

# Tuning the energy gap and charge balance property of bipolar host by molecular modification: Efficient blue electrophosphorescence devices based on solution-process



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## ABSTRACT

Three bipolar hosts composed of electron-accepting diphenylphosphine oxide and electron-donating carbazole/triphenylamine have been synthesized and characterized. With structural topology modification, the particular physical properties of the materials can be subtly optimized, such as the thermal stability, singlet–triplet energy gap and charge balance ability. Both DFT calculation and experiment results demonstrate that the introduced triphenylamine can effectively minimize the HOMO–LUMO energy gap, while the carbazole units can prevent the excited energy loss and keep high triplet energy ( $E_T = 3.0$  eV) due to the enhanced molecular rigidity. As a result, solution-processed blue PHOLEDs exhibited a high current efficiency of  $25.2 \text{ cd A}^{-1}$  and a power efficiency of  $11.5 \text{ lm W}^{-1}$ , which implies that the unique molecular modulation is very cost-effective and competitive for the device performance improving.

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## 1. Introduction

Solution-based fabrication techniques, such as spin-coating, inkjet-printing and roll to roll, are fascinating due to their potential advantages for the cost-effective production of large area solid state lighting and flexible display [1–3]. Although the phosphorescent emitter has led to the internal quantum yield close to unity by using the effective inter-system crossing from excited singlet to highly emissive triplet states, the performance of solution-processed phosphorescent organic light-emitting diodes (PHOLEDs) was also moderate to the vacuum deposited counterpart [4–8]. Actually, several reasons exist for restricting the development of solution technology: (1) the difficulty in deposition of multilayer due to the interface mixing and erosion during spin-coating the subsequent layers [9–11], (2) the inevitable conflict between high triplet energy and the solution-processible required large molecular weight [12–14], (3) the unbalanced carrier transfer in the EML due to the solvent impurity and oxygen diffusion induced electron traps [15].

The common concept to improve the efficiency of PHOLEDs is the realization of the charge-recombination zone inside the emission layer by utilizing multilayer device configuration and suitable host/guest system, which can reduce the non-radiative energy losses of the triplet extensions [12,16]. However, sequential

deposition of hole-transport layers (HTLs) or electron-transport layers (ETLs) will be inherently difficult for the solution-processing technique, because the solvent used to deposit the subsequent layer tends to dissolve or swell the underlying layer. Therefore, great experimental efforts have focused on developing of suitable host materials. Ding and coworkers synthesized a series of dendritic hosts by incorporating carbazole dendrons to the 2,2'-dimethyl-biphenyl core, which can ensure the solution-processible ability while keeping the triplet energy as high as possible [17,18]. However, the unipolar carbazole-based dendrimer must physically blend electron transporting materials to balance the charge transfer in the EML and the multi-disperse molecular structure may induce the potential phase separation effect to destroy the application of device [19]. Besides the carbazole-based dendrimers, a well-established approach to prepare efficient host material is the incorporation of hole- and electron-transporting moieties into one molecule to provide more balanced carrier fluxes and better charge transport properties in the emission layer (EML) [20–22]. Xu et al. have demonstrated that the using of bipolar host could not only enhance the charge balance property of the EML, but also potentially simplifying the device structure (i.e., free of using an HTL and/or ETL) [23–25]. Despite these advantages, an essential compromise between the triplet energy ( $E_T$ ) and molecular weight is inevitable for designing solution-processable host materials, since the former requires a small conjugated length, whereas the large conjugated group benefits the latter. Apart from the high triplet energy, in order to

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enhance the power efficiency of the PHOLEDs, it is necessary to adjust singlet energy ( $E_S$ ) as low as possible to reduce the operating voltage [25]. In other words, small energy difference between  $E_S$  and  $E_T$  (so-called  $\Delta E_{ST}$ ) and high triplet energy are essentially required to design an effective host material [26]. However, as most of the modification approaches have the same effect on both singlet and triplet states, the development of a promising bipolar host material with small  $\Delta E_{ST}$ , especially for solution processed PHOLEDs, is a highly challenging task due to the severe limitation of molecular design [27–33].

In this work, three novel bipolar hosts composed of electron-transporting diphenylphosphine oxide (PO) moieties and hole-transporting carbazole/triphenylamine, namely TPAPO, pCzPO and mCzPO, were designed, synthesized and characterized. Interestingly, the slight move in one part of the molecule can finely affect the optoelectronic property as a whole, and consequently modulating the triplet state distributions, HOMO–LUMO energy gaps and charge balance abilities. Therefore, the soluble-based blue emission PHOLEDs were fabricated and the corresponding relationships between molecular structure and device performance were systematically researched.

## 2. Experimental

### 2.1. General information

All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received.  $^1\text{H}$  NMR and  $^{13}\text{C}$  HMR spectra were measured on a BRUKER AMX 300-MHz instrument with tetramethylsilane as the internal standard. Elemental analysis was performed on an Elementar Vario EL CHN elemental analyzer. Molecular masses were determined by a BRUKER DALTONICS Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS), with  $\alpha$ -cyano-hydroxycinnamic acid as a matrix. Absorption and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUOROMAX-4 spectrophotometer, respectively. Phosphorescence spectra at 77 K were measured in a dichloromethane solvent. Thermogravimetric analysis (TGA) was recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) under a dry nitrogen gas flow at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Glass-transition temperature was recorded by (DSC) at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  with a thermal analysis instrument (DSC 2910 modulated calorimeter). Cyclic voltammetry (CV) was performed on a CHI750C voltammetric analyzer in a typical three-electrode cell with a platinum plate working electrode, a silver wire reference electrode and a platinum wire counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected to determine the potential of the silver wire electrode. The solutions were bubbled with a constant nitrogen flow for 15 min before measurements. The film surface morphology was measured with AFM (Seiko Instruments, SPA-400).

### 2.2. Quantum chemical calculations

The molecular structures for the three compounds in their neutral, cationic and anionic states were optimized by DFT method using the B3LYP functional, which employs the gradient correction of the exchange functional with three parameters by Becke and the correlation functional by Lee et al. The 6-31G(d) basis set was applied to the studied compounds. The values of  $k^+$  and  $k^-$  were also calculated for the DFT-optimized structures by both

B3LYP/6-31G(d) level. All calculations were carried out using the Gaussian 09 program.

### 2.3. Device fabrication and performance measurements

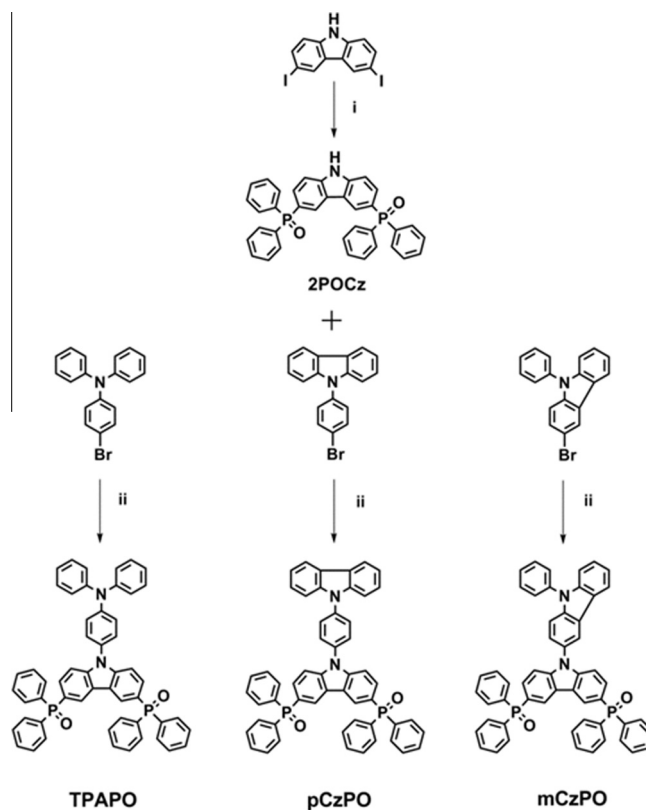
In a general procedure, indium–tin oxide (ITO)-coated glass substrates were pre-cleaned and treated with UV ozone. The poly (ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) aqueous solution was pin-coated onto the ITO substrate and baked at  $200\text{ }^\circ\text{C}$  for 10 min under vacuum. The substrates were then taken into a nitrogen glove box, where the emitting layers consist of hosts and Flrpic was deposited by spin-coating from solution. The substrate was then transferred into an evaporation chamber, where the TmPyPB electron-transporting layer was evaporated at an evaporation rate of  $1\text{--}2\text{ \AA s}^{-1}$  under a pressure of  $8 \times 10^{-5}\text{ Pa}$  and the  $\text{Cs}_2\text{CO}_3/\text{Al}$  bilayer cathode was evaporated at evaporation rates of 0.2 and  $10\text{ \AA s}^{-1}$  for  $\text{Cs}_2\text{CO}_3$  and Al, respectively, under a pressure of  $1 \times 10^{-3}\text{ Pa}$ . 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 device were carried out in ambient atmosphere without further encapsulations.

### 2.4. Materials

TPAPO, pCzPO and mCzPO were synthesized according to the procedure in Scheme 1. All manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere.

### 2.5. 3,6-bis(diphenylphosphoryl)-9H-carbazole (2POCz)

A mixture of 3,6-diiodo-9H-carbazole (4.20 g, 10.0 mmol), diphenylphosphine (4.46 g, 24.0 mmol),  $\text{Pd}(\text{OAc})_2$  (0.22 g,



Scheme 1. Synthetic routes and chemical structures of TPAPO, pCzPO and mCzPO.

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