



Blue organic light-emitting diodes using novel spiro[fluorene-benzofluorene]-type host materials

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ABSTRACT

Deep blue colored, fluorescent, spiro-type host materials, 5-[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] and 5,9-bis[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] were designed and successfully prepared by the Suzuki reaction. The electroluminescence characteristics of the two compounds as blue host materials doped with blue dopant materials, diphenyl[4-(2-[1,1;4,1]terphenyl-4-yl-vinyl)phenyl]amine and 1,6-bis[(*p*-trimethylsilylphenyl)amino]pyrene (SPP) were evaluated. The device used comprised ITO/*N,N'*-bis-[4-(*di-m*-tolylamino)phenyl]-*N,N'*-diphenylbiphenyl-4,4'-diamine)/bis[*N*-(1-naphthyl)-*N*-phenyl]benzidine/Host:5% dopant/tris(8-hydroxyquinolinato)aluminum/Al-LiF. The device obtained from 5-[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] doped with 1,6-bis[(*p*-trimethylsilylphenyl)amino]pyrene displayed high color purity (0.138, 0.138) and high efficiency (3.70 cd/A at 7 V).

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1. Introduction

Organic light-emitting diodes (OLEDs) are the subject of intense research owing to their promising full-color display application. Although a large number of valuable red and green emitters that satisfy the requirements for OLEDs have been developed, efficient and stable blue emitters are still rare and have been the subject of considerable interest [1,2]. Major focus has been on various material systems, including anthracene [3–5], distyrylarylene [6–11], fluorene [12,13] and tetra(phenyl)silyl derivatives [14,15].

Spiro compounds with specific steric configurations have attracted attention as organic functional materials on account of their specific physical properties. An important class of spiro compounds with high glass transition temperatures was recently developed for use as optoelectric materials [16]. In particular, the most recent research into blue light-emitting materials has centered on spiro-based derivatives on account of their high solution and solid state photoluminescence quantum yield. Evidence suggests that amorphous, thin film OLEDs which have a high glass transition temperature (T_g) are less vulnerable to

heat damage and, hence, are more stable during use. Thus, high T_g materials are always desirable in OLED applications. Spirofluorenes can be functionalized easily with a variety of substituents as blue host and dopant materials, such as aryl, alkyl and diarylamine. Many attempts have been made to develop new amorphous spirobifluorenes with high morphological stability. The introduction of the spiro linkage has resulted in the generation of spiro-type host and dopant materials with higher T_g values [5,17–20]. Recently, spiro[fluorene-benzofluorene] derivatives with various aromatic and aromatic amine groups on the 5-position were synthesized and their electroluminescence (EL) characteristics were investigated as both host and dopant materials for blue OLEDs [21–24].

This paper reports the synthesis two new deep blue-emitting host materials consisting of 5-[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] (BH-1PN) and 5,9-bis[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] (BH-1DPN) along with their characterization using the following techniques: ¹H nuclear magnetic resonance (NMR), ¹³C NMR, Fourier transform infrared (FT-IR), Mass spectroscopy, thermal analysis, and ultraviolet (UV)–visible and photoluminescence (PL) spectroscopy. The EL properties of multilayered OLEDs fabricated using a BH-1PN and BH-1DPN host and BD-1 and SPP as the dopant were evaluated.

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2. Experimental

2.1. Materials and measurements

Tetrakis(triphenylphosphine)palladium(0) and bromine (Aldrich Chem. Co.) were used without further purification. 4-(Naphthalene-1-yl)phenylboronic acid and 5-[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] (BH-1PN) were prepared using the method reported elsewhere [25]. Tetrahydrofuran and toluene were distilled over sodium and calcium hydride. Diphenyl-[4-(2-[1,1;4,1]terphenyl-4-yl-vinyl)-phenyl]-amine (BD-1, band gap, 2.87 eV; HOMO 5.44 eV; λ_{\max} (Absorption) = 383 nm; λ_{\max} (Emission) = 472 nm) [6] and 1,6-bis[*p*-trimethylsilylphenyl]amino]pyrene (SPP; band gap, 2.73 eV; HOMO 5.47 eV; T_{sub} , 340 °C; λ_{\max} (Absorption) = 426 nm; λ_{\max} (Emission) = 460 nm) [26] were used as dopant materials. 5-Bromo-spiro[fluorene-7,9'-benzofluorene] (**1**) was prepared using a previously reported method [21].

The FT-IR spectra were obtained using a Biorad Excaliber FTS-3000MX spectrophotometer, and the ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker, Avance 500 (500 MHz for ^1H and 125 MHz for ^{13}C) spectrometer. The photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500) and the UV-vis spectra were obtained using a UV-vis spectrophotometer (Shimadzu, UV-1601 PC). Elemental analyses were performed using a CE Instrument (EA1110), and the differential scanning calorimetry (DSC) measurements were performed using a Mettler DSC 822^e 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 programmable electrometer with current and voltage sources (Keithley 237 model). The luminance and EL spectra were measured using a PR650 system (Photo Research Co. Ltd.).

2.2. Synthesis of 5,9-dibromo-spiro[fluorene-7,9'-benzofluorene] (**2**)

Compound **1** (4.43 g, 10 mmol) was dissolved in chloroform (100 mL) in a two-necked flask. Bromine (1.6 g, 0.2 mmol) was then added dropwise over a period of 20 min. The mixture was stirred at room temperature for 24 h. The precipitated solid was filtered and

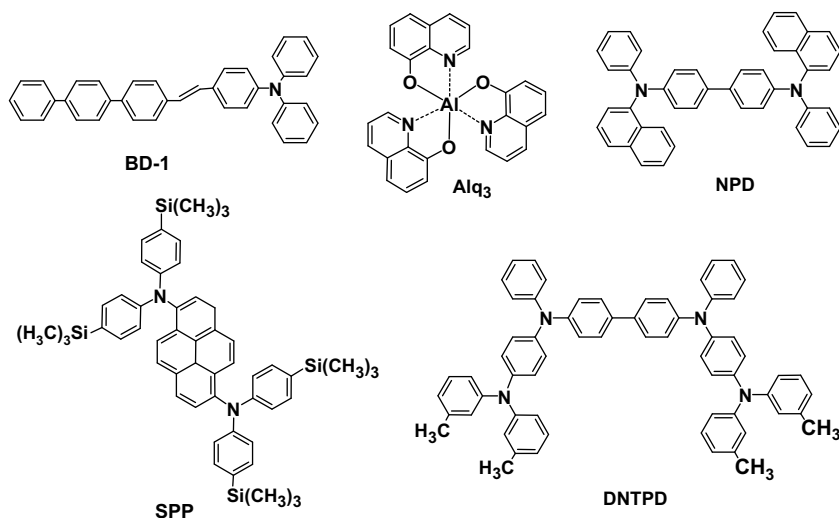
dried in vacuo to give the crude product, which was then purified by recrystallization from acetonitrile to give a white powder.

Yield 76%. Mp 243 °C. ^1H NMR (500 MHz, CDCl_3): δ 8.78–8.76 (d, 1H, Ar-CH-benzene), 8.42–8.40 (d, 1H, Ar-CH-naphthalene), 8.35–8.33 (d, 1H, Ar-CH-benzene), 7.88–7.87 (s, 1H, Ar-CH-benzene), 7.75–7.72 (t, 2H, Ar-CH-fluorene), 7.65–7.63 (t, 2H, Ar-CH-fluorene), 7.47–7.44 (t, 2H, Ar-CH-fluorene), 7.41–7.37 (t, 2H, Ar-CH-fluorene), 7.17–7.15 (d, 1H, Ar-CH-benzene), 6.89–6.87 (d, 1H, naphthalene-CH-Br), 6.69–6.67 (d, 1H, Ar-CH-Br), 6.71–6.69 (d, 1H, Ar-CH-benzene). FT-IR (KBr, cm^{-1}) 3057, 3040, 3012 (aromatic C-H), 745 (aromatic C-Br). MS (FAB) m/z 523.96 [(M+1)⁺]. UV-vis (THF): λ_{\max} (Absorption) = 356 nm, λ_{\max} (Emission) = 422 nm.

2.3. Synthesis of 5,9-bis[4-(1-naphthyl)phenyl]-spiro[fluorene-7,9'-benzofluorene] (BH-1PN)

Compound **2** (5.23 g, 10 mmol), 4-(naphthalene-1-yl)phenylboronic acid (4.87 g, 20 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.81 g, 0.70 mmol) were dissolved in THF (150 mL) in a two-necked flask with constant stirring under nitrogen for 1 h. A solution of potassium carbonate (2 M, 100 mL) was added dropwise to the above reaction mixture over a period of 30 min, and the reaction mixture was heated under reflux for 24 h in a nitrogen atmosphere. After cooling to ambient temperature, the reaction mixture was extracted with methylene chloride and water. The organic layer was evaporated using a rotary evaporator, and the residue was subjected to column chromatography using methylene chloride/*n*-hexane (1/3) as the eluant. A yellow powdery product was obtained.

Yield: 65%. Mp 371.8 °C. ^1H NMR (500 MHz; CDCl_3) δ 9.03–9.01 (d, J = 8.43 Hz, 1H, Ar-CH-benzene), δ 8.60–8.58 (d, J = 8.19 Hz, 1H, Ar-CH-benzene), δ 8.19–8.17 (d, J = 8.44 Hz, 1H, Ar-CH-benzene), δ 7.97–7.95 (d, J = 8.40 Hz, 1H, Ar-CH-benzene), δ 7.90–7.88 (t, 4H, Ar-CH-naphthalene), δ 7.86–7.83 (t, 4H, Ar-CH-naphthalene), δ 7.81–7.78 (t, 1H, Ar-CH-benzene), δ 7.62–7.60 (d, 1H, Ar-CH-benzene), δ 7.59–7.57 (d, 2H, Ar-CH-fluorene), δ 7.54–7.51 (d, 4H, Ar-CH-benzene), δ 7.50–7.47 (d, 4H, Ar-CH-benzene), δ 7.47–7.45 (d, 4H, Ar-CH-naphthalene), δ 7.43–7.40 (d, 2H, Ar-CH-naphthalene), δ 7.40–7.39 (d, 2H, Ar-CH-fluorene), δ 7.16–7.14 (d, 2H, Ar-CH-fluorene), δ 7.14–7.13 (d, 1H, Ar-CH-benzene), δ 6.89–6.88 (d, 2H, Ar-CH-fluorene), δ 6.88 (d, 1H, Ar-CH-benzene). ^{13}C NMR (CDCl_3) δ 150.6, 147.9, 147.5, 142.2, 142.1, 140.7, 139.8, 139.7, 139.6, 139.5, 135.9, 133.9, 132.3, 131.6, 130.5, 130.2, 129.9, 128.3, 128.0.



Scheme 1. Chemical structure of HTL, ETL, HIL and dopant materials.

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