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Ethylcarbazole Based Phosphine Oxide Derivatives as Hosts for Blue Phosphorescent Organic Light-Emitting Diodes

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Blue phosphorescent organic light-emitting diodes were developed using host materials with 9-ethylcarbazole and phosphine oxide units and they could be used in blue phosphorescent organic light-emitting diodes. Efficient energy transfer from the ethylcarbazole based hosts to the blue phosphorescent dopant material was observed due to the high triplet energy of the host material.

Keywords Blue phosphorescent light-emitting diodes; ethylcarbazole dimer; phosphine oxide; triplet host

Introduction

The development of blue phosphorescent organic light-emitting diodes (PHOLEDs) is important to reduce the power consumption of passive or active matrix type OLED devices. It has been known that the PHOLEDs can achieve four times higher quantum efficiency than fluorescent OLEDs and they are effective to decrease the power consumption of OLEDs [1].

There have been many researches to develop blue PHOLEDs. Several host and dopant materials were synthesized to improve the quantum efficiency of the blue PHOLEDs [2–6]. The most common triplet host materials for blue PHOLEDs are carbazole based materials because of wide triplet bandgap of the carbazole moiety. The carbazole unit was combined with phenyl group or Si based conneting unit [2,3]. Silane based host materials were also reported to have a wide triplet bandgap for an energy transfer to blue phosphorescent dopant [4,5]. Several derivatives of the silane materials were synthesized and they could be used as host materials for blue PHOLEDs. In addition to these materials, a spirobifluorene based host material was found to be effective as a host material for blue PHOLED [6].

In this work, 9-ethylcarbazole based host materials with phosphine oxide moiety in the backbone structure were developed and their performances as host materials

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in the blue PHOLEDs were studied. Blue phosphorescent devices were fabricated and an efficient energy transfer from the phosphine oxide host materials to the blue phosphorescent dopant materials was demonstrated.

Experimental

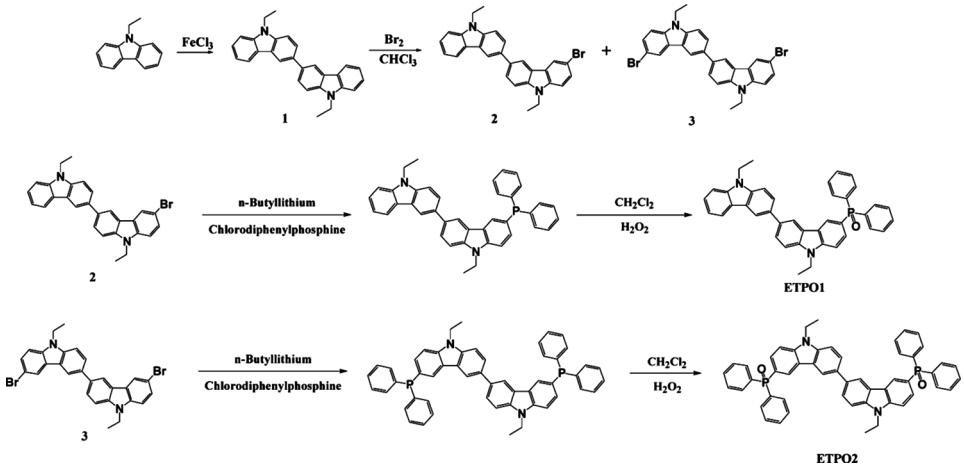
The synthetic scheme of the ETPO1 and ETPO2 is shown in Scheme 1.

Synthesis of 9,9′-diethyl-9H,9′H-3,3′-bicarbazole (1). A solution of 9-carbazole (5 g, 25.6 mmol) and anhydrous iron trichloride (8.3 g, 51.2 mmol) were dissolved in 20 ml of dry chloroform. This mixture was vigorously stirred at room temperature for 16 h. Then the solution was extracted water and dichloromethane, dried over anhydrous magnesium sulphate. This was filtered off and the resulting materials purified by column chromatography to give a white powder.

Synthesis of 6-bromo-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (2). N-bromosuccinimide (NBS) (5.5 g, 30.0 mmol) was added in small portions to a solution of 9,9′-diethyl-9,9′-3,3′-bicarbazole (12 g, 30.0 mmol) in tetrahydrofuran at room temperature under nitrogen atmosphere. After being stirred for 2 h, water and dichloromethane were added. The organic phase was separated, washed with water, brine solution, dried over anhydrous magnesium sulphate, filtered and dried to remove the solvents. Purification by column chromatography with a mixture of dichloromethane and n-hexane gave white solids.

Synthesis of 6,6′-dibromo-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (3). The **3** was synthesized by the same procedure as the **2** except that the amount of the NBS was doubled.

Synthesis of 6-(diphenylphosphoryl)-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (ETPO1). 6-bromo-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (2) (4.4 mmol) was dissolved in 20 mL of anhydrous tetrahydrofuran under argon and cooled to −78°C and 1.2 equiv of *n*-butyllithium (10.0 M in hexanes, 5.3 mmol) was added slowly



Scheme 1. Synthetic scheme of the ETPO1 and ETPO2.

dropwise to give a bright yellow solution that thickened to a slurry. Stirring was continued for 3 h at −78°C after which 0.99 mL (5.3 mmol) of chlorodiphenylphosphine was added giving a clear, pale yellow solution. The reaction was stirred for 3 h more at −78°C before quenching with 2 mL of degassed methanol. Volatiles were removed under a reduced pressure to give an off-white solid that was digested in methanol, filtered, then digested in water, and filtered. The crude material was purified by column chromatography. 6-(diphenylphosphino)-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (1.8 mmol), 10 mL of methylene chloride, and 2 mL of 30% hydrogen peroxide were stirred overnight at room temperature. The organic layer was separated and washed with water and then brine. The extract was evaporated to dryness affording a white solid.

ETPO1 Yield 93%. MP 278.8°C. Tg 130.8°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 8.58–8.52 (d, 1H, Ar-CH-carbazole), 8.37 (s, 2H, Ar-CH-carbazole), 8.20–8.16 (d, 1H, Ar-CH-carbazole), 7.90–7.68 (m, 5H, Ar-CH-carbazole), 7.56–7.47 (m, 10H, Ar-CH-fluorene), 7.46–7.22 (m, 3H, Ar-CH-benzene), 4.46–4.36 (q, 4H, CH_2), 1.53–1.44 (t, 6H, CH_3). MS (FAB) m/z 589 [(M + 1)+].

Synthesis of 6,6′-bis(diphenylphosphoryl)-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (ETPO2). The ETPO2 was synthesized by the same procedure as the synthesis of the ETPO1 except that 6,6′-dibromo-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (3) was used instead of the 6-bromo-9,9′-diethyl-9H,9′H-3,3′-bicarbazole (2).

ETPO2 Yield 93%. MP 347°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 8.55–8.48 (d, 2H, Ar-CH-carbazole), 8.29 (s, 2H, Ar-CH-carbazole), 7.83–7.70 (m, 11H, Ar-CH-carbazole), 7.54–7.46 (m, 15H, Ar-CH-carbazole), 7.26 (m, 2H, Ar-CH-carbazole), 4.44–4.40 (q, 4H, CH_2), 1.52–1.45 (t, 6H, CH_3). MS (FAB) m/z 789 [(M + 1)+].

Device Fabrication

The device structure of indium tin oxide (ITO, 150 nm)/ N,N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (60 nm)/N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine(30 nm)/host: iridium(III) bis((4,6-difluorophenyl)-pyridinato-N,C2) picolinate (FIrpic, 30 nm, 15%)/4,7-diphenyl-1,10-phenanthroline (Bphen, 25 nm)/LiF (1 nm)/Al (200 nm) was used to evaluate the ETPO1 and ETPO2 as host materials for the blue PHOLEDs. In addition to the ETPO1 and ETPO2 devices, the blue PHOLED with a dimer of the 9-ethylcarbazole (ETPO) as a host was also fabricated. Current density-voltage-luminance characteristics of the devices were measured with Keithley 2400 source measurement unit and CS-1000 spectroradiometer.

Results and Discussion

Two host materials with a dimeric ethylcarbazole and phosphine oxide units were synthesized by the phosphonation reaction of the dimeric ethylcarbazole unit. Synthetic scheme of the two host materials is shown in Scheme 1. A dimer of the 9-ethylcarbazole was brominated with bromine and the brominated carbazole compounds were reacted with chlorodiphenylphosphine followed by oxidation. The ETPO1 and ETPO2 were synthesized in good yield over 99% and high purity over 99%.

The dimeric ethylcarbazole group has a high triplet energy of 2.76 eV and it is suitable as the backbone structure of the blue phosphorescent host materials.

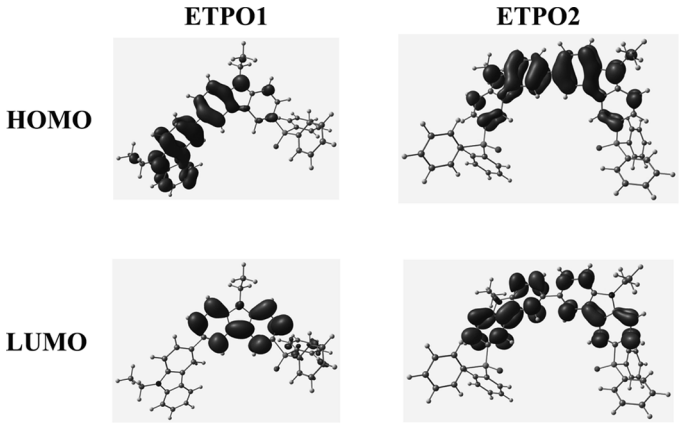


Figure 1. Molecular simulation results of the ETPO1 and ETPO2.

However, the dimeric ethylcarbazole unit has hole transport properties and an electron transport moiety should be introduced in the molecular structure for use in the blue PHOLEDs. The phosphine oxide unit has a strong electron withdrawing character and it can contribute to improve the electron transport properties of the ethylcarbazole [7]. In addition, the phosphine oxide unit does not affect the triplet energy level of the ethylcarbazole dimer through the isolation of the ethylcarbazole unit. Therefore, the combination of the dimeric ethylcarbazole and phosphine oxide groups can be effective to develop host materials for blue PHOLEDs.

Molecular simulation of the synthesized materials was carried out to understand the physical properties of the two materials at the molecular level. The highest occupied molecular orbital (HOMO) and the lowest unoccupired molecular orbital (LUMO) of the two materials are shown in Figure 1. The LUMO of the ETPO1 was concentrated on the ethylcarbazole unit next to the phosphine oxide unit, while the HOMO was rather localized in the other ethylcarbazole. The phosphine oxide group has a strong electron withdrawing character, affecting the HOMO and LUMO distribution of the ETPO1. Compared with the ETPO1, the ETPO2 showed both HOMO and LUMO in the dimer structure of the ethylcarbazole, indicating that the HOMO and LUMO are determined by the ethylcarbazole dimer. The ETPO2 has a symmetric molecular structure and the HOMO and LUMO are uniformly distributed in the core structure.

The HOMO and LUMO levels of the materials are dependent on the orbital distribution and the HOMO/LUMO levels of the ETPO1 and ETPO2 were 5.49/2.14 eV and 5.66/2.33 eV, respectively. The HOMO levels were measured with cyclic voltametry and the LUMO levels were calculated by subtracting the bandgap from the HOMO levels. The bandgap of the ETPO1 and ETPO2 was similar each other although the HOMO/LUMO levels of the ETPO1 and ETPO2 were different. The diphenylphosphine oxide unit just shifted the HOMO/LUMO levels without affecting the bandgap of the ETPO1 and ETPO2. The bandgap of the ETPO1 and ETPO2 is mainly determined by the dimeric ethylcarbazole core structure and similar bandgap was obtained in the ETPO1 and ETPO2. The HOMO and LUMO levels of the ETPO1 and ETPO2 were shifted downward from the vacuum level due to the electron withdrawing character of the diphenylphosphine oxide group.

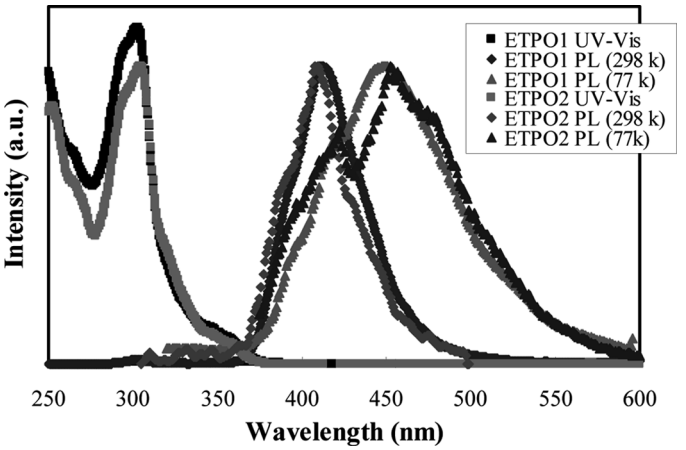


Figure 2. UV-Vis and PL spectra of the ETPO1 and ETPO2.

The shift of the energy levels was more significant in the ETPO2 than in the ETPO1 because two diphenylphosphine oxide groups were introduced in the ETPO2.

Ultraviolet-Visible (UV-Vis) absorption and photoluminescence (PL) spectra of the ETPO1 and ETPO2 are shown in Figure 2. The spectra were obtained in solution. The wavelength for maximum absorption was 304 nm in the ETPO1 and ETPO2 due to the absorption of the carbazole dimer. The PL peak of the two materials showed similar tendency as the UV-Vis absorption and similar PL spectra were obtained in the ETPO1 and ETPO2. The triplet bandgap of the ETPO1 and ETPO2 was also measured from the phsphorescence PL peak at 77 K. The triplet bandgap of the ETPO1 was 2.76 eV, while that of the ETPO2 was 2.73 eV. The two materials showed almost the same triplet energy irrespective of the diphenylphosphine oxide groups. The phosphine oxide group isolates the carbazole dimer from the diphenyl groups attached to the phosphine oxide and there was little change of the triplet energy irrespective of the number of diphenylphosphine oxide groups [7]. The triplet energy of the ethylcarbazole dimer without the phosphine oxide was also 2.75 eV.

Blue PHOLEDs with the ETPO1 and ETPO2 were fabricated to investigate the effect of host material on the device performances. The Blue PHOLED with the ETPO host was also prepared to study the effect of the phosphine oxide group on the device performances. The FIrpic was a blue dopant in the ETPO1 and ETPO2 devices. Current density-voltage-luminance curves of the ETPO1 and ETPO2 devices are shown in Figure 3. The current density of the ETPO2 device was higher than that of the ETPO1 device. The current density is determined by the hole and electron density in the device and the ETPO2 is better than the ETPO1 in terms of electron density. The LUMO levels of the ETPO1 and ETPO2 were 2.14 eV and 2.33 eV respectively. The LUMO level of the ETPO2 is more suitable for electron injection from the Bphen to the emitting layer due to the reduced energy barrier for electron injection. The energy barrier for electron injection was 0.47 eV in the ETPO2 device, while it was 0.66 eV in the ETPO1 device (Figure 4). The reduced energy barrier in the ETPO2 device increased the electron density in the ETPO2 device [8]. Although there was an energy barrier of 0.16 eV for hole injection between the ETPO2 and

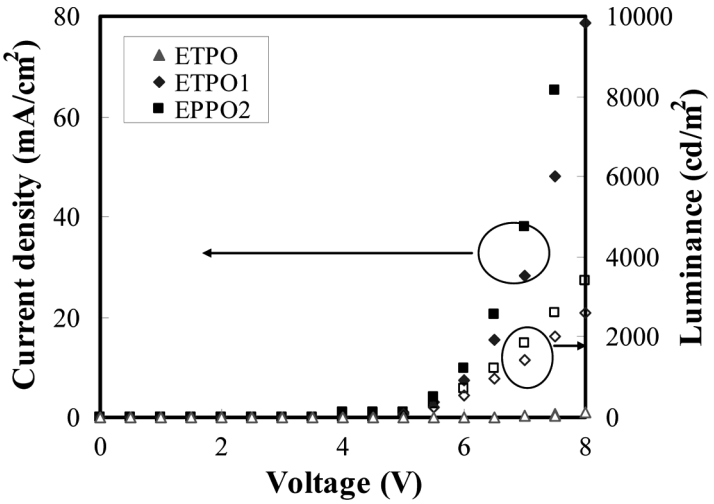


Figure 3. Current density-voltage-luminance characteristics of the blue phosphorescent organic light-emitting diodes with the ETPO1 and ETPO2 host materials.

NPB, it could not greatly affect the current density because of the low energy barrier. The current density of the ETPO1 and ETPO2 was much higher than that of the ETPO without any phosphine oxide group. The electron injection was suppressed in the ETPO device and low current density was obtained. The luminance followed the similar trend as the current density.

The current efficiency-current density curves of the ETPO1 and ETPO2 blue PHOLEDs are shown in Figure 5. The current efficiency of the ETPO2 blue PHOLED was a little higher than that of the ETPO1 device and the improved current efficiency of the ETPO2 device compared with ETPO1 device can be explained by the holes and electrons balance in the emitting layer [9]. In the case of the ETPO1, the hole injection is efficient due to the HOMO level of 5.49 eV, while the electron injection is limited due to the LUMO level of 2.14 eV. The electron

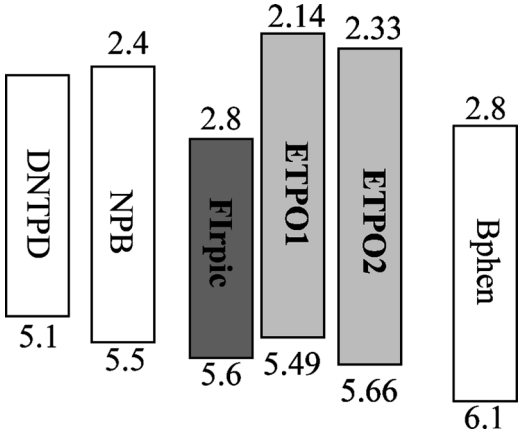


Figure 4. Energy level diagram of the ETPO1 and ETPO2 devices.

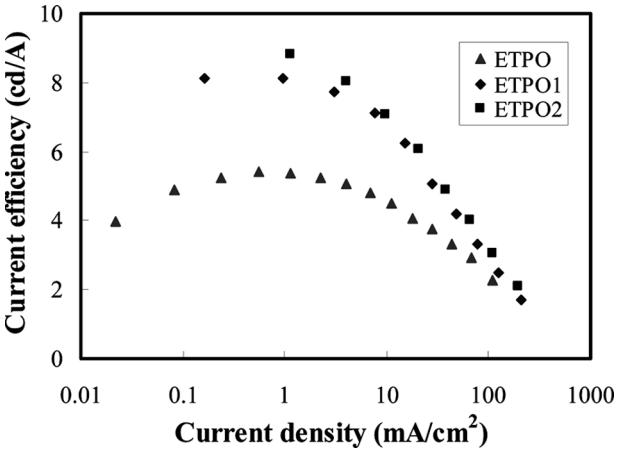


Figure 5. Quantum efficiency-current density curves of the blue PHOLEDs with the ETPO1 and ETPO2 host materials.

injection is improved in the ETPO2, resulting in better charge balance in the emitting layer. The two diphenylphosphine oxide groups assist the electron injection and transport in the ETPO2. The ETPO1 has one diphenylphosphine oxide and it is inferior to ETPO2 in terms of electron injection and transport. The current efficiency of the ETPO1 and ETPO2 was much better than that of the ETPO due to the phosphine oxide group with electron transport properties. However, the efficiency roll-off was significant in the ETPO1 and ETPO2 devices due to the large energy barrier for electron injection even though the electron injection was improved by the phosphine oxide groups [10,11].

Conclusions

In summary, high triplet energy host materials with the phosphine oxide unit and 9-ethylcarbazole dimer were effectively synthesized by the phosphonation and they could be used as the host materials in the blue PHOLEDs. The ETPO2 with the 9-ethylcarbazole dimer and two phosphine oxide groups was better than the ETPO1 with the 9-ethylcarbazole dimer and one phosphine oxide group in terms of current density and current efficiency. The introduction of the phosphine oxide group was effective to control the energy levels and charge balance in the emitting layer.

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