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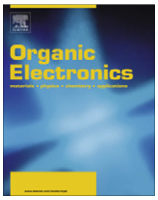

Blue light-emitting OLED using new spiro[fluorene-7,9′-benzofluorene] host and dopant materials

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ABSTRACT

A new spiro-type compound, 2-(10-biphenylanthracene)-spiro[fluorene-7,9′-benzofluorene] (BH-3B) containing anthracene moiety was prepared for the blue host material. Also new dopant materials, 2-[4′-(phenyl-4-vinylbenzeneamine)phenyl-spiro[fluorene-7, 9′-benzofluorene] (BH-3BD) and 4-[2-naphthyl-4′(phenyl-4-vinylbenzeneamine)]phenyl (BD-1N) were successfully synthesized and a blue OLEDs were made from them. The structure of the device was as follows; ITO/DNTPD/α-NPD/Host:5% dopant/Alq_3/Al-LiF. Among all of the devices, the device obtained from BH-3B host doped with 5% BH-3BD showed the best electroluminescence characteristics. The emission peak of EL is at 456 nm and the CIE value is (0.15,0.14). The brightness of the device is up to 5407 cd/m^2 at 10 V with the maximum EL efficiency of 3.4 cd/A.

1. Introduction

Polyfluorenes are promising new materials for blue light-emitting diodes because of their high photoluminescence (PL) quantum efficiencies and thermal stability [1–3]. However, an optical output of higher luminance or higher conversion efficiency is required under the present conditions. In addition, many problems still remain to be solved regarding the durability with respect to a change with time due to a long-term usage, deterioration caused by an atmospheric gas including oxygen, moisture. Besides, it is not still insufficient for solving problems related to the needs for luminescence of blue having good color purity in the case of considering the applications to a full color display and so on [4,5].

On the other hand, a spiro compound having a specific steric configuration has been attracting attention as an organic functional material in terms of the specific physical properties of the material. The important class of spiro compounds as organic molecular materials with high glass transition temperature that evolved as a very promising approach for optoelectric materials have been investigated [6–13]. 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 [14,15]. Representative organic spiro materials as blue light-emitting materials include spiro-oligophenyl [16], spirobifluorenes with asymmetric substitution [17–20], spiro-substituted spiro fluorene [21,22], spirofluorene-linked phenylanthracene [23,24],

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spirofluorene-linked anthracene [25], heteroatom- and aromatic amine-substituted spiro compound [26], pyrene-substituted spiro compound [27] and difluorene-indenofluorene compound [28].

In this paper, we report the synthesis of new host and dopant materials 2-(10-biphenylanthracene)-spiro[fluorene-7,9′-benzofluorene] (BH-3B) and 2-[4′-(phenyl-4-vinylbenzeneamine)phenyl-spiro[fluorene-7,9′-benzofluorene] (BH-3BD) by Suzuki reaction. Various properties such as UV–Vis absorption, photoluminescence, electroluminescence including EL efficiency and color purity were evaluated.

2. Experiment

2.1. Material and measurements

9-(4-Biphenylanthracene)-10-boronic acid was synthesized according to the method previously reported [7–9]. Tetrakis(triphenylphosphine)palladium(0) and potassium carbonate (Aldrich Chem. Co.) were used without further purification. Tetrahydrofuran was distilled over sodium and calcium hydride. 1-(2-Bromophenyl)naphthalene (**1**) was prepared by the method previously reported [29,30]. Diphenyl-[4-(2-[1,1;4,1]terphenyl-4-yl-vinyl)-phenyl]-amine (BD-1) was used as one of the dopants.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker, Avance 500 (500 MHz) spectrometer. Photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500) and UV–Vis spectra were obtained by a UV–Vis spectrophotometer (Shimadzu, UV-1601PC). Energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki AC-2). The FT-IR spectra were obtained with a Biorad Excaliber FTS-3000MX spectrophotometer and elemental analyses were performed using a CE Instrument, EA1110. The DSC measurements were performed on a Mettler DSC 822^e under nitrogen at a heating rate of 10 °C/min. Low and high resolution mass spectra were recorded using a JEOL, JMS-AX505WA spectrometer in FAB mode.

2.2. Synthesis of 2-bromo-spiro[fluorene-7,9′-benzofluorene] (**2**)

To a two-necked flask (250 mL), was placed a solution of 1-(2-bromophenyl)naphthalene (10 g, 35.3 mmol) dissolved in THF (50 mL). The reaction flask was cooled to −78 °C and *n*-BuLi (2.5 M in hexane, 16.8 mL) was added dropwise slowly. The whole solution was stirred at this temperature for 1 h, followed by addition of a solution of 2-bromo fluorenone (10.8 g, 41.7 mmol) dissolved in THF (30 mL) under argon atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by saturated, aqueous NaHCO$_3$ (80 mL). The reaction mixture was extracted with dichloromethane. The combined organic layers were dried with magnesium sulfate, and filtered. After the solvent was evaporated under reduced pressure, the yellow powdery product was obtained.

The above solid product was placed in a two-necked flask (100 mL) and dissolved in acetic acid (30 mL). Catalytic amount of aqueous HCl (5 mol%, 12 N) was then added and the whole solution was refluxed for 12 h. After having been cooled to ambient temperature, the purification by silica gel chromatography using dichloromethane/*n*-hexane (1/1) gave a white powdery product. Yield 73%. Mp 152 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.85-8.83 (d, 1H, Ar-*H* in fluorene), 8.44–8.43 (d, 1H, Ar-*H* in fluorene), 7.92–7.90 (d, 1H, Ar-*H* in benzofluorene), 7.85–7.83 (d, 1H, Ar-*H* in fluorene), 7.73–7.70 (t, 2H, Ar-*H* in benzofluorene), 7.64–7.62 (d, 1H, Ar-*H* in benzofluorene), 7.57–7.54 (t, 1H, Ar-*H* in fluorene), 7.50–7.46 (t, 2H, Ar-*H* in benzofluorene), 7.39–7.36 (t, 1H, Ar-*H* in fluorene), 7.17–7.15 (t, 1H, Ar-*H* in benzofluorene), 7.12–7.09 (t, 1H Ar-*H* in fluorene), 6.82–6.78 (m, 2H, Ar-*H* in benzofluorene), 6.70–6.69 (d, 1H, Ar-*H* in fluorene). FT-IR (KBr, cm^{-1}) 3055 (aromatic C-*H*), 1580 (aromatic C=C), 657 (aromatic C–Br).

2.3. Synthesis of 2-(10-biphenylanthracene)-spiro[fluorene-7,9′-benzofluorene] (BH-3B)

Compound **2** (5.0 g, 11.18 mmol) and 9-(4-biphenylanthracene)-10-boronic acid (5.01 g, 13.41 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.68 g, 0.59 mmol) were dissolved in THF (100 mL) in a two-necked flask under nitrogen atmosphere for 30 min. A solution of potassium carbonate (1.63 g, 11.18 mmol) dissolved in distilled water (50 mL) was added dropwise over a period of 20 min. The resulting solution was refluxed overnight at 80 °C. The reaction mixture was extracted with dichloromethane and water. The organic layer was evaporated with a rotary evaporator. The resulting powdery product was purified by column chromatography from *n*-hexane to give a white crystalline solid. Yield 60%. Mp 350 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.75–8.33 (2d, 2H, Ar-C*H*-benzofluorene), 8.12–7.99 (2d, 2H, Ar-C*H*-benzofluorene), 7.88–7.73 (2d, 2H, Ar-C*H*-benzofluorene), 7.71-7.45 (m, 8H, Ar-C*H*-anthracene), 7.66–7.64 (m, 4H, Ar-*H* in fluorene), 7.63–7.49 (2d, 2H, Ar-C*H*-benzofluorene), 7.41–7.39 (d, 1H, Ar-*H* in fluorene), 7.39–7.38 (t, 1H, Ar-*H* in fluorene), 7.21–7.18 (m, 4H, –*Ph*–Ph), 7.18–7.15 (m, 5H, –Ph–*Ph*), 7.02–6.84 (2d, 2H, Ar-C*H*-benzofluorene), 6.79–6.78 (d, 1H, Ar-*H* in fluorene). ^{13}C NMR (CDCl$_3$) δ 148.6, 147.5, 141.0, 138.8, 131.8, 129.4, 129.1, 129.0, 127.5, 127.3, 127.2, 127.0, 126.9, 125.2, 125.1, 124.4, 120.4, 77.4, 77.2, 76.9, 66.5 ppm. FT-IR (KBr, cm^{-1}) 3059, 3040, 3012 (aromatic C–H), 1578 (aromatic C=C). MS (FAB) m/z 694.0 [(M + 1)$^+$]. Anal. Calcd. for C$_{55}$H$_{34}$ (694.86): C, 95.07; H, 4.93. Found: C, 94.53; H, 4.87. UV–Vis (THF) λ_{max} (Absorption) = 369, 388 nm, λ_{max} (Emission) = 432, 447 nm.

2.4. Synthesis of 2-[4′-(phenyl-4-vinylbenzeneamine)phenyl]-spiro[fluorene-7,9′-benzofluorene](BH-3BD)

Compound **3** (5.0 g, 12.13 mmol), *N*-[4-[2-(4-bromophenyl)vinyl]phenyl]-*N*,*N*-diphenylamine (4.3 g, 10.11 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.58 g, 0.51 mmol) were dissolved in THF (100 mL) under nitrogen atmosphere for 30 min. To an above solution, was added a solution of potassium carbonate (1.40 g, 10.11 mmol) dissolved in distilled water