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Carbazolyldibenzofuran-type high-triplet-energy bipolar host material for blue phosphorescent organic light-emitting diodes

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ABSTRACT

A high-triplet-energy material, 9′-(4,4′-(phenylphosphoryl)bis(dibenzo[b,d]furan-6,2-diyl))bis(9H-carbazole) (44DFCzPO), was synthesized as a bipolar host material for blue phosphorescent organic light-emitting diodes (PHOLEDs). 44DFCzPO was synthesized by the selective lithiation of the 4-position of a carbazole-modified dibenzofuran, followed by phosphorylation. 44DFCzPO showed a high triplet energy of 2.91 eV for energy transfer to a blue phosphorescent dopant, and bipolar charge transport properties for balanced hole and electron density in the emitting layer. A high quantum efficiency of 16.7% at a low doping concentration of 3% was obtained using 44DFCzPO as the host in blue PHOLEDs.

1. Introduction

High-triplet-energy bipolar materials have been found to be effective as host materials for phosphorescent organic light-emitting diodes (PHOLEDs) to improve the quantum efficiency, because holes and electrons can be balanced in the emitting layer [1–8]. They are effective in red, green, and blue PHOLEDs as a host material to achieve high quantum efficiency. High quantum efficiency above 20% was achieved in the red, green, and blue PHOLEDs using bipolar host materials with high triplet energy.

In the case of blue PHOLEDs, bipolar host materials with high triplet energy above 2.80 eV are required to obtain high quantum efficiency. The high-triplet-energy host materials transfer triplet energy to a blue phosphorescent dopant and suppress the back energy transfer from the dopant to the host materials. There have been many high-triplet-energy bipolar host materials based on carbazole [9–13], dibenzofuran [14–20], and dibenzothiophene [21,22] cores for blue PHOLEDs. Among these core structures, dibenzofuran was effective as a core structure for high-triplet-energy host materials. However, only a few bipolar host materials based on dibenzofuran have been developed and further developments are needed.

In this work, a high-triplet-energy bipolar host material, 9′-(4,4′-(phenylphosphoryl)bis(dibenzo[b,d]furan-6,2-diyl))bis(9H-carbazole) (44DFCzPO), was developed as the host material for blue PHOLEDs. The basic photophysical properties of 44DFCzPO were studied, and the device performance of blue PHOLEDs were optimized using 44DFCzPO. A high quantum efficiency of 16.7% at a low doping concentration of 3% was demonstrated in the blue PHOLEDs with the 44DFCzPO host material.

2. Experimental

General information about synthesis and basic material measurements was reported in other work[14].

3. Synthesis

3.1. 9,9′-(4,4′-(phenylphosphoryl)bis(dibenzo[b,d]furan-6,2-diyl))bis(9H-carbazole) (44DFCzPO)

Into a 100 mL two-neck flask was placed 9-(dibenzo[b,d]furan-2-yl)-9H-carbazole (2.00 g, 5.99 mmol) in tetrahydrofuran (30 mL). The reaction flask was cooled to -78 °C and n-butyllithium (2.5 M in hexane, 2.73 mL) was added dropwise slowly. The whole solution was stirred for 3 h, followed by addition of a solution of dichlorophenylphophine (0.49 g, 2.73 mmol) under argon. The resulting mixture was gradually warmed to ambient temperature and quenched by methanol (10 mL). The mixture was extracted with dichloromethane and the combined organic layer was dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The white powdery product was obtained to 1.80 g (yield 39%). It was dissolved in dichloromethane (20 mL) solution with hydrogen

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peroxide (5 mL), which was stirred overnight at room temperature. The organic layer was separated and washed with dichloromethane and water. The extract was evaporated to dryness affording a white solid.

44DFCzPO Yield 39%. ^{1}H–NMR (500 MHz, $CDCl_3$): δ 8.32 (s, 2H), 8.12 (d, J=8.0 Hz, 6H), 8.00–7.93 (m, 10H), 7.55 (d, J=7.6 Hz, 8H), 7.45–7.41 (m, 3H), 7.27–7.23 (m, 10H). ^{13}C–NMR (125 MHz, $CDCl_3$) δ 157.1, 141.2, 133.1, 132.8, 132.0, 131.9, 130.4, 130.3, 128.9, 128.8, 128.6, 126.9, 126.1, 124.0, 123.7, 123.4, 122.8, 121.1, 120.4, 120.2, 112.4, 109.4. MS (FAB) m/z 789 $[(M+H)^+]$. Anal. Calcd. for $C_{54}H_{33}N_2O_3P$: C, 82.22; H, 4.22; N, 3.55. Found: C, 82.82; H, 4.20; N, 3.50.

4. Device fabrication

Device structure of the blue PHOLED used in this work was indium tin oxide (ITO, 50 nm)/N,N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD, 30 nm)/N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine (NPB, 15 nm)/N,N′-dicarbazolyl-3,5-benzene (mCP, 10 nm)/44DFCzPO:bis((3,5-difluorophenyl)pyridine) iridium picolinate (FIrpic) (30 nm, *x*%)/4-(triphenylsilyl)phenyldiphenylphosphine oxide (TSPO1, 20 nm)/LiF(1 nm)/Al (200 nm). Doping concentrations of FIrpic in the emitting layer were 3, 5, and 10%. A hole only device with a device structure of ITO (50 nm)/DNTPD (30 nm)/NPB (15 nm)/mCP (10 nm)/44DFCzPO (30 nm)/DNTPD (5 nm)/Al(200 nm) and an electron only device with a device structure of ITO (50 nm)/TSPO1 (5 nm)/44DFCzPO(30 nm)/TSPO1 (20 nm)/LiF (1 nm)/Al (200 nm) was also fabricated to study hole and electron density of the host material. All devices were encapsulated with a glass lid with CaO getter after metal deposition. Device performances were measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

5. Results and discussion

The basic design concept of 44DFCzPO was to obtain bipolar charge transport properties by connecting two hole-transport-type 9-(dibenzo[b,d]furan-2-yl)-9H-carbazole units with an electron-withdrawing phenylphosphine oxide unit. Another design motivation was to increase the triplet energy by integrating two 9-(dibenzo[b,d]furan-2-yl)-9H-carbazole units using a tetrahedral phenylphosphine oxide unit, because a tetrahedral bridging unit does not extend the conjugation of aromatic units. Additionally, the thermal stability can be improved by increasing the molecular size of the host material.

The synthetic scheme of 44DFCzPO is shown in Scheme 1. 9-(Dibenzo[b,d]furan-2-yl)-9H-carbazole was directly lithiated at the 4-position of dibenzofuran due to the electron-withdrawing character of oxygen. The lithiated intermediate was reacted with dichlorophenylphosphine followed by oxidation using hydrogen peroxide. The synthetic yield of the reaction was 39%. The identity of 44DFCzPO was confirmed by chemical analysis using ^{1}H and ^{13}C nuclear magnetic resonance and mass spectrometry.

The photophysical properties of 44DFCzPO were studied using ultraviolet–visible (UV–vis) and photoluminescence (PL) spectrometry. Fig. 1 shows the UV–vis absorption, solution PL, and low-temperature PL spectra of 44DFCzPO. UV–vis absorption peaks were observed at 326 nm and 338 nm, and were assigned to the $n-\pi^*$ transition of carbazole linked to the dibenzofuran and absorption peaks below 300 nm, which is attributed to the $\pi-\pi^*$ transition of 9-(dibenzo[b,d]furan-2-yl)-9H-carbazole. The phosphine oxide unit did not affect the UV–vis absorption spectra. The bandgap was calculated from the absorption edge of the UV–vis spectrum as 3.51 eV. The solution PL spectrum was measured in tetrahydrofuran solvent, and the maximum emission peak was observed at 410 nm. Low-temperature PL measurement was carried out in liquid nitrogen to calculate the triplet energy from the first phosphorescent emission peak. Fluorescent emission peak was shifted to short wavelength at low temperature due to restricted molecular motion. The phosphorescent emission peak wavelength was 426 nm, which corresponded to a triplet energy of 2.91 eV. The triplet energy of 44DFCzPO was suitable for energy transfer to common blue-emitting FIrpic dopant with a triplet energy of 2.65 eV.

As the 44DFCzPO host material was designed as a thermally stable host material, the thermal stability was studied by exposing the vacuum-deposited 44DFCzPO film to high temperature. Fig. 2 shows AFM pictures of the 44DFCzPO film after thermal treatment at different temperatures. There was little change in the film morphology until 120 °C, and crystallization of the film was observed at 140 °C. This indicates that the 44DFCzPO film is thermally stable at up to 120 °C without any crystallization. The surface roughness of the 44DFCzPO film annealed at 100 °C and 120 °C was 0.5 nm, while it was 0.6 nm after annealing at 140 °C.

Thermal stability of 44DFCzPO was further analyzed using thermogravimetric analyzer (TGA). TGA thermogram of 44DFCzPO is shown in Fig. 3. There was no change of the weight up to 400 °C, which indicates that the 44DFCzPO host is thermally stable even at 400 °C without any decomposition. Thermal decomposition temperature at 5% weight loss was 444 °C,

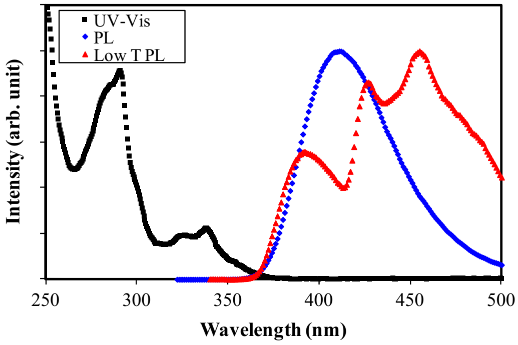
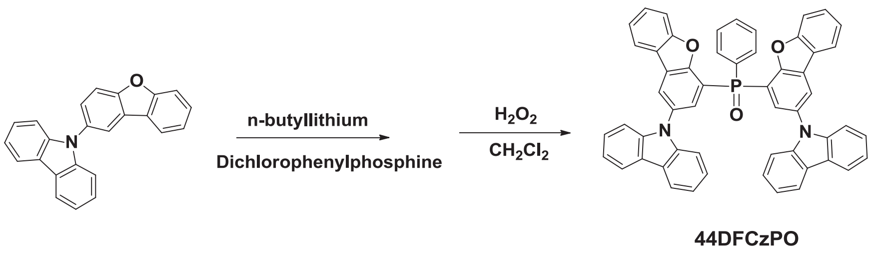


Fig. 1. UV–vis absorption, PL and low temperature PL spectra of 44DFCzPO. Low temperature PL was measured at 77 K in tetrahydrofuran.



Scheme 1. Synthetic scheme of 44DFCzPO.