



Design of high triplet energy electron transporting material for exciplex-type host: Efficient blue and white phosphorescent OLEDs based on solution processing



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ABSTRACT

A high triplet energy electron transporting material 1,3,5-tris(diphenylphosphoryl)benzene (TPO) was successfully designed and synthesized to form an efficient exciplex with the commonly used hole transporting molecule tris(4-carbazoyl-9-ylphenyl)amine (TCTA). The singlet-triplet energy difference in this exciplex was only 0.03 eV, which leads to the successive triplet up-conversion and delayed fluorescence. In addition, due to the high triplet energies of TPO and TCTA, the energy leakage from exciplex-state to the constituting molecule was eliminated. By employing this exciplex as host, solution-processed white phosphorescent OLEDs have been realized with a low turn-on voltage of 3 V and a high power efficiency of 20.5 lm W⁻¹. These results indicate that the well-designed exciplex can be used as efficient host material for low-cost solution-processed OLEDs.

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1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted a great deal of attention due to their potential application in solid state lighting and 100% internal quantum efficiency [1–5]. However, the host matrixes, which are used to prevent triplet-triplet annihilation of the phosphorescence emitter, usually lead to a high operating voltage because of the large energy band gap [6–9]. Recently, developing host material with small singlet-triplet split (ΔE_{ST}) has been demonstrated to be an effective way to reduce the operating voltage of PHOLEDs [10–12]. As a result, the turn-on voltages of vacuum-deposited blue and green PHOLEDs have approached the theoretical limits by using host materials with small ΔE_{ST} [13–15]. Nevertheless, the design of donor/acceptor molecule to attain sufficiently small ΔE_{ST} is nontrivial, which requires the ingenious separation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) within one framework [16–20]. Up to now, only a few of hosts with small ΔE_{ST} have been successfully developed to reduce the operating voltage of solution-processed PHOLEDs due to the

severe limitation of molecular design [21–26]. Alternatively, the excited states with intrinsically small ΔE_{ST} (≈ 0 –50 meV) can also be achieved by the formation of exciplex via intermolecular charge transfer between physically blended electronic donor and acceptor molecules [27–29]. Kim et al. have reported the vacuum deposited blue PHOLEDs achieved a very low driving voltage of 2.75 V at 100 cd A⁻¹ by using the exciplex formation co-host [30–32]. As for wet technology, Wang et al. demonstrated a maximum power efficiency of 96 lm W⁻¹ with a turn on voltage of 2.36 V for solution-processed yellow PHOLEDs by incorporating interfacial exciplex into the device architecture [33]. However, several challenges make it difficult to generate a solution-processible exciplex-type host used for blue and white PHOLEDs. Primary design criteria are as following: (1) both the donor and acceptor materials possess high solubility and good film forming ability through wet-process; (2) The difference between energy levels of the two components should be large enough for efficient exciplex formation [34–37], while a high-lying HOMO and a low-lying LUMO of donor and acceptor are needed to match the Fermi levels of charge injection layers; (3) More importantly, the excited-state energy of the exciplex should be greater than the blue dopant but less than the constituting molecules to confine the back energy transfer from guest to host and eliminate the energy leakage from exciplex to components, respectively [38–41]. In view of these requirements,

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the development of solution-processible electron-transporting molecules, which possess high triplet energy and exciplex-formation property, seems to be imminent.

In this work, we designed and synthesized a new phosphine oxide-based electron-acceptor 1,3,5-tris(diphenylphosphoryl)benzene (TPO). The high triplet energy of TPO can be well-preserved due to disruption of conjugation by the phosphine oxide linkage. The star shaped molecular structure effectively hinders π - π stacking in the solid state and endows the compound good film-forming ability through spin-coating. In addition, an efficient exciplex state was achieved by equal blending TPO with the widely used electron donor tris(4-carbazoyl-9-ylphenyl)amine (TCTA). Moreover, the photo energy of the formed exciplex is higher than that of blue dopant and the unwanted energy leakage is completely eliminated. By employing this exciplex as host, a solution-processed white phosphorescent OLED has been realized with a very low turn-on voltage of 3.0 V and a high power efficiency of 20.5 lm W⁻¹, which are among the best values reported up to now. Noticeably, the efficiency roll-off of this white PHOLED is extremely small even the luminance up to 10,000 cd m⁻², which further demonstrates the superiority of our exciplex used for solution-processed devices.

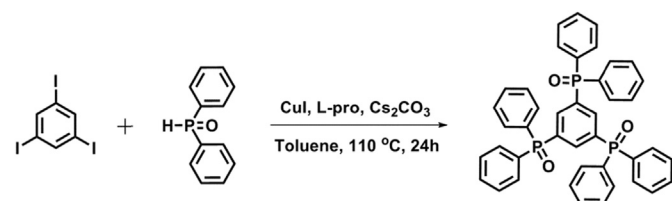
2. Experimental section

2.1. General methods

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. ¹H NMR and ¹³C NMR spectra were recorded on a BRUKER AMX 300-MHz instrument. Elemental analysis was determined by an Elementar Vario EL CHN elemental analyzer. Mass spectrometry was performed with a Thermo Electron Corporation Finnigan LQ mass spectrometer. The UV-Vis absorption spectra of the compounds were measured by SHIMADZU UV-2450. The photoluminescence emission spectra were recorded on HORIBA FLUOROMAX-4 and liquid nitrogen was placed into the optical Dewar flask for low-temperature (77 K) photophysical measurements. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) curves were recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) and DSC 2910 modulated calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹. Cyclic voltammetry (CV) was performed on a CHI750C voltammetric analyzer in a typical three-electrode cell with a platinum plate working electrode, a platinum wire counter electrode and a silver wire reference electrode. The electrochemical experiment was carried out after bubbled with a constant nitrogen flow for 20 min at room temperature.

2.2. Materials

The synthetic procedure for TPO was illustrated in Scheme 1. The dry nitrogen atmosphere was used in the reactions involving



Scheme 1. Synthetic route and chemical structure of TPO.

air-sensitive reagents.

2.2.1. 1,3,5-tris(diphenylphosphoryl)benzene (TPO)

A mixture of 1,3,5-triiodobenzene (0.46 g, 1.0 mmol), diphenylphosphine oxide (0.73 g, 3.6 mmol), CuI (0.06 g, 0.30 mmol), L-proline (0.04 g, 0.30 mmol), and Cs₂CO₃ (1.5 g, 4.5 mmol) was added to toluene solution (30 mL). The mixture was refluxed under nitrogen for 48 h. After the reaction finished, the reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried by anhydrous MgSO₄ and filtered. The product was isolated by silica gel column chromatography using methanol/ethyl acetate (1:5) as eluent to afford a white solid (0.64, 52%). ¹H NMR (300 MHz, CDCl₃, δ): 8.08 (t, J = 11.9 Hz, 3H), 7.52 (dd, J = 12.9, 7.2 Hz, 18H), 7.39 (dd, J = 9.8, 4.8 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃, δ): 141.05, 141.02, 140.91, 134.89, 134.66, 134.39, 133.00, 131.36, 131.19, 31P NMR (121 MHz, CDCl₃, δ): 27.59. HRMS [m/z]: calcd for C₄₂H₃₃O₃P₃, 678.1643; found, 679.1711 [M+H⁺]. Anal. Calcd. for C₄₂H₃₃O₃P₃: C, 74.33; H, 4.90. Found: C, 74.36; H, 4.88.

2.3. Device fabrication and measurement

In a general procedure, indium-tin oxide (ITO)-coated glass substrates were pre-cleaned and treated with UV ozone. The poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) aqueous solution was pin-coated onto the ITO substrate and baked at 200 °C for 10 min under vacuum. The substrates were then taken into a nitrogen glove box, where the emission layer of TCTA:TPO doped with Flrpic or (fbi)₂Ir(acac) was spin-coated onto the PEDOT:PSS layer from 1,2-dichloroethane solution and annealed 80 °C for 30 min. The substrate was then transferred into an evaporation chamber, where the Cs₂CO₃/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å s⁻¹ for Cs₂CO₃ and Al, respectively, under a pressure of 1 × 10⁻³ Pa. The current-voltage-brightness characteristics of the devices were characterized with Keithley 2400 semiconductor characterization system. The electroluminescent spectra were collected with a Photo Research PR655 Spectrophotometer. All measurements of the device were carried out in ambient atmosphere without further encapsulations.

3. Results and discussion

TPO was easily synthesized by the Ullmann coupling reaction of 1,3,5-triiodobenzene with excess diphenyl phosphine oxide using CuI/L-proline/Cs₂CO₃ catalyst system. Prior to device fabrication, the product was purified by silica gel column chromatography and recrystallization to give white powders. ¹H NMR, ¹³C NMR, HRMS, and elemental analysis were used to confirm the chemical structure of the new compounds.

The electrochemical property of TPO was investigated by cyclic voltammetry (CV) as shown in Fig. 1. On the basis of the onset potentials for reduction, the LUMO energy level of TPO was estimated to be -2.75 eV, with regard to ferrocene (LUMO = -(E_{red}^{onset} + 4.8) eV). The low-lying LUMO energy level of TPO suggests the potential for good electron-injection from high work function metals such as Al. From the onset absorption in CH₂Cl₂ (Fig. S1), the optical energy band gap (E_g) of TPO was determined to be 4.35 eV. As a result, the HOMO level was further calculated to be -7.1 eV by subtraction of the E_g from the LUMO level. The thermal properties of TPO were also investigated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) under a nitrogen atmosphere. As shown in Fig. 3, the TGA curve confirmed the high thermal stability of TPO with a decomposition temperature (T_d, 5% weight loss) of 428 °C.

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