Supporting Information

Bis(phosphine oxide)/ triphenylamine based material for solutionprocessed blue electrofluorescent and green electrophosphorescent

devices

Wei Jiang*, Peng Cui, Xinxin Ban, Yueming Sun*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu, 211189, P. R. China.

E-mail: jiangw@seu.edu.cn (W. Jiang); sun@seu.edu.cn (YM. Sun)

General information:

All chemical and reagents were obtained from commercial suppliers and used without further purification. ¹H NMR and ¹³C HMR spectra were measured on a Bruker ARX300 NMR spectrometer with tetramethylsilane as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Mass spectrometry was performed with a Electron Corporation Finnigan LTQ mass spectrometer. Absorption Thermo and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUOROMAX-4 spectrophotometer, respectively. The film PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 330 nm. The transient photoluminescence characteristics were measured using a transient spectrometer (Edinburg FL920P). TGA was recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC). Glass-transition temperature was recorded by DSC with a thermal analysis instrument (DSC 2910 modulated calorimeter). The film surface morphology was measured with AFM (Seiko Instruments, SPA-400). Cyclic voltammetry (CV) was performed on a CHI760D voltammetric analyzer in CH₂Cl₂ solutions at a scan rate of 100 mV s^{-1} with a glassy carbon rod as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M) and ferrocene was selected as the external standard. The film surface morphology was measured with AFM (Seiko Instruments, SPA-400).

Quantum chemical calculations:

All computations were done with Gaussian09 program package with different parameters for structure optimizations and vibrational analysis. The singlet ground states and triplet states of molecules were optimized by the restricted and unrestricted formalism of Becke's three-parameter exchange functional along with the Lee-Yang-Parr correlation functional with the restricted (B3LYP) at the standard split valence plus polarization function 6-31G(d) basis set. The inner reorganization energies were obtained by comparing the energies in charged and uncharged optimized configurations, for both neutral and ionized states:

 $\lambda_{+} = \lambda_{1} + \lambda_{2} = (E_{0}^{+} - E_{+}^{+}) + (E_{+}^{0} - E_{0}^{0}); \lambda_{-} = \lambda_{3} + \lambda_{4} = (E_{0}^{-} - E_{-}^{-}) + (E_{-}^{0} - E_{0}^{0})$

where E_{+}^{+} , E_{-}^{-} and E_{0}^{0} denote the energy of the cationic, anionic and neutral species at their respective optimized geometries. E_{0}^{+} and E_{0}^{-} denote the energy of the cationic and anionic species in the optimized neutral geometry respectively. Similarly, E_{+}^{0} and E_{-}^{0} represent the energy of the neutral molecule in the optimized cationic and anionic species geometries respectively. To compare the magnitudes of hole and electron mobility, we calculate the relative hopping rates of holes versus electrons, k_{+}/k_{-} , according to $(\lambda_{-}/\lambda_{+})^{1/2} \exp[(\lambda_{-} - \lambda_{+})/4kT]$ assuming *T* to be 300 K and neglecting the difference in the charge transfer integral (H_{ab}). *k* is the Boltzman constant.

Device fabrication:

In a general procedure, indium-tin oxide (ITO)-coated glass substrates were pre-cleaned carefully and treated by UV ozone for 6 min. A 40 nm PEDOT:PSS (Baytron P VP CH 8000) aqueous solution was spin coated onto the ITO substrate and baked at 120 °C for 30 min to remove the residual water. Then, 60 nm TPA-BPhPO was deposited onto the PEDOT:PSS layer by spincoating from 1,2-dichloroethane solution and annealed at 80 °C for 30 min. Another type of substrates were spin coated with the 8 wt% Ir(mppy)₃ doped TPA-BPhPO from 1,2dichloroethane solution and annealed at 80 °C for 30 min. Another type of an evaporation chamber, where the 40 nm TPBi was evaporated at an evaporation rate of $1\sim2$ Å/s under a pressure of 8×10^{-5} Pa and the Cs₂CO₃/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å/s for Cs₂CO₃ and Al, respectively, under a pressure of 1×10^{-3} Pa. The active area of the device was 9 mm². The current–voltage–brightness characteristics of the devices were characterized with Keithley 4200 semiconductor characterization system. The electroluminescent spectra were collected with a Photo Research PR705 Spectrophotometer. All measurements of the devices were carried out in ambient atmosphere without further encapsulations

Experimental section:

(5-bromo-1,3-phenylene)bis(diphenylphosphine oxide) (BPhPO-Br).

The mixture of 1-bromo-3,5-diiodobenzene (4.08 g, 10.0 mmol), diphenylphosphine (4.46 g, 24.0 mmol), $Pd(OAc)_2$ (0.22 g, 1.0 mmol), K_3PO_4 (6.4 g, 30 mmol), and dried Toluene 50 mL was refluxed under an argon atmosphere for 24 h. After cooling to room temperature, the solvent was

removed under vacuum. The crude material was dissolved in 1, 2-dichloromethane (30 mL) and to the solution was added 30% aqueous H_2O_2 (10 mL). The mixed solution was stirred for 2 h at room temperature. The organic and aqueous portions in the mixed solution were separated and the aqueous portion was extracted with dichloromethane two times and the combined organic layer was dried over MgSO₄. The product was then obtained by column chromatography on silica gel with dichloromethane/methanol (30:1) as the eluent, to yield a white solid (2.82 g, 50.6%). ¹H-NMR (300 MHz, CDCl₃, δ): 8.08 (s, 1H), 8.04 (s, 1H), 7.58-7.50 (m, 13H), 7.43-7.33 (m, 8H). ¹³C-NMR (300 MHz, CDCl₃, δ): 140.6, 140.5, 135.0, 134.5, 134.4, 134.3, 131.4, 131.2. MS (MALDI-TOF) [m/z]: calcd for C₃₀H₂₃BrO₂P₂, 557.3; found, 557.4. Anal. Calcd. for C₃₀H₂₃BrO₂P₂: C, 64.65; H, 4.16. Found: C, 64.60; H, 4.22.

(4'-(diphenylamino)-[1,1'-biphenyl]-3,5-diyl)bis(diphenylphosphine oxide) (TPA-BPhPO).

The mixture of BPhPO-Br (0.56 g, 1.0 mmol), N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)aniline (0.45 g, 1.2 mmol), and Pd(PPh₃)₄ (0.14 g, 0.15 mmol) were dissolved in 50 mL of 1,4-dioxane. After adding 10 mL of aqueous 2 N potassium phosphate solution, the reaction mixture was heated at 110 °C for 24 h. The cooled crude mixture was poured into water and extracted with dichloromethane and dried over MgSO₄, filtered, and evaporated to yield a crude product. The product was then obtained by column chromatography on silica gel with dichloromethane/methanol (30:1) as the eluent, to yield a white solid (0.47 g, 65%). ¹H-NMR (300 MHz, CDCl₃, δ): 8.20 (s, 1H), 8.16 (s, 1H), 7.64 (t, J=7.5 Hz, 8H), 7.54 (d, J=7.2 Hz, 4H), 7.45-7.39 (m, 10H), 7.30-7.26 (m, 6H), 7.12-7.06 (m, 7H). ¹³C-NMR (300 MHz, CDCl₃, δ): 132.8, 132.7, 131.6, 131.5, 131.4, 128.8, 128.2, 128.0, 127.4, 124.4, 124.3, 123.0, 122.6. MS (MALDI-TOF) [m/z]: calcd for C₄₈H₃₇NO₂P₂, 721.7; found, 721.7. Anal. Calcd. for C₄₈H₃₇NO₂P₂: C, 79.88; H, 5.17; N, 1.94. Found: C, 79.76; H, 5.20; N, 1.96.





Figure S1. ¹H-NMR and ¹³C-NMR of BPhPO-Br and TPA-BPhPO.



Figure S2. TGA and DSC curves of TPA-BPhPO recorded at a heating rate of 10 °C min⁻¹.



Figure S3. AFM images of neat TPA-BPhPO and 8 wt% Ir(mppy)₃-doped TPA-BPhPO films on ITO/PEDOT:PSS.



Figure S4. *I-V-L* characteristics of TPA-BPhPO based devices.