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# Carboline modified dibenzofuran as a high triplet host material for blue phosphorescent organic light-emitting diodes

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#### Abstract

A carboline modified dibenzofuran compound, 2,8-bis(pyrido[2,3-b]indol-9yl)dibenzofuran (DBFCb), was synthesized and evaluated as the host material for blue phosphorescent organic light-emitting diodes by doping iridium (III) bis((3,5difluorophenyl)pyridine) picolinate (FIrpic) as a blue triplet emitter. The DBFCb host showed balanced charge density in the emitting layer and a triplet energy of 2.88 eV by carboline moiety. The FIrpic doped DBFCb devices realized high external quantum efficiency of 21,3% at a low doping concentration of 3%.

Key words : dibenzofuran, carboline, charge balance, blue device, high quantum efficiency

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#### Introduction

There have been a lot of researches about developing high triplet energy host materials to enhance the quantum efficiency of blue phosphorescent organic light-emitting diodes (PHOLEDs). Generally, carbazole derivatives have been extensively studied as the high triplet energy host materials, but relatively poor electron transport properties of the carbazole derivatives limited the device performances of the blue PHOLEDs[1-7]. Therefore, several moieties have been developed as alternatives of the carbazole moiety and one of the most useful unit structures was carboline[8-15]. The carboline moiety is composed of conjugated pyridine and indole sub-units and has better electron transport properties than carbazole due to electron deficiency of the pyridine sub-unit. The good electron transport properties of carboline balanced holes and electrons, contributing to the high quantum efficiency of the blue PHOLEDs. There have been several papers reporting high external quantum efficiency above 20% in blue PHOLEDs using host materials derived from carboline[10-15]. However, the molecular structure of the carboline compounds was not diversified in spite of high quantum efficiency of the carboline derivatives. Typically, the carboline moiety was combined with the carbazole moiety for both hole and electron transport properties[12,13] although a carboline compound with two carboline moieties linked via a biphenyl core was reported[15].

In this work, a new carboline derivative, 2,8-bis(pyrido[2,3-b]indol-9-yl)dibenzofuran (DBFCb), was developed as a host material for blue PHOLEDs. The synthesis and device application of DBFCb as the host material of blue PHOLEDs were investigated and high external quantum efficiency 21.3% at a low doping concentration of 3% in blue PHOLEDs was demonstrated.

#### **Experimental Section**

#### **General information**

Dibenzofuran (TCI Chem. Co.) was used without further purification. Periodic acid, copper iodide (CuI), *trans*-1,2-diaminocyclohexane (Aldrich Chem. Co.), sodium thiosulfate, sulfuric acid, acetic acid, 1,4-dioxane (Duksan Sci. Co.), iodine (Samchun Sci. Co.), 9*H*-pyrido[2,3-*b*]indole ( $\alpha$ -carboline) (P&H tech Co.), and potassium phosphate (K<sub>3</sub>PO<sub>4</sub>) (Daejung Sci. Co.) were also used as received. Synthesized material was analyzed according to the method reported in the literature[10].

#### **Synthesis**

Synthetic scheme of the DBFCb is described in Scheme 1.

#### 2, 8-Diiododibenzofuran (1)

Dibenzofuran (7.00 g, 41.62 mmol) and periodic acid (11.38 g, 49.94 mmol) were dissolved in acetic acid (300 ml). And then, iodine (9.34 g, 73.6 mmol) was added to the solution. The reaction mixture was stirred at 60 °C for 30 min followed by addition of distilled water (60 ml) and sulfuric acid (0.6 ml). The solution was refluxed for 38 h, cooled to room temperature and poured into distilled water. The mixture was filtered and diluted with ethyl acetate and washed with distilled water and sodium thiosulfate. The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo. The crude product was washed with hexane after drying in vacuum. The synthesized 2, 8-diiododibenzofuran was used in the next reaction without further purification. A white powder was obtained as a product (7.70 g, yield : 44%)

#### 2, 8-Bis(pyrido[2,3-b]indol-9-yl)dibenzofuran (DBFCb) (2)

2, 8-Diiododibenzofuran (1.15 g, 2.74 mmol),  $\alpha$ -carboline (1.02 g, 6.03 mmol), K<sub>3</sub>PO<sub>4</sub> (2.33 g, 10.96 mmol) and CuI (0.53 g, 2.74 mmol) were dissolved in 1,4-dioxane (60 ml) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min and *trans*-1,2-diaminocyclohexane (0.34 ml, 2.74 mmol) was added to the solution followed by reflux overnight. After cooling to room temperature, the mixture was filtered and diluted with methylene chloride and washed with distilled water. The organic layer was dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo. The product was purified by

column chromatography using methylene chloride/n-hexane as an eluent. A white powder was obtained by vacuum train sublimation. (0.30 g, yield : 42%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (d, 1H, J = 6.40 Hz), 8.40 (d, 1H, J = 8.80 Hz), 8.20 (d, 1H, J = 1.60 Hz), 8.14 (d, 1H, J = 7.60 Hz), 7.86 (d, 1H, J = 8.80 Hz), 7.76 (d, 1H, J = 11.20 Hz), 7.49-7.47 (m, 2H), 7.36-7.33 (m, 1H), 7.26-7.23 (m, 1H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.14, 152.49, 146.71, 140.79, 131.64, 128.52, 127.57, 127.22, 125.43, 121.13, 120.94, 120.90, 120.70, 116.46, 116.26, 113.16, 110.45, MS (FAB) m/z 501 [(M+H)<sup>+</sup>]. Elemental Analysis (calculated for C<sub>34</sub>H<sub>20</sub>N<sub>4</sub>O) : C, 81.58; H, 4.03; N, 11.19; O, 3.20. Found : C, 81.57; H, 4.05; N, 11.18; O, 3.19.

#### **Device fabrication and measurements**

Blue PHOLEDs were fabricated by growing organic materials on poly(3,4ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, 60 nm) coated indium tin oxide (ITO, 120 nm) substrate by vacuum thermal evaporation. 4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 20 nm) was a hole transport layer and N,N'-dicarbazolyl-3,5-benzene (mCP, 10 nm) was used as a hole transport type exciton blocking layer. Iridium (III) bis((3,5-difluorophenyl)pyridine) picolinate (FIrpic) doped DBFCb (25 nm) was a blue emitting layer and diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 35 nm) was deposited as an electron transport type exciton blocking layer. LiF(1 nm)/Al(200 nm) double layer was evaporated as a cathode for the blue PHOLEDs. Single carrier devices had device structures of ITO (120 nm)/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/DBFCb (25 nm)/TAPC (5 nm)/Al (200 nm) (hole only device) and ITO (120 nm)/Ca (5 nm)/DBFCb (25 nm)/TSPO1 (35 nm)/LiF (1 nm)/Al (200 nm) (electron only device). Encapsulation of the blue PHOLEDs and single carrier devices was carried out to protect the devices from moisture and oxygen using a glass cover. A desiccant was inserted inside the device and the glass cover was sealed with an epoxy adhesive by ultraviolet curing. Electrical performances of the devices were characterized using Keithley 2400 source measurement unit and luminance performances were measured using CS 2000 spectroradiometer.

#### **Results and discussion**

The carboline based host material, DBFCb, has a weak electron transport type dibenzofuran core and two carboline moieties. Compared with other carboline compounds reported earlier[10-15], the dibenzofuran core can allow more electron transport character to the host material and can produce electron transport type host materials. The DBFCb host was simply synthesized by the reaction of 2,8diiododibenzofuran with  $\alpha$ -carboline using CuI. Synthetic yield of the product after column chromatography and vacuum train sublimation was 42%. Purity of the final sublimed compound was 99.9% and the final compound was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, mass and elemental analysis.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of DBFCb were studied by calculating electron distribution of optimized geometrical structure. B3LYP 6-31G\* basis set of Gaussian 09 program was used for the molecular simulation. **Figure 1** represents the electron distribution of DBFCb. The HOMO was widespread over the entire molecule with more HOMO dispersion on the carboline and the LUMO was centered on the dibenzofuran moiety. Relatively low electron density of the aromatic units of dibenzofuran by electron withdrawing oxygen allowed the localization of LUMO on the dibenzofuran moiety and dominant HOMO distribution on the carboline moiety. As the carboline and dibenzofuran moieties are weak hole transport and electron transport units, respectively, DBFCb may show bipolar charge transport properties.

Ionization potential (IP) and electron affinity (EA) of DBFCb were analyzed by measuring the oxidation and reduction potentials. Oxidation and reduction curves obtained from cyclic voltammetry (CV) measurement were plotted against voltage in **Figure 2**. The oxidation and reduction potentials of DBFCb were 1.30 V and -2.13 V from the onset of oxidation and reduction curves, which were -6.17 eV and -2.74 eV as IP and EA using ferrocene as the standard material. The IP of DBFCb was stabilized by the HOMO dispersion on the carboline moiety. The pyridine unit of the carboline moiety decreased electron density and deepened the HOMO level of DBFCb compared to carbazole derived molecules. The EA was also stabilized by the LUMO distribution on the dibenzofuran. The HOMO and LUMO of DBFCb can be estimated to be -6.17 eV and -2.74 eV, respectively, from the IP and EA.

Photophysical parameters of DBFCb were extracted using UV-vis absorption and PL emission analysis. **Figure 3** shows UV-vis absorption, solution PL and low temperature PL spectra of DBFCb. Solution and low temperature PL measurements were carried out in tetrahydrofuran solvent at a concentration of  $1.0 \times 10^{-5}$  M. UV-vis absorption assigned to  $\pi$ - $\pi$ \* and n- $\pi$ \* absorption of DBFCb was observed below 360 nm and solution PL peak position was 379 nm. First phosphorescent peak position was 427 nm and the triplet energy of DBFCb was 2.90 eV from the low temperature PL measurement at 77 K. The high triplet energy of DBFCb is due to the distortion of the carboline moiety from the dibenzofuran plane by 53.86 ° as presented in **Figure 4**. The

distortion of the carboline moiety limited p-orbital overlap between dibenzofuran and carboline, which lead to the high triplet energy.

Thermal transition temperatures of DBFCb were measured using differential scanning calorimeter (DSC) to elucidate thermal stability of DBFCb. **Figure 5** shows a DSC themogram of DBFCb. Glass transition temperature ( $T_e$ ) is an important parameter for the thermal stability and the  $T_e$  of DBFCb was 132 °C. As the  $T_e$  of DBFCb was well above 100 °C, the DBFCb host can be considered as a thermally stable host material. The  $T_e$  of DBFCb was higher than that of the carboline host material with a biphenyl core[15]. Thermal decomposition temperature ( $T_d$ ) of DBFCb was investigated by thermogravimetric analysis (TGA). TGA curve of DBFCb is displayed in **Figure 6**. The  $T_d$  at 5 % weight loss was 378 °C, which supports the thermal stability of DBFCb as a host material.

The high triplet energy of DBFCb allowed us to grow blue PHOLEDs by doping common FIrpic as a blue triplet emitter because the triplet energy of FIrpic (2.65 eV) is lower than that of DBFCb (2.90 eV). FIrpic was doped at doping concentrations of 3% and 5%. Current density-voltage-luminance plots of the DBFCb:FIrpic devices at 3% and 5% doping concentrations are presented in **Figure 7**. The current density was sharply increased at a turn-on voltage of 3.0 V. Low energy barrier for hole injection

(0.07 eV) and electron injection (0.22 eV) lowered the turn-on voltage of the DBFCb device by facilitating charge injection from the charge transport layers to the emitting layer as shown in the energy level diagram of the device in **Figure 8**. Driving voltage at 1,000 cd/m<sup>2</sup> was 5.7 V and 6.7 V at 3% and 5% doping concentrations, respectively. The high driving voltage of the DBFCb device at 5% doping concentration is originated by the low recombination efficiency and low current density compared to the DBFCb device at 3% doping concentration.

External quantum efficiency of the DBFCb device was presented against luminance in **Figure 9**. The external quantum efficiency was optimized at 3% doping concentration by concentration quenching effect at 5% doping concentration and the maximum quantum efficiency of the DBFCb device was 21.3%. The high quantum efficiency above 20% was maintained up to a luminance of 3,500 cd/m<sup>2</sup>. Several factors can explain the origins of the high external quantum efficiency of the DBFCb devices. One key factor is the suppression of triplet exciton quenching of FIrpic by the DBFCb host due to high triplet energy of DBFCb (2.90 eV). Another factor is complete energy transfer from DBFCb to FIrpic as can be ensured by the electroluminescence (EL) spectra in **Figure 10**. Pure emission of FIrpic without DBFCb emission supports the complete energy transfer in the DBFCb device. Although DBFCb was synthesized as an electron transport type host as shown in current density-voltage curves of single carrier devices (**Figure 11**), the triplet exciton harvesting and good energy transfer increased the quantum efficiency. Additionally, electron trapping effect by FIrpic in the emitting layer contributed to the high quantum efficiency through balancing holes and electrons in the emitting layer[16]. The quantum efficiency of the DBFCb devices was higher than that of mCP device over all luminance range and efficiency roll-off was also reduced.

#### Conclusions

In summary, a carboline and dibenzofuran derived material, DBFCb, was synthesized as an electron transport type host material for FIrpic triplet emitter. The high triplet energy of 2.90 eV and good energy transfer characteristics of DBFCb contributed to high external quantum efficiency and the maximum external quantum efficiency of DBFCb reached 21.3%. Therefore, the DBFCb host can be diversely applied as the host material for blue PHOLEDs.

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Figure 8. Energy level diagram of the blue phosphorescent organic light emitting diodes with DBFCb host material.

Figure 9. External quantum efficiency-luminance plots of DBFCb devices doped with FIrpic at doping concentrations of 3% and 5%. Device data of mCP device was also added for comparison.

Figure 10. Electroluminescence spectra of DBFCb devices doped with FIrpic at doping

concentrations of 3% and 5%.

Figure 11. Current density-voltage curves of the hole only and electron only devices of DBFCb.









Figure 3















Figure 9





Carboline modified dibenzofuran as an electron transport type host High triplet energy of 2.88 eV as a host for blue phosphorescent organic light-emitting diodes High quantum efficiency of 21.3% in blue phosphorescent organic light emitting diodes