



Blue emitting materials based on bispiro-type anthracene derivatives for organic light emitting diodes



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ABSTRACT

Three bispiro-type molecules, 2-(10-phenylanthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (**1**), 10-([naphthalen-2-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (**2**), and 10-([naphthalen-1-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (**3**), were synthesized by Pt-catalyzed Suzuki coupling reactions. To explore electroluminescence properties of these materials, devices were fabricated with the following structures: Indium-tin-oxide (180 nm)/4,4'-Bis(*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (60 nm)/blue emitting materials (30 nm)/Bathophenanthroline (30 nm)/Lithium quinolate (2 nm)/Al (100 nm). Among devices, device using 2-(10-phenylanthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) showed the efficient blue emission with a luminous efficiency of 1.57 cd/A, a power efficiency of 1.83 lm/W and an external quantum efficiency of 1.83% at 20 mA/cm², respectively. The CIE coordinates of this device were (0.16, 0.10).

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1. Introduction

Over the recent years, organic light-emitting diodes (OLEDs) have been studied and developed in display industry due to their potential of application in solid-state lighting, full color display, flexible, and transparent display [1–4]. Among three primary colors emitters, red and green ones have good properties to apply in industry. However, blue emitter has problem in efficiencies as well as color purity because of intrinsic large band gap in the blue materials [5–7].

To overcome these problems, various blue emitters based on carbazole [8], triphenylamine [9], and anthracene [10,11] were investigated. Particularly, anthracene derivatives were widely studied because of intrinsic properties of anthracene, such as high quantum yield, good thermal stability, and superior electrochemical properties. However, representative anthracene units undergo intermolecular interaction like excimer or exciplex

formation resulting in the decrease of their electroluminescent (EL) performances, therefore adequate molecular design is necessary for advanced anthracene derivatives [12–16].

To overcome these problems and enhance the EL properties of anthracene derivatives, we designed and synthesized the three bispiro-type blue emitting materials, (2-(10-phenylanthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene)) (**1**), 10-([naphthalen-2-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (**2**), and 10-([naphthalen-1-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (**3**). In these materials, anthracene backbones were end-capped with phenyl and naphthyl group at C-10 position and bispiro-type moieties at C-9 position. Spiro-type materials such as spirobifluorenes have been shown to be good EL building units for OLED materials, due to their excellent fluorescent properties and good morphological, thermal, and electrochemical stabilities [17–19]. However, only a few systematic studies have investigated the EL properties of blue-emitting materials based on bispiro-type materials. As will be shown below, these bispiro-type materials **1–3** show the excellent deep blue EL properties.

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2. Experimental details

2.1. Synthesis and characterization

General procedure for the Suzuki Cross Coupling Reaction: arylanthracenyl boronic acid such as 9-phenylanthracen-10-yl-10-boronic acid, 9-(naphthalen-3-yl)anthracen-10-yl-10-boronic acid, and 9-(naphthalen-1-yl)anthracen-10-yl-10-boronic acid (1.2 mol) and 2-bromo-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (1.0 mol), Pd(PPh₃)₄ (0.04 mol), aqueous 2.0 M Na₂CO₃ (10.0 mol), ethanol, and toluene were mixed in a flask. The mixture was refluxed for 4 h. After the reaction was completed, water was added to quench the reaction. After cooling, the crude solid was collected by filtration, washed with water and ethanol. The product was purified recrystallization from CH₂Cl₂/EtOH.

¹H NMR was recorded on a Varian Unity Inova 300Nb or Bruker Avance III 500 MHz NMR spectrometer. FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Low-resolution mass spectra were measured using a Jeol JMS-600W spectrometer in the APCI mode. Elemental analyses (EA) were determined by a Flash 2000 autoanalyzer.

2-(10-phenylanthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (1). Yield: 65% (white powder). ¹H NMR (CDCl₃ 500 MHz) [δ ppm]: 7.95 (d, *J* = 8.0 Hz, 2H), 7.74 (m, 2H), 7.54–7.48 (m, 6H), 7.47–7.41 (m, 6H), 7.39–7.31 (m, 8H), 7.20–7.16 (m, 3H), 7.09–7.05 (m, 2H), 6.94 (dd, 1H), 6.85–6.81 (m, 2H). ¹³C NMR (CDCl₃ 125 MHz) [δ ppm]: 157.3, 157.2, 140.6, 140.5, 136.5, 132.4, 131.2, 130.4, 129.7, 129.3, 128.7, 128.6, 128.4, 128.3, 127.7, 127.5, 126.9, 126.8, 126.7, 126.6, 125.7, 125.3, 124.8, 124.7, 120.3, 120.2, 58.3, 56.6. FT-IR (ATR): ν 3811, 3056, 1826, 1614, 1259, 1026, 861, 811, 749, 706, 645 cm⁻¹. MS (APCI⁺) (*m/z*): 732 [M⁺]. Anal. Calcd: C, 95.05; H, 4.95. Found: C, 94.95; H, 4.91.

10-([naphthalen-2-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (2). Yield: 66% (white powder). ¹H NMR (CDCl₃ 500 MHz) [δ ppm]: 8.00–7.95 (m, 4H), 7.85–7.81 (m, 2H), 7.58–7.49 (m, 6H), 7.48–7.38 (m, 9H), 7.37–7.34 (m, 4H), 7.17 (dd, 1H), 7.15 (dd, 1H), 7.09 (dd, 1H), 7.07 (dd, 1H), 6.97 (ddd, 1H), 6.86–6.82 (m, 2H), 6.65 (d, *J* = 8 Hz, 1H), 6.57 (dd, 1H), 6.49–6.46 (m, 2H). ¹³C NMR (CDCl₃ 125 MHz) [δ ppm]: 157.4, 157.2, 140.7, 140.5, 136.5, 133.3, 132.7, 128.9, 128.7, 128.4, 127.7, 127.5, 126.9, 126.8, 125.7, 125.3, 124.9, 124.7, 120.3, 120.2, 58.1, 58.0. FT-IR (ATR): ν 3717, 2984, 2873, 1804, 1686, 1268, 1162, 1052, 814,

752, 697, 642 cm⁻¹. MS (APCI⁺) (*m/z*): 758 [M⁺]. Anal. Calcd: C, 95.11; H, 4.89. Found: C, 95.07; H, 4.86.

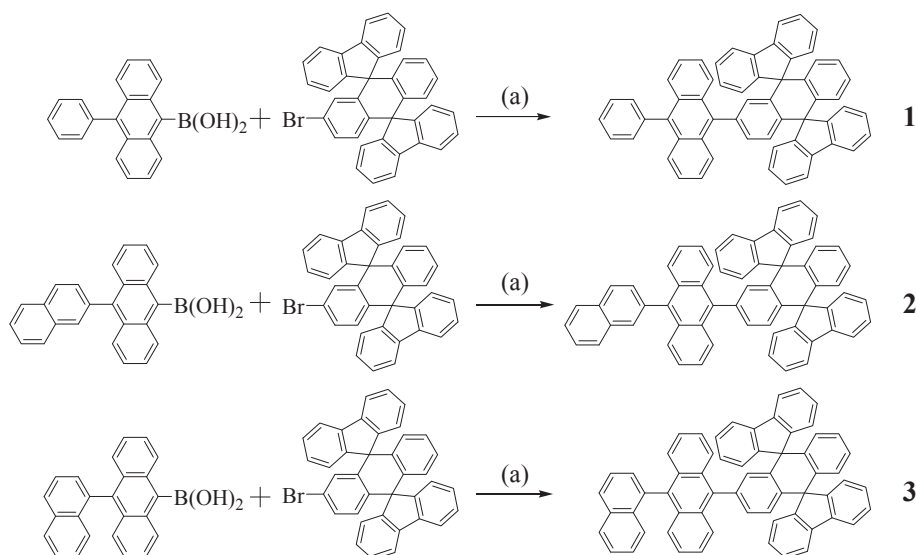
10-([naphthalen-1-yl]anthracen-9-yl)-bispiro(9,10-dihydro-anthracene-9,7'-7''H-fluorene-10,7''-7''H-fluorene) (3). Yield: 65% (white powder). ¹H NMR (CDCl₃ 500 MHz) [δ ppm]: 8.01–7.94 (m, 4H), 7.82–7.79 (m, 1H), 7.75 (dd, 1H), 7.64–7.60 (m, 1H), 7.53–7.50 (tdd, 2H), 7.48–7.35 (m, 14H), 7.28–7.27 (m, 1H), 7.25 (m, 1H), 7.17–7.11 (m, 1H), 7.09–7.02 (m, 5H), 6.97 (dd, 1H), 6.85–6.83 (m, 2H), 6.86 (t, *J* = 8 Hz, 1H), 6.60 (dd, 1H), 6.49–6.46 (m, 2H). ¹³C NMR (CDCl₃ 125 MHz) [δ ppm]: 157.4, 157.2, 140.7, 140.5, 136.5, 133.3, 132.7, 129.9, 129.4, 129.3, 128.9, 128.7, 128.6, 128.4, 128.0, 127.8, 127.7, 127.5, 126.9, 126.8, 126.3, 125.7, 125.3, 124.9, 124.7, 120.3, 120.2, 58.1, 56.0. FT-IR (ATR): ν 3718, 2989, 1796, 1686, 1268, 1168, 1050, 809, 754, 700 cm⁻¹. MS (APCI⁺) (*m/z*): 758 [M⁺]. Anal. Calcd: C, 95.11; H, 4.89. Found: C, 95.01; H, 4.82.

2.2. Physical measurements

The UV–Vis absorption and photoluminescent (PL) spectra were measured in dichloromethane (10⁻⁵ M) using Shimadzu UV-1650PC and AMINCO-Bowman series 2 luminescence spectrometers. The fluorescence quantum yields of the emitting materials were determined in dichloromethane at 293 K against DPA (9,10-diphenylanthracene) as a reference ($\Phi_{\text{DPA}} = 0.90$) [20]. Fluorescence quantum yields of thin films were determined using BDAVB film as a standard ($\Phi = 0.30$ measured by the calibrated integration sphere system). The HOMO (highest occupied molecular orbital) energy levels were measured with a low energy photo-electron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and PL spectra. The LUMO (lowest unoccupied molecular orbital) energy levels were estimated by subtracting the corresponding optical band gap energies from the HOMO energy values. Thermogravimetric analysis (TGA) was carried out using a SEIKO EXSTAR 6000 TG/DTA 7300 unit under a nitrogen atmosphere at a heating rate of 10 °C/min.

2.3. OLED fabrication and measurement

For fabricating OLEDs, the indium-tin-oxide (ITO) thin films coated on glass substrates were used, which was 30 Ω/square of the sheet resistivity and 180 nm of thickness. The ITO coated glass was



Scheme 1. Structures and Synthetic routes of compounds 1–3. (a) Pd(PPh₃)₄, 2 M Na₂CO₃, Toluene, Ethanol.

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