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Simple Bipolar Molecules Constructed from Biphenyl Moieties as Host Materials for Deep-Blue Phosphorescent Organic Light-Emitting Diodes

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Phosphorescent organic light-emitting diodes (PhOLEDs) that have heavy-metal complexes as phosphorescent emitters can harvest both singlet and triplet excitons by spin-orbit coupling in the emitting layer to achieve 100% internal quantum efficiency in theory.[1] This makes OLEDs very promising candidates for the next commercial full-color, flat-panel, solid-state displays and lighting products.[2] To avoid the triplet–triplet (T–T) annihilation and concentration quenching, phosphorescent emitters of heavy-metal complexes are usually doped in host materials to guarantee the device performance.[3] Of the three primary colors, green and red PhOLEDs have achieved satisfactory efficiency and stability.[4] However, the efficiency and stability of blue PhOLEDs are still far away from practical application.

Nowadays, most research about blue PhOLEDs is focused on the development of new host materials and blue phosphorescent emitters. Significant advances have been made with sky-blue PhOLEDs based on iridium(III) bis(4,6-difluorophenylpyridinato-*N*,$C^{2'}$) picolinate (FIrpic) that have a maximum external quantum efficiency of over 20% and a maximum power efficiency of over 35 lm W^{-1}.[5] However, the FIrpic-based sky-blue PhOLEDs do not satisfy the blue color standards recommended by the National Television Committee. Deep-blue phosphors, such as, [bis(4,6-difluorophenylpyridinato-*N*,$C^{2'}$)][tetrakis(1-pyrazolyl)borate]iridium(III) (FIr6), need to be developed.[6] Unfortunately, it is not easy to obtain high efficiencies for FIr6-based deep-blue PhOLEDs by virtue of the scarcity of host materials, especially bipolar hosts that possess both hole- and electron-transporting abilities. The key problem to design bipolar host materials for deep blue PhOLEDs is how to maintain high triplet energy (E_T) above 2.8 eV, which is necessary to prevent energy back from the blue phosphors to the hosts.[7] Simultaneously, the bipolar host materials should have matched HOMO/LUMO levels with adjacent layers to decrease carrier-injection barriers, as well as high carrier drift mobility to increase current and power efficiency. However, introducing hole- and electron-transporting moieties into a single molecule usually brings about intramolecular charge transfer, causing a depreciation of the triplet energy. A design strategy to overcome these problems is to employ insulating linkages, such as adamantane and tetraaryl silane, to interrupt the π conjugation. So far, only a few bipolar host materials for FIr6-based deep-blue PhOLEDs have been reported.[8]

The biphenyl molecule has high triplet energy of 2.84 eV,[9] but direct functionalization usually brings down the triplet energy due to the enlarged π conjugation, such as 4,4′-(*N*,*N*′-dicarbazolyl)biphenyl (CBP) with $E_T = 2.56$ eV and 4,4′-bis(diphenyloxophosphinoyl)biphenyl (PO1) with $E_T = 2.72$ eV.[10] Interestingly, when bulky groups are placed at the 2,2′-positions of the biphenyl molecule, a twist configuration of biphenyl molecule can reduce the π conjugation and therefore increase the triplet energy, for example, 4,4′-(*N*,*N*′-dicarbazolyl)-2,2′-dimethylbiphenyl (CDBP) with $E_T =$ 3.0 eV.[11] In this paper, with the aim to develop simple bipolar host materials with high triplet energy, we introduce the hole-transporting carbazole moiety and the electron-transporting diphenylphosphine oxide moiety into the 2,2′-positions of a biphenyl molecule. We anticipate that the carbazole group and the diphenylphosphine oxide group will cause biphenyl molecule to twist through steric effects, and thus minimize the π conjugation of the two moieties. Meanwhile, the different spatial orientations of the two groups can avoid intramolecular charge transfer, and thus maintain their individual functionality. The two new hosts, POBPCz and POBP*t*Cz, show triplet energies of approximately 3.0 eV, which are significantly higher than that of biphenyl molecule itself and qualify their application as bipolar hosts to fabricate deep blue PhOLEDs.

The two host materials were synthesized according to Scheme 1. Firstly, the intermediate (2-bromo-2′-diphenyloxophosphinoyl)biphenyl was prepared from three steps: regioselective lithiation of 2,2′-dibromobiphenyl, coupling with chlorodiphenylphosphine, and finally oxidation with hydrogen peroxide to afford (2-bromo-2′-diphenyloxophosphinoyl)biphenyl with a overall yield of 50%. Secondly, carba-

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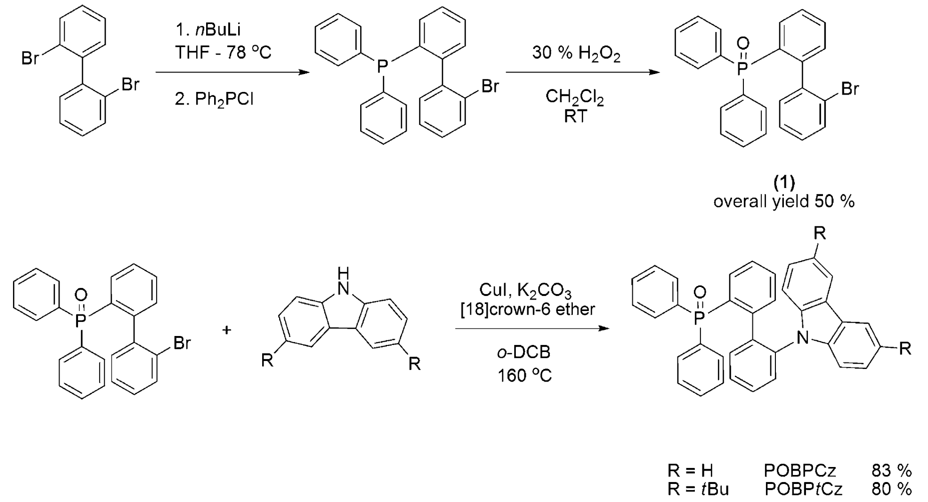

Scheme 1. Synthesis of the intermediate (2-bromo-2′-diphenyloxophosphinoyl)biphenyl (**1**) and the final products POBPCz and POBP*t*Cz.

zole or 3,6-di-*tert*-butylcarbazole was coupled with (2-bromo-2′-diphenyloxophosphinoyl)biphenyl by means of the Ullmann reaction to get the final POBPCz and POBP*t*Cz with yields of 83 and 80 %, respectively. All the compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis. The structure of POBPCz was further confirmed by single-crystal X-ray diffraction analysis. As shown in Figure 1, the C13-C18-C19-C24 torsion angle in the biphenyl molecule is almost 60°, consequently the free rotation through the C18−C19 bond is partially suppressed by the two bulk groups at the 2,2′-positions. The rotation through C13−N1 bond is also suppressed due to the molecular configuration, as indicated by the different chemical shift of two *tert*-butyl groups of POBP*t*Cz in the ^{1}H NMR spectra. The detailed preparation and characterization of the compounds can be found in Supporting Information.

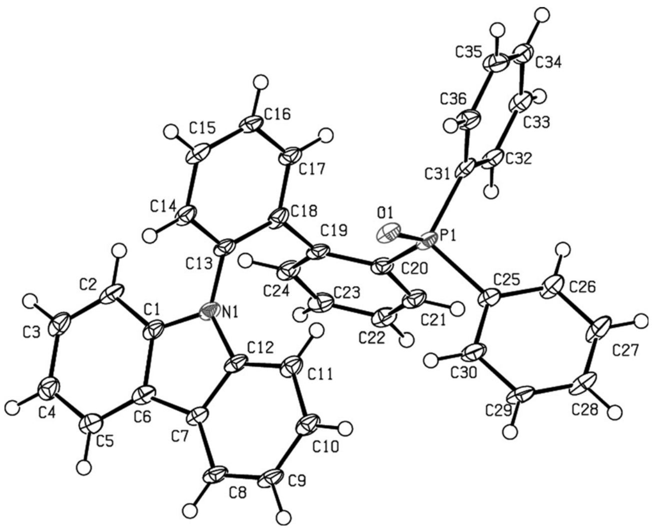

Figure 1. Oak Ridge thermal ellipsoidal plot (ORTEP) diagram of POBPCz.

Figure 2 shows the absorption and photoluminescence spectra of POBPCz and POBP*t*Cz in CH_2Cl_2. Both compounds show two characteristic peaks of absorption in the range of 320–350 nm, which can be attributed to n–π* transition of the carbazole moiety and the π–π* transition of biphenyl moiety. Their energy gaps (E_g), calculated from the onsets of absorption spectra, are 3.57 and 3.50 eV for POBPCz and POBP*t*Cz, respectively, and they exhibit emission at 399 and 418 nm, respectively, in CH_2Cl_2. Both absorption and emission spectra of POBP*t*Cz show a red-shift relative to POBPCz. The inset of Figure 2 depicts the phosphorescence spectra of the two compounds measured from a frozen 2-methyltetrahydrofuran (2-MeTHF) matrix at 77 K. Their triplet energies (E_T) are determined to be 3.01 and 2.98 eV for POBPCz and POBP*t*Cz, respectively, from the highest-energy vibronic sub-band of the phosphorescence spectra. The triplet energies of POBPCz and POBP*t*Cz are significantly higher than that of biphenyl molecule itself ($E_T = 2.84$ eV), which is caused by minimizing the π conjugation of biphenyl molecule.

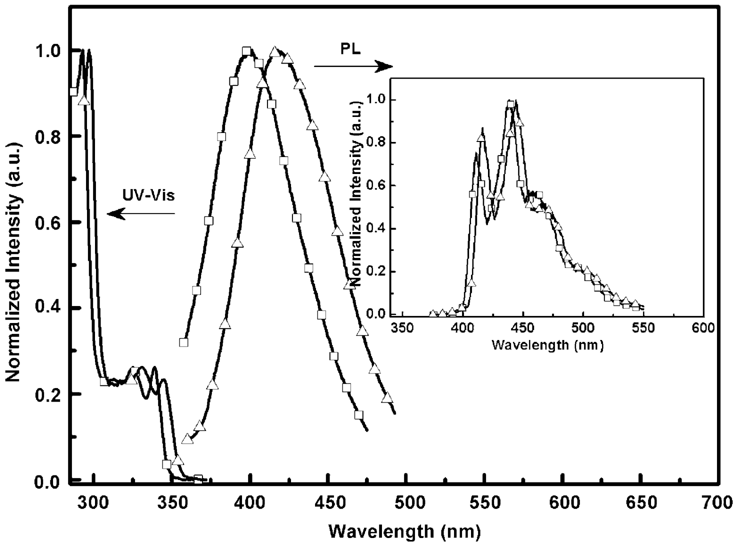

Figure 2. UV/Vis absorption spectra, PL spectra of POBPCz (□) and POBP*t*Cz (△) in CH_2Cl_2 solution at room temperature, and their phosphorescence spectra in 2-MeTHF at 77 K (inset).

The thermal stability of the two host materials, POBPCz and POBP*t*Cz, is indicated by the high decomposition temperatures (T_d, corresponding to 5% weight loss) of 352 °C for POBPCz and 346 °C for POBP*t*Cz through thermogravimetric analysis (TGA; Figure S1 in the Supporting Information). Their glass transition temperatures (T_g) appear at 170 °C for POBPCz and 140 °C for POBP*t*Cz in the differential scanning calorimetry (DSC) thermograms (inset of Figure S1). The T_g temperatures of POBPCz and POBP*t*Cz are much higher than that of CBP (62 °C).[12] Both high decomposition temperatures and high glass transition temperatures implicate that the two host materials form thermally durable and morphologically stable amorphous thin-films, which is essential for fabrication of PhOLEDs during thermal evaporation

The electrochemical behaviors of POBPCz and POBP*t*Cz were examined by the cyclic voltammetry (CV; Figure S2 in the Supporting Information). POBPCz exhibits a quasi-reversible oxidation process, whereas POBP*t*Cz shows a reversible oxidation process, because the active sites of carbazole are blocked by the *tert*-butyl groups. Their HOMO energy levels determined from the oxidation potentials are −5.69 and −5.51 eV for POBPCz and POBP*t*Cz, respectively. The higher HOMO level of POBP*t*Cz can be attributed to the electron-denoting property of *tert*-butyl groups. Their LUMO energy levels, deduced from the HOMO energy levels and the energy gaps, are −2.12 and −2.01 eV for POBPCz and POBP*t*Cz, respectively.

The geometrical configurations of POBPCz and POBP*t*Cz were optimized at B3LYP/6-31g(d) level and their triplet energies were calculated at wB97x/6-311+g(d,p) level using a polarized continuum solvent model (IEFPCM) with THF. The electronic properties of the compounds were studied by density functional theory (DFT) calculations by using B3LYP hybrid functional. All the computations were carried out with Gaussian 09 program.[13] The calculated triplet energies are 3.03 and 2.99 eV for POBPCz and POBP*t*Cz, respectively, very close to their measured values. As shown in Figure S3 in the Supporting Information, the HOMO orbitals of the two molecules are mainly located on carbazole moiety, while their LUMO orbitals are distributed on biphenyl moiety and phenyl groups of diphenyl phosphine oxide. The complete separation between HOMO and LUMO levels is favorable for efficient hole and electron injection and thus benefit to the electroluminescence performance of the devices.

The triplet energies of POBPCz and POBP*t*Cz are high enough to host the deep-blue phosphorescent emitter [bis(4,6-difluorophenylpyridinato-*N,C*$^{2'}$)][tetrakis(1-pyrazolyl)borate]iridium(III) (FIr6 with an E_T of ca. 2.72 eV);[14] hence we fabricated devices with the following configurations: ITO/MoO_3 (10 nm)/NPB (80 nm)/TCTA (5 nm)/POBPCz (device A) or POBP*t*Cz (device B): FIr6 (20 nm)/Tm (5 nm)/TPBi (30 nm)/LiF (1 nm)/Al (120 nm). The device structure and energy level diagram of materials used in the devices are shown in Figure S4 in the Supporting Information. In these devices, 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) was used as the hole-transporting material; hole-transporting material 4,4′,4′′-tri(*N*-carbazolyl)triphenylamine (TCTA) and electron-transporting material 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (Tm) were used for blocking excitons due to their high triplet energies.[15] 1,3,5-Tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi) was utilized as electron transporting material; FIr6 was used as the deep blue triplet emitter, with optimized doping level at 10 %; MoO_3 and LiF served as hole- and electron-injecting materials, respectively.

Current-density–voltage–luminance (*J*–*V*–*L*) characteristics and current efficiency, power efficiency versus current density of the devices are shown in Figure 3. Both devices show typical emission from the deep blue phosphor of FIr6 (inset of Figure 3 c,d). Device A with POBPCz as host displays a turn-on voltage of 3.1 V and achieves a maximum current efficiency of 40 cd A^{-1}, a maximum power efficiency of 36 lm W^{-1} and a maximum external quantum efficiency of 19.5 % at 0.01 mA cm^{-2}. At practical brightness of 100 cd m^{-2} (0.41 mA cm^{-2}), device A shows a current efficiency of 27 cd A^{-1} and power efficiency of 17 lm W^{-1}. At brightness of 1000 cd m^{-2} (6.4 mA cm^{-2}), device A still shows current efficiency of 16 cd A^{-1} and power efficiency of 7 lm W^{-1}. Device B with POBP*t*Cz as host shows a turn-on voltage of 3.8 V and reveals a maximum current efficiency of 38 cd A^{-1}, a maximum power efficiency of 31 lm W^{-1} and a maximum external quantum efficiency of 19.5% at 0.01 mA cm^{-2}. At brightness of 100 (0.35) and 1000 cd m^{-2} (7.26 mA cm^{-2}), device B exhibits current efficiency of 27 and 14 cd A^{-1} and power efficiency of 17 and 6 lm W^{-1}, respectively. To the best of knowledge, these efficiencies of the devices are comparable with the best results recently reported,[8] and even better than the device with p–i–n structure.[16]

In conclusion, we rationally designed two new and simple bipolar host materials, POBPCz and POBP*t*Cz, based on the biphenyl molecule. The molecular structure of POBPCz and POBP*t*Cz shows a twist configuration due to the steric effect, and thus can minimize the π conjugation of biphenyl molecule. Meanwhile, the hole-transporting carbazole group and the electron-transporting diphenylphosphine oxide group in the two molecules still retain their individual attributes on account of their different spatial orientations. Both POBPCz and POBP*t*Cz show high triplet energies of about 3.0 eV and can be used as hosts to fabricate deep blue PhOLEDs. The FIr6-based deep blue device A with POBPCz as host achieves a maximum current efficiency of 40 cd A^{-1}, a maximum power efficiency of 36 lm W^{-1}, and a maximum external quantum efficiency of 19.5%, which are among the best results ever reported. The impressing efficiencies are mainly attributed to the high triplet energies of hosts and their bipolar carrier-transporting abilities.

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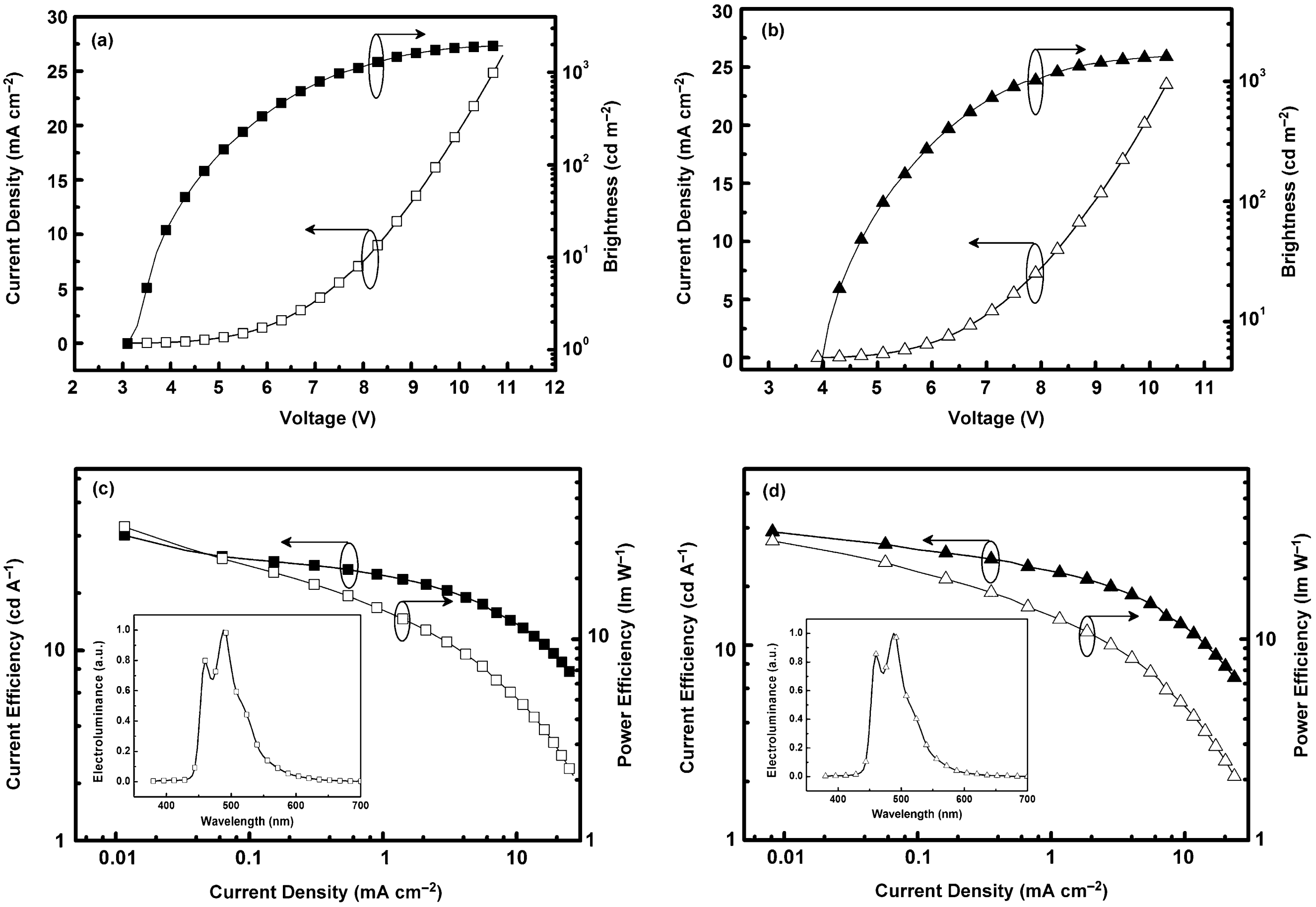

Figure 3. *J–V–L* characteristics of a) device A and b) device B. Current efficiency and power efficiency versus current density of c) device A (EL spectrum inset) and d) device B (EL spectrum inset).

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