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Tuning of Charge Balance in Bipolar Host Materials for Highly Efficient Solution-Processed Phosphorescent Devices

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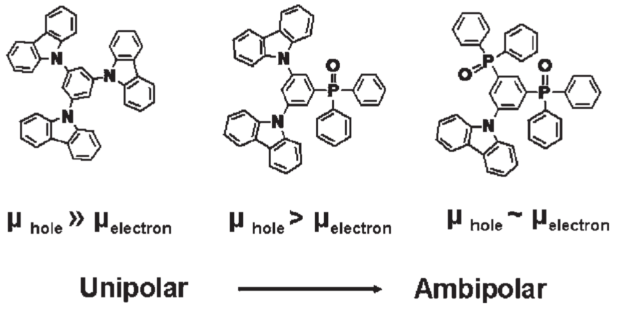
ABSTRACT



A novel bipolar host material, which meets the requirements of high triplet energy, good charge carrier transport properties, high solubility, and film-forming ability at the same time, has been designed and synthesized. Utilizing a new compound as host material, high-efficiency solution-processed blue and white phosphorescent organic light-emitting diodes (PHOLEDs) have been achieved.

White organic light-emitting diodes (WOLEDs) have attracted considerable interest because of their potential applications in full-color display panels, flexible displays, and lighting sources.[1] The most promising approach to manufacture highly efficient WOLEDs is phosphorescent OLED (PHOLED) technology because the phosphors could harvest both singlet and triplet excitons, yielding an internal quantum efficiency as high as 100%.[2] Most recently, Reineke et al. achieved WOLEDs with a record efficiency of 120 lm W^{-1} by using phosphorescent emitters with improved out-coupling structures.[3] This efficiency was comparable to that of fluorescent tubes.[4] Another challenge for WOLED lighting is to reduce the fabrication cost. A solution process based device fabrication is considered to open the way to true low-cost mass production of large-area lighting devices.[5] Other than polymer-based materials, solution processable small-molecule materials can be conventionally synthesized and purified. However, fabrication of high-performance solution-processed WOLEDs based on small molecules is limited by the relatively low efficiency of blue PHOLEDs. Hence, promotion of small-molecule host materials for solution-processed blue PHOLEDs is the key of power-efficient WOLEDs.

A good host material for solution-processed blue PHOLEDs should have the following features: high triplet

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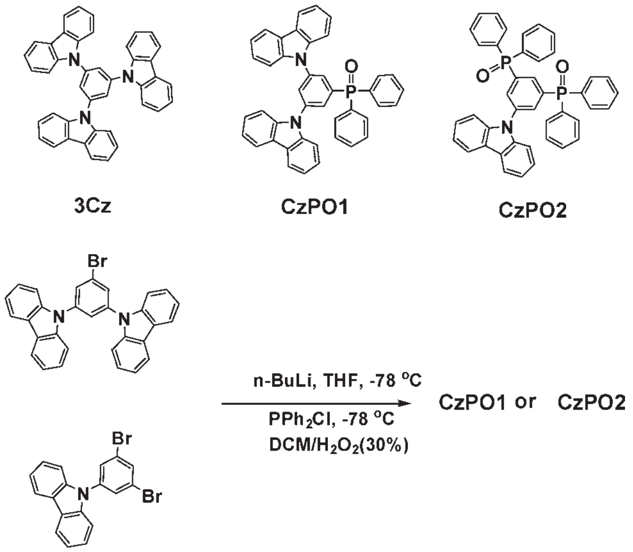
energy, good charge carrier transport properties, high solubility, and film-forming ability. Recently, during the search for the host materials for blue PHOLEDs, a great deal of attention has been given to bipolar transporting molecules containing electron-transporting diphenylphosphine oxide[6] and hole-transporting carbazole[7] units. Utilization of bipolar host materials can balance the charge carriers and broaden the recombination zone in the emitting layer, therefore reduce the efficiency roll-off. Most importantly, it could allow the fabrication of efficient single-layer devices.[8]

Scheme 1. Synthetic Route for CzPO1 and CzPO2



In this paper, we report the use of carbazole and diphenylphosphine oxide as the bulky units, which are connected to the phenyl core to build novel star-shaped host materials, 9,9′-(5-(diphenylphosphoryl)-1,3-phenylene)bis(9*H*-carbazole) (CzPO1) and 9-(3,5-bis(diphenylphosphoryl)phenyl)-9*H*-carbazole (CzPO2) (illustrated in Scheme 1). There are several strategies to the design of bipolar host materials for solution-processed blue PHOLEDs. (i) The unique star-shaped structure of molecules greatly enhances the thermal stability of these materials, and the nonconjugation linkage mode keeps the triplet energy gap at a very high level.[9] (ii) Phosphine oxide units are introduced to replace the carbazole units in unipolar hole-transport host material 1,3,5-tri(*N*-carbazolyl)benzene (3Cz) to achieve bipolar transporting character. (iii) The polar nature of the phosphine oxide helps to increase the solubility of the host materials in the most common solvents. The solution-processed devices with our new hosts showed excellent performance, with a luminous efficiency (LE) of 23.6 cd A^{-1} and an external quantum efficiency (EQE) of 12.2% for blue PHOLEDs and a LE of 33.8 cd A^{-1} and an EQE of 12.0% for white PHOLEDs, which are among the highest reported values for small molecule based solution-processed blue and white PHOLEDs.

As shown in Scheme 1, the starting materials were treated with excess *n*-BuLi at −78 °C to give lithiated intermediates, which were subsequently quenched with chlorodiphenylphosphine to give the corresponding phosphine-containing intermediates. Oxidation of the phosphine-containing intermediates with aqueous H_2O_2 (30%) led to the desired CzPO1 and CzPO2 in 60% and 51% yields, respectively. Additionally, CzPO1 and CzPO2 exhibited excellent thermal stability with the 5% weight-loss decomposition temperatures of 391 and 386 °C, with the glass transition temperatures of 111 and 96 °C, respectively, which suggests that they could form morphologically stable and uniform amorphous films. The phosphine oxide group also increased the solubility of the host materials in the common solvents, and the smooth surface roughness less than 0.5 nm was obtained from the spin-coated films.

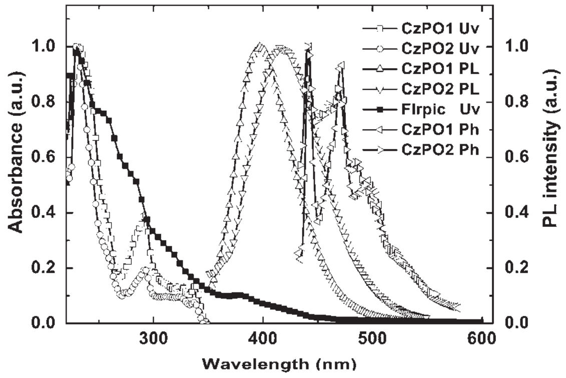


Figure 1. Absorption and emission spectra of CzPO1, CzPO2, and FIrpic in CH_2Cl_2 and phosphorescent spectra of CzPO1 and CzPO2 in 2-methyltetrahydrofuran at 77 K.

Figure 1 depicts the UV–vis absorption and photoluminescence (PL) spectra of the compounds. The absorption peaks at around 292 nm could be assigned to the $n-\pi^*$ transitions of the carbazole moiety, while the longer wavelength absorption at around 339 nm could be attributed to $\pi-\pi^*$ transitions from the electron-donating carbazole moiety to the electron-accepting diphenylphosphine oxide

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moiety. Their PL spectra exhibit peaks at 418 and 397 nm for CzPO1 and CzPO2, respectively, which were well overlapped with the metal-to-ligand charge-transfer absorption peaks of the iridium(III) bis(4,6-difluorophenylpyridinato)-picolinate (FIrpic), indicating that the Förster energy transfer from the host materials to the FIrpic would be efficient. The triplet energies of CzPO1 and CzPO2, measured from the low-temperature photoluminescence spectra, were 2.81 and 2.82 eV, respectively, larger than that of the guest blue-emitter of FIrpic.

The electrochemical properties of CzPO1 and CzPO2 compared with 3Cz were investigated by cyclic voltammetry (Figure 2a). CzPO1, CzPO2, and 3Cz exhibited similar quasi-reversible oxidation process, which can be assigned to the oxidation of electron-donating carbazole moiety, with onset potentials of 1.79, 1.72, and 1.59 V, respectively. Upon cathodic sweeping in THF, CzPO1, and CzPO2 exhibited reversible reduction waves, arising from their electron-accepting diphenylphosphine oxide moiety, with onset potentials of -1.84 and -1.70 V, respectively. In contrast, the diphenylphosphine oxide-free counterpart 3Cz exhibited no reduction wave during the cathodic scan, which implies that the incorporation of the electron-accepting diphenylphosphine oxide functionalities in CzPO1 and CzPO2 would facilitate electron-transporting in the emitting layer.[5b] On the basis of the onset potentials for oxidation and reduction, we estimated the HOMO and LUMO energy levels of CzPO1 and CzPO2 to be -5.78, -2.20, -5.85, and -2.34 eV, respectively, with regard to ferrocene (-4.8 eV below vacuum).[10] This reversible reductive and quasi-reversible oxidative behaviors indicate that CzPO1 and CzPO2 possess both hole- and electron-transporting characteristics.[6a,11] DFT calculations were performed to understand the physical properties of CzPO1 and CzPO2 at the molecular level (Figure 2b). The HOMO and LUMO levels of CzPO1 and CzPO2 are mainly located at the electron-donating carbazole and electron-accepting diphenylphosphine oxide fragments, respectively, consistent with the electrochemical studies that the carbazole groups control the HOMO levels and the diphenylphosphine oxide groups are responsible for the LUMO levels of CzPO1 and CzPO2.

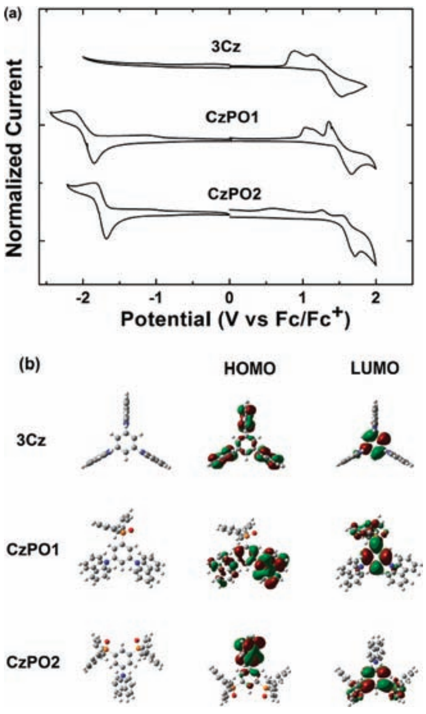

Figure 2. (a) Electrochemical properties of 3Cz, CzPO1, and CzPO2. (b) Optimized geometries and calculated HOMO and LUMO density maps for 3Cz, CzPO1, and CzPO2.

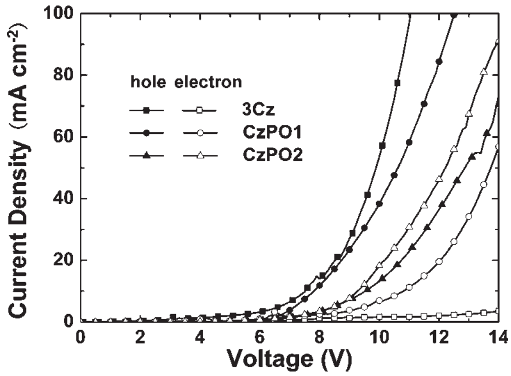

Figure 3. Current density versus voltage for the hole-only and electron only devices of 3Cz, CzPO1, and CzPO2.

Hole-only and electron-only devices were fabricated to investigate the bipolar character of CzPO1 and CzPO2 (Figure 3). The hole-only device consists of the following structure: ITO/PEDOT:PSS (40 nm)/hosts (60 nm)/NPB (20 nm)/Al (100 nm). The electron-only devices contain the following layers: ITO/hosts (60 nm)/TPBI (30 nm)/Cs_2CO_3 (2 nm)/Al (100 nm). According to the $J-V$ curves of hole-only devices, a decrease in the numbers of carbazole groups contained in the molecule structures leads to a decrease in hole-current densities of 3Cz, CzPO1 and CzPO2, which can be explained by the higher HOMO energy level and the increased hole mobility of 3Cz compared with those of CzPO1 and CzPO2.[6d] In contrast, the CzPO2-based device shows the highest electron-current density, relative to those in the 3Cz- and CzPO1-based devices, because of the appropriate LUMO level for better electron injection and high electron mobility. Furthermore, there was a slight difference between the hole- and electron-current densities in the CzPO2, which can be expected since holes and electrons can be balanced by the incorporation of both donor (carbazole) and acceptor (diphenylphosphine oxide) units into molecule structures.

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These results indicate that the CzPO2 shows the bipolar charge-transport property.[6c]

The single-layer devices A with the configuration ITO/PEDOT/PSS (40 nm)/host/FIrpic (10 wt %) (80 nm)/Cs_2CO_3 (2 nm)/Al (100 nm) have been fabricated. Excellent performance was observed in device using CzPO2 as host, which was turned on at 5.4 V (corresponding to 1 cd m^{-2}), with the maximum LE of 10.2 cd A^{-1} and the maximum EQE of 5.4%. In contrast, the single-layer device based on CzPO1 and 3Cz showed poor performance with the maximum LE (3.8 cd A^{-1}, 0.2 cd A^{-1}), the maximum EQE (2.0%, 0.1%), and the turn-on voltage (7.0 V, 13.6 V), respectively. The increased driving voltage can be attributed to the low electron mobility of CzPO1 and 3Cz. However, efficiency of the device based on CzPO2 is much higher than that of the devices based on CzPO1 and 3Cz, maybe because of the bipolar transporting nature of CzPO2 that increasing carrier balance in the emitting layer.

To further improve the performance of the device on the basis of CzPO2, a thin 30 nm TPBI electron-transporting and exciton-confining layer was inserted between the light-emitting layer and the cathode.[12] Devices B with configurations of ITO/PEDOT/PSS/host/FIrpic(10 wt %) (80 nm)/TPBI(30 nm)/Cs_2CO_3 (2 nm)/Al (100 nm) have been fabricated. After the insertion of the TPBI layer, the maximum LE of the $CzPO_2$-based device was largely improved to 23.6 cd A^{-1} and the corresponding maximum EQE to 12.2%, which was comparable to the vacuum-deposited multilayer devices previously reported.[7g,13]

Furthermore, a two-color-based single-layer phosphorescent WOLED via solution process was fabricated by codoping the blue phosphorescent dye FIrpic and the orange phosphorescent dye bis[2-(9,9-diethyl-9*H*-fluoren-2-yl)-1-phenyl-1*H*-benzoimidazol-N,C^3]-iridium(acetylacetonate) [$(fbi)_2Ir(acac)$] into the emitting layer with the configuration ITO/PEDOT/PSS/host/FIrpic (10 wt %)/$(fbi)_2Ir(acac)$ (0.2 wt %)/Cs_2CO_3 (2 nm)/Al (100 nm) (device C). The maximum efficiency was achieved in the $CzPO_2$-based single-layer device C with a LE of 21.4 cd A^{-1} and an EQE of 7.4%. The best solution-processed phosphorescent WOLED performance was achieved in devices D with a configuration of ITO/PEDOT/PSS/$CzPO_2$/FIrpic (10 wt %)/$(fbi)_2Ir(acac)$ (0.2 wt %)/TPBI (30 nm)/Cs_2CO_3 (2 nm)/Al (100 nm), which show the maximum LE of 33.8 cd A^{-1} and an EQE of 12.0%. The performance of $CzPO_2$-based device D is among the highest for solution-processed phosphorescent WOLEDs. Additionally, the electroluminescence (EL) spectra of device D are show in Figure 4. The Commission Internationale de L'Eclairage (CIE) coordinates of device D remain almost invariable when the driving voltage goes from 8 V (0.36, 0.45) to 14 V (0.35, 0.45).

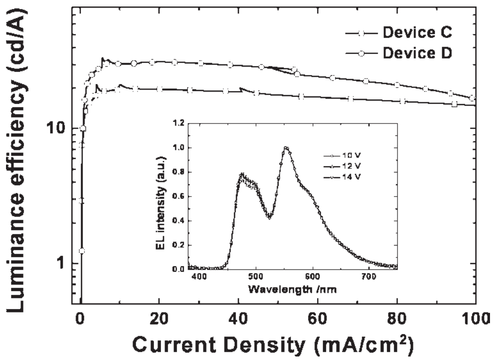

Figure 4. Current efficiency versus current density of device C and device D. Inset: normalized EL spectra of device D.

In summary, we have designed and synthesized a novel series of solution processable bipolar host materials by incorporating carbazole and diphenylphosphine oxide units into the star-shaped structure. Utilizing these compounds as host materials, high-efficiency solution-processed blue and white PHOLEDs have been achieved because of their high triplet energies, excellent morphological stability, and bipolar nature.

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Supporting Information Available. Experimental and characterization details for all new compounds.This material is available free of charge via the Internet at http://pubs.acs.org.

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