as a working electrode, and a scan rate of 100 mV s⁻¹.

Device Fabrication and Measurement. ITO coated glasses with a sheet resistance of 30 Ω per square were used as substrates. The substrates were first cleaned with isopropyl alcohol and deionized water, then dried in an oven at 120 °C, treated with UV-ozone, and finally transferred to a deposition system with a base pressure of about 1 × 10⁻⁶ Torr. Thermally evaporated organic materials were sequentially deposited at a rate of 1-2 Å s⁻¹ onto the ITO substrates. The cathode was completed by thermal deposition of LiF at a deposition rate of 0.1 Å s⁻¹, and then capped with Al metal deposited at a rate of 10 Å s⁻¹. EL luminescence, spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current-voltage characteristics were measured with a computer-controlled Keithley 2400 SourceMeter under ambient atmosphere.

Synthesis of 4'-bromo-N, N-diphenylbiphenyl-4-amine: A mixture of 4,4'-dibromobiphenyl (14.04 g, 45 mmol), Pd(OAc)₂ (175 mg, 0.75 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (420 mg, 0.75 mmol), diphenylamine (2.54 g, 15 mmol), and sodium tert-butoxide (2.16 g, 22.5 mmol) in 30 mL dry toluene was placed in a two-necked flask under a nitrogen atmosphere and was stirred at 90 °C for 15 h. After cooling, the reaction was quenched by water and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The product was purified by silica gel column chromatograph eluted with dichloromethane/petroleum ether (1: 5). White solid was obtained in a yield of 73%. ¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.50 (m, 2H), 7.45 – 7.39 (m, 4H), 7.31 – 7.25 (m, 4H), 7.12 (ddd, *J* = 9.2, 4.0, 1.8 Hz, 6H), 7.04 (dd, *J* = 10.5, 4.2 Hz, 2H). HRMS (EI, *m/z*): [M]⁺ calcd for C₂₄H₁₈BrN, 399.0623; found, 399.0621.

Synthesis of 4'-(diphenylphosphoryl)-N,N-diphenylbiphenyl-4-amine (POA): 4'-bromo-N, N-diphenylbiphenyl-4-amine (0.80 g, 2.0 mmol) was dissolved in anhydrous THF (20 mL) under nitrogen atmosphere. Then the mixture was cooled to -78 °C and n-BuLi (2.72 M in hexane, 1.0 mL) was added dropwise. After stirring for 1 h, chlorodiphenylphosphine (0.5 mL, 2.5 mmol) was added slowly. The resulting mixture was gradually warmed to ambient temperature and stirred for another 4 h.

The reaction was quenched by water and the mixture was extracted with dichloromethane. The combined organic layer was concentrated under reduced pressure. Then the concentrate was dissolved in dichloromethane (100 mL) and hydrogen peroxide (30 mL) was added, followed by stirring overnight at room temperature. The organic layer was extracted and washed with dichloromethane and distilled water. The extract was concentrated and then purified by silica gel column chromatograph eluted with acetone/petroleum ether (20: 1). White solid of POA was obtained with a yield of 58%. ^1H NMR (400 MHz, DMSO-d_6) δ 7.80 (dd, $J = 8.3, 2.3$ Hz, 2H), 7.70 – 7.60 (m, 10H), 7.60 – 7.51 (m, 4H), 7.34 (t, 4H), 7.13 – 6.99 (m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.93, 148.25, 144.98, 134.01, 133.43, 132.98, 132.89, 132.75, 130.18, 129.40, 129.28, 128.72, 127.34, 125.58, 124.14. HRMS (EI, m/z): $[\text{M}]^+$ calcd for $\text{C}_{36}\text{H}_{28}\text{NOP}$, 521.1909; found, 521.1909. Anal. calcd. for $\text{C}_{36}\text{H}_{28}\text{NOP}$: C, 82.90; H, 5.41; N, 2.69. Found: C, 82.87; H, 5.45; N, 2.65.

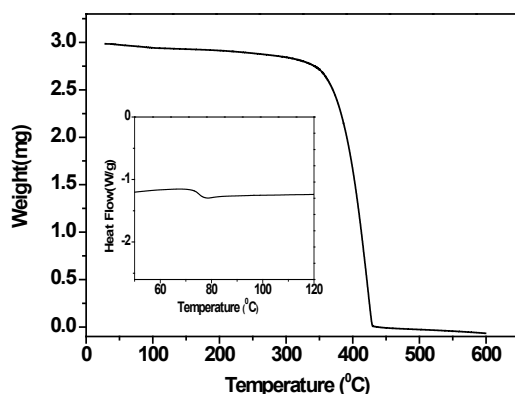


Figure S1. TGA and DSC (inset) curves of POA.

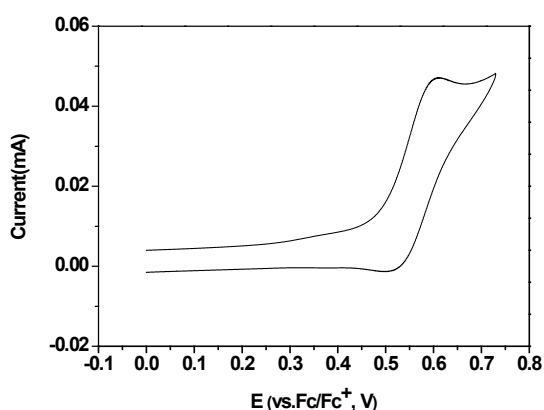


Figure S2. Cyclic voltammogram of POA in DMF.

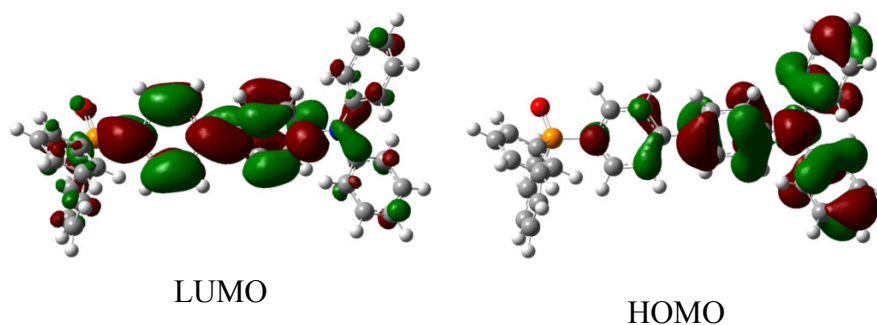


Figure S3. Calculated spatial distributions of the HOMO and LUMO of POA.

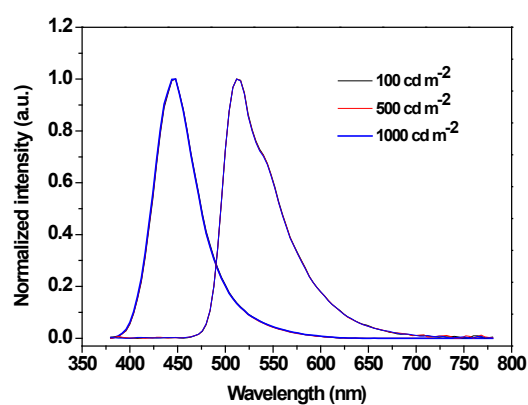
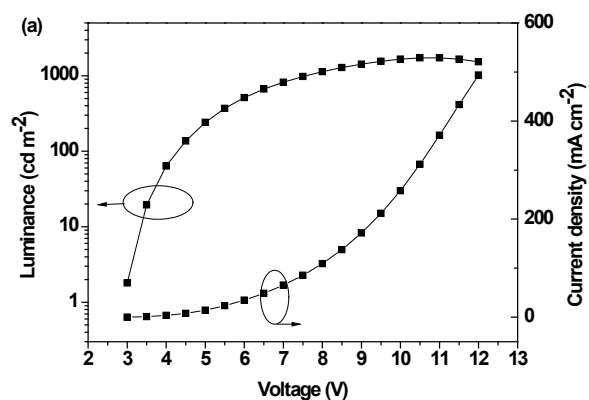


Figure S4. EL spectra of the POA-based blue fluorescence device and green phosphorescent device at different luminance.



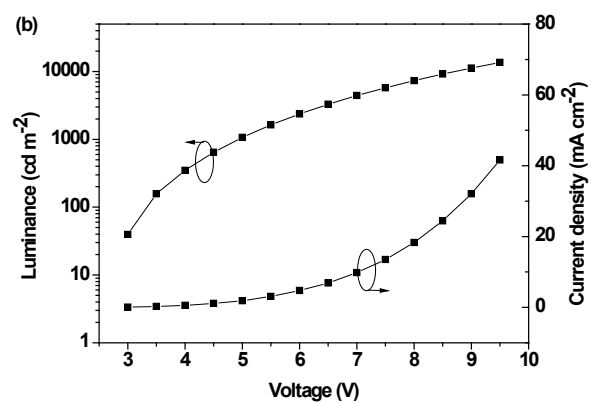


Figure S5. Luminance-voltage-current density characteristics of (a) the non-doped blue fluorescence device and (b) the green phosphorescent device doped with Ir(ppy)₃.