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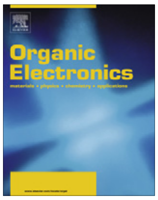

Dibenzofuran derivative as high triplet energy host material for high efficiency in deep blue phosphorescent organic light-emitting diodes

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ABSTRACT

A high efficiency deep blue phosphorescent organic light-emitting diodes was developed using an weak electron transport type high triplet energy host material with dibenzofuran and phosphine oxide units. The host material showed a high triplet energy of 3.01 eV and was effective as the host material for deep blue phosphorescent organic light-emitting diodes. The device performances could be optimized by managing the doping concentration of phosphorescent dopants and a high quantum efficiency of 25.9% with a color coordinate of (0.14, 0.22) was achieved.

1. Introduction

Deep blue phosphorescent organic light-emitting diodes (PHOLEDs) have been actively studied to overcome the low external quantum efficiency of current fluorescent deep blue organic light-emitting diodes (OLEDs) [1–8]. Compared with the external quantum efficiency of deep blue fluorescent OLEDs (5–9%), the external quantum efficiency of deep blue PHOLEDs was improved up to 25% [3].

The significant improvement of quantum efficiency in deep blue PHOLED was accomplished by the development of high triplet energy host materials [3,4,6–10] in addition to dopant materials and device architecture [1,11–15]. As the triplet energy of the deep blue dopant materials is in the range from 2.7 eV to 2.8 eV, host materials with a triplet energy over 2.9 eV have been developed for deep blue PHOLEDs. The high triplet energy host materials include carbazole [16], silane [17,18] and phosphine oxide (PO) [3,4,6,7,19–27] derivatives. In particular, PO derivatives were very effective to enhance the quantum efficiency of deep blue PHOLEDs.

Several high triplet energy PO type host materials were reported, which include carbazole based PO [3,4,6,7,19–22] dibenzofuran based PO [23–25] and dibenzothiophene based PO materials [20,26]. A high external quantum efficiency over 20% was achieved in PO based host materials and the best quantum efficiency value of deep blue PHOLEDs was 25.4% [3]. However, it is necessary to further improve the quantum efficiency of deep blue PHOLEDs using a better host material. In addition, high quantum efficiency in deep blue PHOLEDs was mostly obtained by using bipolar host materials [3–11].

In this work, a high triplet energy electron transport type host material, bis(dibenzo[b,d]furan-2-yl)(phenyl) phosphineoxide (DFPO3), was synthesized as the high triplet energy host material for deep blue PHOLEDs and the device performances of the DFPO3 devices were investigated according to the doping concentration. A high quantum efficiency of 25.9% was demonstrated from the deep blue PHOLEDs with the DFPO3 host material, which is higher than any other data reported in deep blue PHOLEDs.

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2. Experimental

2.1. Synthesis

2.1.1. Bis(dibenzo[b,d]furan-2-yl)(phenyl)phosphineoxide (DFPO3)

2-Bromo-dibenzofuran (3.00 g, 12.14 mmol) was dissolved in 30 mL of anhydrous tetrahydrofuran under argon and cooled to −78 °C and *n*-butyllithium (2.5 M in hexane, 5.83 mL) was added slowly to give a bright yellow solution that thickened to a slurry. Stirring was continued for 3 h at −78 °C after 1.65 mL (8.50 mmol) of dichlorophenylphophine was added giving a clear, pale yellow solution under argon atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by methanol (10 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The white powdery product was obtained to 1.34 g (yield: 25%). It was dissolved in dichloromethane (20 mL) and hydrogen peroxide (4 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.

DFPO3 yield 25%. NMR-^{1}H (500 MHz, $CDCl_3$): δ 8.45 (d, 2H, *J* = 10 Hz), 7.93 (d, 2H, *J* = 10 Hz), 7.65 (d, 2H, *J* = 17.5 Hz), 7.70 (d, 4H, *J* = 10 Hz), 7.64–7.33 (m, 9H). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 132.2, 132.1, 132.0, 130.9, 130.8, 128.7, 128.6, 128.0, 125.5, 125.4, 123.4, 123.3, 121.1, 112.0, 111.9, 111.8. MS (FAB) m/z 459 $[(M + H)^+]$. Anal. Calcd. for $C_{30}H_{19}O_3P$: C, 78.60; H, 4.18; O, 10.47; P, 6.76. Found: C, 78.44; H, 4.14.

2.2. Device fabrication

The device structure of blue PHOLEDs was indium tin oxide (ITO, 150 nm)/*N*,*N*′-diphenyl-*N*,*N*′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (DNTPD, 60 nm)/*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (NPB, 10 nm)/*N*,*N*′-dicarbazolyl-3,5-benzene (mCP, 10 nm)/ DFPO3: bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (FCNIrpic) (30 nm, x%)/4-(triphenylsilyl)phenyldiphenylphosphine oxide (TSPO1, 15 nm)/LiF(1 nm)/ Al(200 nm). The doping concentrations of FCNIrpic were 3%, 5%, and 10%. All devices were fabricated by vacuum thermal evaporation. Deposition rate of organic materials was 0.1 nm/s and doping concentration was controlled by changing the deposition rate of dopant material. Devices were encapsulated with CaO getter and a glass lid after metal electrode deposition. The device performances of the blue PHOLEDs was measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

2.3. Measurements

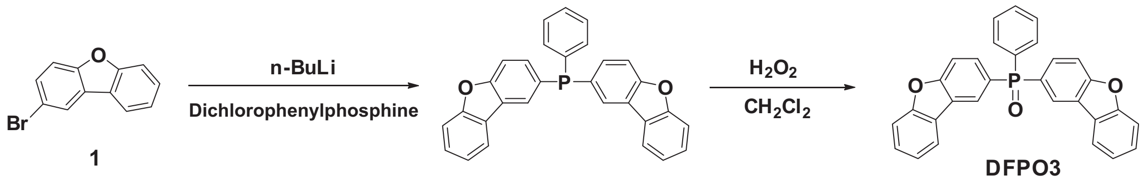
Photophysical properties of the DFPO3 were analyzed using ultraviolet–visible (UV–Vis) and photoluminescence (PL) spectrometer. DFPO3 was dissolved in tetrahydrofuran at a concentration of 1.0×10^{-4} M for UV–Vis and PL measurements. Triplet energy analysis of the DFPO3 was carried out using low temperature PL measurement in liquid nitrogen. Energy levels of the DFPO3 were measured using cyclic voltametry (CV). Cyclic voltametry measurement of organic materials was carried out in acetonitrile solution with tetrabutylammonium perchlorate at 0.1 M concentration. Ag was used as the reference electrode and Pt was the counter electrode. Organic materials were coated on indium tin oxide substrate and were immersed in electrolyte for analysis. Ferrocene was used as the internal standard material. Elemental analysis of the materials was carried out using EA1110 (CE instrument). High performance liquid chromatography (HPLC) analysis of the synthesized materials was carried out using HPLC from Youngrin Instrument. A mixed eluent of actonitrile:methanol (90:10) was used for the analysis.

3. Results and discussion

DFPO3 was designed as a weak electron transport type host material with high triplet energy. Dibenzofuran was used as the electron deficient core structure and two dibenzofuran units were connected through electron withdrawing PO unit. The dibenzofuran core has a high triplet energy of 3.14 eV and the PO linking unit does not extend the conjugation between the dibenzofuran and phenyl unit. Therefore, high triplet energy can be obtained in DFPO3. Compared with other PO modified dibenzofuran host materials [24,25,28], DFPO3 may show weak electron transport properties because two dibenzofuran units share one PO unit. Therefore, DFPO3 may function as a weak electron transport type host material for deep blue PHOLEDs.

DFPO3 could be synthesized by the lithiation of the 2-bromobenzofuran followed by the reaction with dichlorophenylphosphine and oxidation. Two equivalent of 2-bromobenzofuran was used to attach two dibenzofuran units. Synthetic scheme of the DFPO3 is shown in Scheme 1. The DFPO3 could be obtained in high purity level over 99% after purification.

Photophysical properties of DFPO3 were analyzed using UV–Vis and PL spectrometer. Fig. 1 shows UV–Vis and PL spectra of DFPO3. DFPO3 showed strong absorption peaks at 287 nm and 299 nm due to $\pi-\pi^*$ absorption of dibenzofuran unit. As the PO unit does not extend the conjugation of DFPO3, the absorption of dibenzofuran was observed. Bandgap of DFPO3 was 3.96 eV from the absorption edge of UV–Vis spectra. PL emission of DFPO3 was observed at 321 nm. Triplet energy of DFPO3 was 3.01 eV from the first emission peak of low temperature PL spectrum. The triplet energy of DFPO3 was higher than that of deep blue phosphorescent dopant (2.74 eV). Therefore, DFPO3 can be effectively used as the host material for deep blue PHOLEDs. The triplet energy of DFPO3 was similar to that of other PO modified dibenzofuran host materials substituted at 2,8 positions [25], but it was lower than that of dibenzofuran derivatives with the PO unit at 4 position [28] due to extended conjugation through *para* substitution to oxygen moiety. The triplet energy 2,8-bis(diphenylphosphoryl)dibenzo[b,d]furan (DFPO) was 3.04 eV from our measurement, which is similar to that of DFPO3.



Scheme 1. Synthetic scheme of DFPO3.

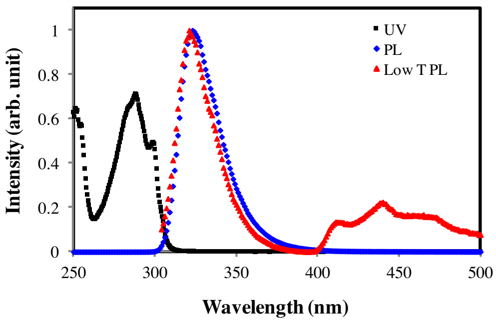


Fig. 1. UV–Vis absorption, PL and low temperature PL spectra of DFPO3.

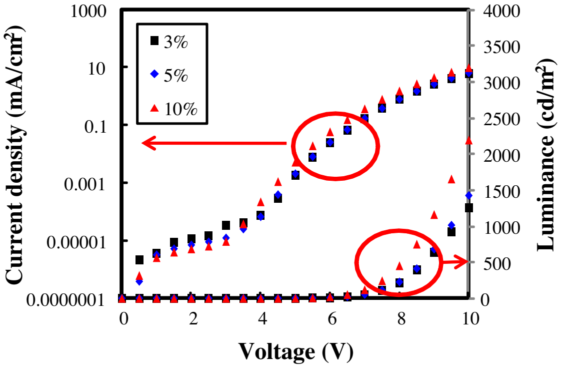


Fig. 3. Current density–voltage-luminance curves of DFPO3 deep blue PHOLEDs according to doping concentration.

Molecular simulation of DFPO3 was performed to study the molecular orbital distribution of DFPO3. Fig. 2 shows highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distribution of DFPO3. Both HOMO and LUMO were dispersed over dibenzofuran of DFPO3 due to strong electron withdrawing character of phosphine oxide unit. As dibenzofuran is an electron deficient unit, the molecular orbital simulation results indicate that DFPO3 is an electron transport type host material with weak hole transport properties. Simulated HOMO and LUMO levels of DFPO3 were −6.16 eV and −1.16 eV, respectively. The HOMO of DFPO3 measured by cyclic voltametry was −6.66 eV from the onset of oxidation curve and the LUMO was −2.70 eV from the HOMO and bandgap.

DFPO3 was evaluated as the host material for deep blue PHOLEDs because of its high triplet energy of 3.01 eV. The doping concentration of the blue dopant was changed from 3% to 10% to optimize the device performances. Fig. 3 shows current density–voltage-luminance curves of the DFPO3 devices according to the doping concentration of FCNIrpic. The current density of the device was not changed up to doping concentration of 5%, but it was increased at 10% doping concentration. The increased current density of the device is due to the charge hopping effect between dopant materials at high doping concentration. In particular, hole transport is improved at high doping concentration because of large HOMO level difference between DFPO3 (−6.66 eV) and FCNIrpic (−5.74 eV). Hole trapping and hopping by FCNIrpic dominate the current density of the device, resulting in high current density at 10% doping concentration. The luminance also followed the same trend as the current density although the luminance of the 5% FCNIrpic doped device was slightly higher than that of the 3% FCNIrpic doped device because of better recombination efficiency in the emitting layer.

The quantum efficiency–luminance curves of the DFPO3 device are shown in Fig. 4. The quantum efficiency was increased according to doping concentration and the best quantum efficiency was obtained in the 10% FCNIrpic doped device. The maximum quantum efficiency of the 10% FCNIrpic doped deep blue PHOLED was 25.9% and the quantum efficiency at 100 cd/m^2 was 23.2%. The quantum efficiency achieved in this work is better than any other data reported in deep blue PHOLEDs [3]. The high quantum efficiency in 10% FCNIrpic doped device is due to the better

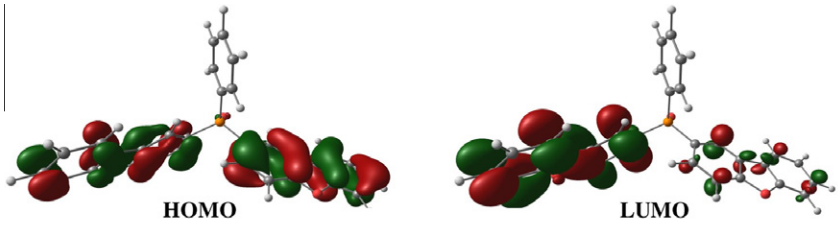


Fig. 2. HOMO and LUMO distribution of DFPO3.

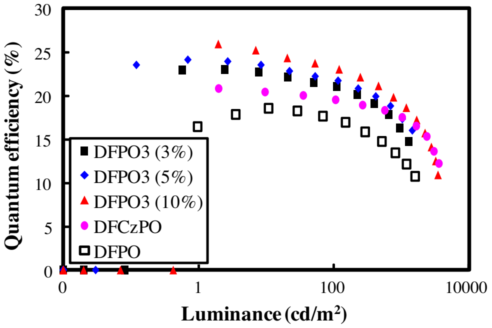


Fig. 4. Quantum efficiency–luminance curves of DFPO3 devices according to doping concentration. Quantum efficiency of DFPO3 was compared with that of DFCzPO and DFPO.

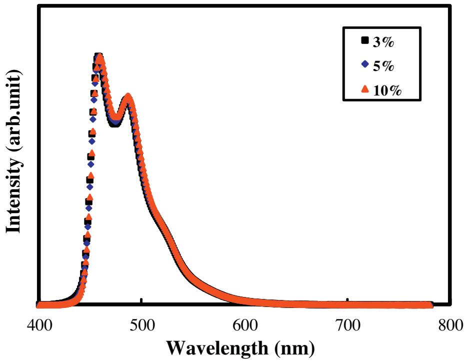


Fig. 5. Electroluminescence spectra of DFPO3 devices.

hole injection at high doping concentration by charge trapping and hopping. As there is 0.56 eV energy barrier for hole injection between the DFPO3 and mCP hole transport material, the hole injection from the mCP to emitting layer is limited. The hole injection can be improved by the dopant material at high doping concentration because dopant transports holes through hopping between dopant materials. As DFPO3 is an electron transport type host material, holes and electrons are balanced at high doping concentration because of the high hole density. The maximum current efficiency of the 10% FCNIrpic doped device was 37.5 cd/A. Quantum efficiency of strong electron transport and bipolar host materials is also shown in this figure to compare the device performances of weak electron transport type host material with those of strong electron transport and bipolar host materials. 9-(8-(Diphenylphosphoryl)dibenzo[b,d]furan-2-yl)-9H-carbazole (DFCzPO) was used as the bipolar host material and DFPO was adopted as the strong electron transport type host material. It can be seen that DFPO3 showed better quantum efficiency than DFPO and DFCzPO although the quantum efficiency roll-off was worse than that of DFPO3 device. Strong electron transport type DFPO host material showed low quantum efficiency because of poor hole injection. This indicates that weak electron transport type host materials can be as efficient as bipolar host materials in terms of quantum efficiency. Management of doping concentration controls the hole injection and transport in the emitting layer, resulting in the high recombination efficiency in the emitting layer.

Electroluminescence (EL) spectra of the DFPO3 devices are shown in Fig. 5 according to doping concentration. Deep blue emission with a maximum emission peak at 459 nm was observed without any emission by host or charge transport materials, indicating efficient energy transfer from DFPO3 to FCNIrpic. The EL spectra were red-shifted at high doping concentration due to strong intermolecular interaction. The colour coordinate of the 3% FCNIrpic doped device was (0.14, 0.20), while that of the 10% FCNIrpic doped device was (0.14, 0.22).

4. Conclusions

In conclusion, an electron transport type high triplet energy host material, DFPO3, was effectively synthesized and showed good performances as the host material for deep blue PHOLEDs. A high quantum efficiency of 25.9% was achieved, which was higher than any other quantum efficiency value reported in other works.

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