



# Deep-blue OLEDs using novel efficient spiro-type dopant materials

Young-Min Jeon<sup>a</sup>, Jun-Yeop Lee<sup>b</sup>, Joon-Woo Kim<sup>c</sup>, Chil-Won Lee<sup>c</sup>, Myoung-Seon Gong<sup>d,\*</sup>

<sup>a</sup> Department of Chemistry, Dankook University, Chungnam 330-714, Republic of Korea

<sup>b</sup> Department of Polymer Engineering, Dankook University, Yongin, Kyung-gi 448-701, Republic of Korea

<sup>c</sup> OLED Team, Daejoo Electronic Materials, Siheung, Kyung-gi 429-848, Republic of Korea

<sup>d</sup> Department of Nanobiomedical Science and WCU Research Center of Nanobiomedical Science, Dankook University, Cheonan, Chungnam 330-714, Republic of Korea

## ARTICLE INFO

### Article history:

Received 31 March 2010

Received in revised form 16 May 2010

Accepted 6 August 2010

Available online 19 August 2010

### Keywords:

Deep blue

Spiro[fluorene-benzofluorene]

Dopant

Color purity

OLED

Host

## ABSTRACT

The deep blue fluorescent spiro-type dopant materials *N,N,N',N'*-tetraphenylspiro[fluorene-7,9'-benzofluorene] (**SFBF**)-5,9-diamine (BD-6DPA), *N,N'*-di-(2-naphthyl)-*N,N'*-diphenyl-**SFBF**-5,9-diamine (BD-6NPA), *N,N'*-diphenyl-*N,N'*-di-*m*-tolyl-**SFBF**-5,9-diamine (BD-6MDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-(trimethylsilyl)phenyl)-**SFBF**-5,9-diamine (BD-6TMSA) were designed and successfully prepared by amination reactions. The EL characteristics of MADN as the blue host material doped with the above blue dopant materials were evaluated. The electroluminescence spectra of ITO/*N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD/*N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine (NPB)/2-methyl-9,10-di(2-naphthyl)anthracene (MADN):BD-6MDPA/tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>)/LiF/Al devices show a narrow emission band with a full width at half maximum of 48 nm and a  $\lambda_{\text{max}}(\epsilon) = 463$  nm. The device obtained from MADN doped with BD-6MDPA showed a good color purity (0.135, 0.156), high luminance efficiency (9.11 cd/A at 6.5 V) and high external quantum efficiency (8.16%).

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Organic light emitting diodes (OLEDs) have attracted considerable attention due to their many advantages for commercial applications, such as their high brightness, low power consumption, capability of emitting a wide range of colors, and applications in full color organic displays [1]. For full color displays, three primary colors (red, green, blue) are necessary. Many new materials with red, green, and blue emitting colors have been developed to meet these requirements [2]. Developing blue light emitters is essential for the development of full color displays. In spite of the considerable advances that have been made in the field of OLEDs, it is difficult to find appropriate blue emitting materials because of their low solution and low solid-state photoluminescence (PL) quantum yields

[3]. OLED devices have a short lifetime because of the deterioration of the luminescent layers. Their lifetimes can be lengthened by the introduction of thermally stable substituents on the host and dopant materials [4]. Generally, host and supporting layer materials having a high glass transition temperature are needed to obtain a long lifetime. Especially, the lifetime of the luminescent layers is closely related to the specific host material in use [5].

The color purity of a blue light emitter is determined by the dopant, and is improved by shifting the emission region to a shorter wavelength. The maximum emission range of some commercial dopant materials are close to the blue sky region (450–470 nm), but wavelengths lower than 450 nm are also considered to have reasonable color purity [6,7]. In addition, many problems still remain to be solved regarding durability over time due to long-term usage, and deterioration caused by oxygen and moisture in air. In addition, many other problems remain related to the need for good color purity of blue luminescence in applications such as full color displays [8].

\* Corresponding author. Tel./fax: +82 41 5501476.

E-mail address: [msgong@dankook.ac.kr](mailto:msgong@dankook.ac.kr) (M.-S. Gong).

On the other hand, spiro compounds with specific steric configurations has been attracting attention as an organic functional material because of the specific physical properties of the material, such as high glass transition temperature, which makes them a very promising approach for optoelectric materials [9]. Much of the recent research into blue light-emitting materials has centered on spiro-based derivatives because of their high solution and solid-state photoluminescence quantum yields [10]. Representative organic spiro materials as blue light-emitting materials include spiro-oligophenyl [11], spirofluorenes (SFs) with asymmetric substitution [12], spiro-substituted SF [13], SF-linked phenylanthracene [14] and anthracene [15], heteroatom-substituted spiro compounds [16], pyrene-substituted SFs [17] and difluorene-indenofluorene compounds [18]. Many studies have dealt with the spiro[fluorene-7,9'-benzofluorene] (SFBF) as organic electroluminescent host materials. The performance of OLEDs (the color purity and luminescence efficiency) based on SFBF was determined by the position of substitution and aryl moieties with a variety of conjugation chain length [19].

In this study, we report the synthesis of a series of new deep-blue emitting dopant materials, *N,N,N',N'*-tetraphenyl-SFBF-5,9-diamine (BD-6DPA), *N,N'*-di-(2-naphthyl)-*N,N'*-diphenyl-SFBF-5,9-diamine (BD-6NPA), *N,N'*-diphenyl-*N,N'*-di-*m*-tolyl-SFBF-5,9-diamine (BD-6MDPA) and *N,N'*-diphenyl-*N,N'*-bis(4-(trimethylsilyl)phenyl)-SFBF-5,9-diamine (BD-6TMSA) by amination reactions of both 5- and 9-positions on the SFBF. Multilayered OLEDs were fabricated by using these deep-blue materials as the emitting layer and the dopant for MADN. A high quantum efficiency of 8.16% with CIE coordinates of (0.135, 0/156) was achieved, and this is one of the best efficiency value of deep blue fluorescence OLEDs ever reported in the literature.

## 2. Experimental

### 2.1. Materials and measurements

Tetrakis(triphenylphosphine)palladium(0) and bromine (Aldrich Chem. Co.) were used without further purification. Diphenyl-[4-(2-[1,1;4,1]terphenyl-4-yl-vinyl)-phenyl]-amine (BD-1) and 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) were prepared using a method reported elsewhere [22]. Tetrahydrofuran and toluene were distilled over sodium and calcium hydride. Diphenylamine, *N*-phenyl-2-naphthylamine and 3-methyldiphenylamine (Aldrich Chem. Co.) were used as received. *N*-phenyl-4-(trimethylsilyl)aniline was prepared by the literature method previously reported [23]. Tri-*t*-butylphosphine, potassium *t*-butoxide (Aldrich Chem. Co.), palladium(II) acetate (TCI Co.) were used as received for amination. 5-Bromo-SFBF and 9-bromo-SFBF [19] were prepared as previously reported.

The FT-IR spectra were obtained using a Biorad Excaliber FTS-3000MX spectrophotometer, and the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 500 (500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ ) spectrometer. The photoluminescence (PL) spectra were recorded on a fluo-

rescence spectrophotometer (Jasco FP-6500) and the UV-vis spectra were obtained using a UV-vis spectrophotometer (Shimadzu, UV-1601PC). Elemental analyses were performed using a CE Instrument (EA1110), and the differential scanning calorimetry (DSC) measurements were performed using a Mettler DSC 822<sup>e</sup> under nitrogen at a heating rate of 10 °C/min. The low and high resolution mass spectra were recorded using a mass spectrometer (JEOL, JMS-AX505WA) in FAB mode. The energy levels were measured using a low energy photoelectron spectrometer (Riken-Keiki AC-2). The current-voltage characteristics of the encapsulated devices were measured using a Keithley 2400 source measurement unit and CS 1000 spectroradiometer.

### 2.2. General procedure for the coupling reaction

The 5,9-dibromo-SFBF (**1**) (5 g, 9.53 mmol), diarylamine derivative (24.79 mmol) and palladium acetate (0.150 g, 0.67 mmol) were dissolved in anhydrous toluene under nitrogen atmosphere. To the reaction mixture was added a solution of tri-*t*-butylphosphine (1 M, 0.42 g, 1.91 mmol) and potassium *t*-butoxide (4.28 g, 38.15 mmol) dropwise slowly. The reaction mixture was stirred for 12 h at 100 °C. The mixture was diluted with dichloromethane and washed with distilled water (150 mL) three times. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and evaporated in vacuo to give the crude product, which was purified by column chromatography by *n*-hexane. The final product was obtained, a yellow-green powder.

*N,N,N',N'*-Tetraphenyl-SFBF-5,9-diamine (BD-6DPA). Yield 65%. Mp 270 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77–8.76 (d,  $J$  = 8.47 Hz, 1H, Ar-CH-naphthalene), 8.23–8.22 (d,  $J$  = 8.54 Hz, 1H, Ar-CH-naphthalene), 8.02–8.00 (d,  $J$  = 8.37 Hz, 1H, Ar-CH-benzene), 7.69–7.67 (d,  $J$  = 7.61 Hz, 2H, Ar-CH-fluorene), 7.61–7.59 (t,  $J$  = 8.15 Hz, 1H, Ar-CH-naphthalene), 7.39–7.38 (t,  $J$  = 8.00 Hz, 1H, Ar-CH-naphthalene), 7.28–7.26 (t,  $J$  = 7.05 Hz, 2H, Ar-CH-fluorene), 7.12–7.10 (s, 2H, Ar-CH-benzene), 7.12–7.10 (t, 4H, Ar-CH-benzene), 7.10–7.08 (d, 2H, Ar-CH-fluorene), 6.96–6.94 (t, 4H, Ar-CH-benzene), 6.90–6.89 (t, 4H, Ar-CH-benzene), 6.89–6.87 (d, 1H, Ar-CH-naphthalene), 6.82–6.81 (d, 4H, Ar-CH-benzene), 6.71–6.69 (d, 1H, Ar-CH-benzene), 6.56–6.56 (d, 1H, Ar-CH-benzene).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  151.6, 148.0, 147.9, 147.8, 147.5, 146.8, 142.7, 142.1, 137.1, 135.4, 131.9, 130.8, 129.2, 127.9, 127.8, 127.0, 126.1, 125.7, 124.4, 124.1, 123.9, 123.5, 123.4, 122.9, 121.5, 121.4, 120.3, 119.5, 77.4, 77.2, 76.9, 66.4 ppm.

*N,N'*-Di-(2-naphthyl)-*N,N'*-diphenyl-SFBF-5,9-diamine (BD-6NPA). Yield 62%. Mp 295 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80–8.78 (d,  $J$  = 8.50 Hz, 1H, Ar-CH-naphthalene), 8.26–8.24 (d,  $J$  = 8.54 Hz, 1H, Ar-CH-naphthalene), 8.06–8.05 (d,  $J$  = 8.39 Hz, 1H, Ar-CH-benzene), 7.69–7.68 (d,  $J$  = 7.62 Hz, 1H, Ar-CH-naphthalene), 7.65–7.63 (d, 2H, Ar-CH-fluorene), 7.65–7.63 (d, 2H, Ar-CH-naphthalene), 7.60–7.57 (t, 1H, Ar-CH-naphthalene), 7.51–7.50 (d, 1H, Ar-CH-naphthalene), 7.43–7.42 (d, 1H, Ar-CH-naphthalene), 7.40–7.38 (d, 2H, Ar-CH-naphthalene), 7.28–7.27 (t, 2H, Ar-CH-fluorene), 7.26–7.24 (t, 2H,

Download English Version:

<https://daneshyari.com/en/article/1264860>

Download Persian Version:

<https://daneshyari.com/article/1264860>

[Daneshyari.com](https://daneshyari.com)