

Electronic supplementary information (ESI)

Multifunctional Bipolar Triphenylamine/Oxadiazole Derivatives: Highly Efficient Blue Fluorescence, Red Phosphorescence Host and Two-color Based White OLEDs

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Experimental

General Information: ¹H NMR and ¹³C NMR spectra were measured on a MECUYR-VX300 and MECUYR-VX600 spectrometer and in CDCl₃. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from dilute dichloromethane solution (ca. 5*10⁻⁶ mol/L) using the Edinburgh F-900 Instruments integrating sphere excited with Xe lamp. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min⁻¹ from 30 to 320 °C under argon, cooled fast to room temperature, then scanned again from 30 to 320 °C. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their

weight loss while heating at a rate of $15\text{ }^{\circ}\text{C min}^{-1}$ from 25 to $600\text{ }^{\circ}\text{C}$. Cyclic voltammetry (CV) was carried out in nitrogen-purged anhydrous DMF at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1} . Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

OLED Fabrication and measurement: The hole-injection MoO₃, hole-transporting material NPB (1,4-bis(1-naphthylphenylamino)-biphenyl), hole-blocking BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and electron-transporting materials Alq₃ (tris(8-hydroxyquinoline)aluminum) were commercially available. Commercial indium tin oxide (ITO) coated glass with sheet resistance of $10\ \Omega/\square$ was used as the starting substrates. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by UV/O₃ for 2 min. Then the sample was transferred to the deposition system. 10 nm of MoO₃ was firstly deposited to ITO substrate, followed by 80 nm NPB, 20 nm emissive layer, 10 nm BCP, and 30 nm Alq₃. Finally, a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminum were sequentially deposited onto the substrate in the vacuum of 10^{-6} Torr to construct the device. The I-V-B of EL devices was measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All measurements were carried out at room temperature under ambient conditions.

DFT Calculations: The calculated values of HOMO and LUMO energy levels are evaluated by the

DFT level of theory with the three-parameter Becke-style hybrid functional (B3LYP). The 6-31G(d) basis set was used for geometry optimizations of compounds under no constraints, and the 6-311G(d,p) was used for calculations of molecular orbital energies (HOMO and LUMO) and total energies of molecules. All these had been carried out in the Gaussian 03 package.

Preparation of 1 and 2: 4-(diphenylamino)phenylboronic acid ^[1], 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole and 2,5-bis(2-bromophenyl)-1,3,4-oxadiazole ^[2] were prepared according to literature procedures.

Synthesis of 4',4''-(1,3,4-oxadiazole-2,5-diyl)bis(N,N-diphenylbiphenyl-4-amine) (1): A mixture of 4-(diphenylamino)phenylboronic acid (0.58 g, 2 mmol), 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (0.38 g, 1 mmol), Pd(PPh₃)₄ (3 % mmol, 10 mg) and Na₂CO₃ (10 mmol, 1.06 g) in 15 ml of THF and 1.5 ml of distilled water was stirred at 80°C for 24 h under argon condition. After reaction, the resulting mixture was cooled to room temperature and then poured into water and extracted with dichloromethane. The organic extracts were collected and dehydrated with MgSO₄. After removal of the solvent, the crude product was purified by chromatograph using dichloromethane and petroleum ether (1:1) as eluent (R_f value is *ca.* 0.33). Pure compound was obtained by recrystallization from CHCl₃/C₂H₅OH as a yellow powder. Yield: 74%. ¹HNMR (CDCl₃, 300 MHz, δ): 8.18 (t, *J* = 7.6 Hz, 4H), 8.02 (d, *J* = 7.8 Hz, 2H), 7.67-7.75 (m, 6H), 7.53 (d, *J* = 8.1 Hz, 4H), 7.25-7.71 (m, 8H), 7.20 (d, *J* = 7.2 Hz, 8H), 7.06 (t, *J* = 7.4 Hz, 4H). ¹³CNMR (CDCl₃, 150 MHz, δ): 164.7, 148.3, 147.6, 144.1, 133.4, 132.7, 129.6, 128.5, 128.0, 127.6, 127.2, 125.0, 123.6, 122.3. FT-IR (cm⁻¹): 1594, 1485, 1276, 762, 696; MS (ESI): *m/z* 708.6 (M⁺). Anal. Calcd. for C₅₀H₃₆N₄O (%): C 84.72, H 5.12, N 7.90; Found: C 84.37, H 5.53, N 7.87.

Synthesis of 2',2''-(1,3,4-oxadiazole-2,5-diyl)bis(N,N-diphenylbiphenyl-4-amine) (2): A mixture of 4-(diphenylamino)phenylboronic acid (0.58 g, 2 mmol), 2,5-bis(2-bromophenyl)-1,3,4-oxadiazole

(0.38 g, 1 mmol), Pd(PPh₃)₄ (3 % mmol, 10 mg) and KOH^[3] (10 mmol, 0.56 g) in 15 ml of THF and 1.5 ml of distilled water was stirred at 80°C for 24 h under argon condition. The workup process was the same as **1** (Rf value is *ca.* 0.33). Pure compound was obtained by recrystallization from CHCl₃/C₂H₅OH as a white powder. Yield: 85%. ¹HNMR (CDCl₃, 300 MHz, δ): 7.86 (d, *J* = 6.6 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.46-7.51 (m, 4H), 7.10-7.19 (m, 8H), 7.96-7.98 (m, 20H). ¹³CNMR (CDCl₃, 150 MHz, δ): 165.4, 147.7, 147.4, 142.1, 134.3, 131.5, 131.1, 130.4, 129.8, 129.5, 127.6, 124.6, 124.6, 123.2, 123.1, 123.0. FT-IR (cm⁻¹): 1586, 1486, 1282, 757, 694; MS (ESI): *m/z* 708.2 (M⁺). Anal. Calcd. for C₅₀H₃₆N₄O (%): C 84.72, H 5.12, N 7.90; Found: C 84.62, H 5.73, N 7.91.

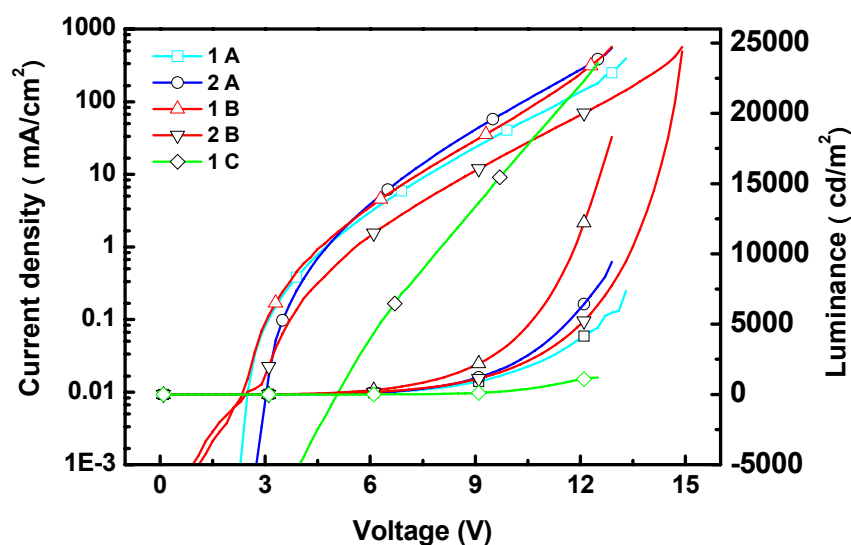


Figure S1. Voltage-Luminance-Current density characteristics of the devices

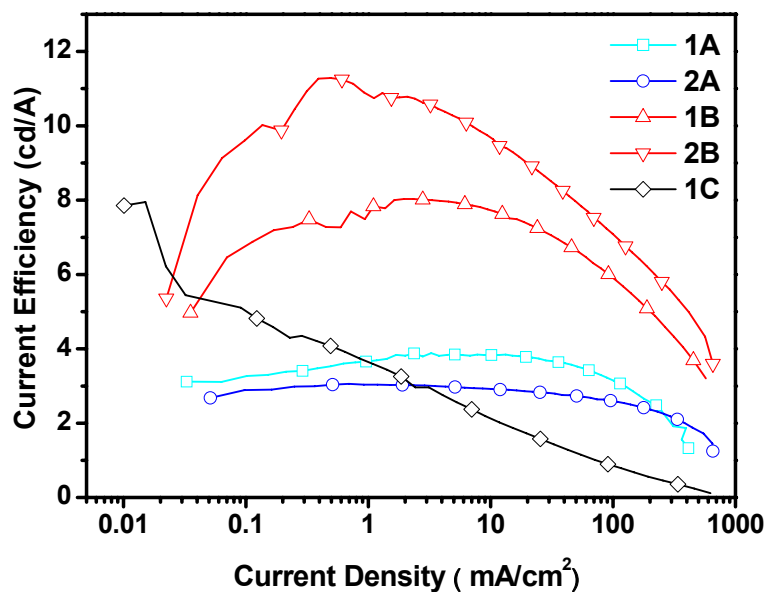


Figure S2. Current efficiency *versus* current density characteristics of the devices

Reference

- [1] Z. H. Li, M.S. Wong. *Org. Lett.*, **2006**, *8*, 1499.
- [2] X. M. Zheng, Z. Li, Y. L. Wang, W. D. Chen, Q. C. Huang, C. X. Liu, G. H. Song. *J. Fluor. Chem.*, **2003**, *123*, 163.
- [3] Y. Jiang, Y. Lu, Y. Cui, Q. Zhou, Y. Ma, J. Pei. *Org. Lett.*, **2007**, *9*, 4539.