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Blue electroluminescent materials based on phenylanthracene-substituted fluorene derivatives for organic light-emitting diodes

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ABSTRACT

Two phenylanthracene-substituted fluorene derivatives, 10-(9,9′-dimethyl-2-(10-phenylanthracen-9-yl)-9*H*-fluoren-7-yl)-phenylanthracene (**1**) and 2′,7′-di-(10-phenylanthracen-9-yl)-9,9′-spirobi[9*H*-fluorene] (**2**) have been designed, synthesized, and characterized. A device using compound **1** as an emitting material exhibited luminous efficiency, power efficiency, external quantum efficiency and CIE coordinates of 3.37 cd/A, 1.50 lm/W, 1.87% at 20 mA/cm^2 and (0.18, 0.25) at 7 V, respectively. Furthermore, by exploiting this efficient blue fluorescent material as a blue emitting material with the combination of red phosphorescent bis(2-phenylquinoline)acetylacetonate [$(pq)_2Ir(acac)$], an efficient white OLED (WOLED) with a external quantum efficiency of 1.70%, luminous efficiency of 1.38 cd/A, power efficiency of 0.94 lm/W at 20 mA/cm^2 and the color coordinates of (0.33, 0.36) at 14 V is demonstrated.

1. Introduction

Over the past years, organic light-emitting diodes (OLEDs) are improved to obtain the condition for full color displays and solid-state lighting [1]. Recently, device performances such as high efficiencies and proper CIE coordinates are required in OLEDs for the practical applications. In this regards, the efficient red, green, and blue emitting materials are required. Especially, blue emitting materials are troublesome due to their wide band gap [2–7].

In the blue electroluminescent (EL) materials, anthracene derivatives have been used because of the wide-energy band gap, high quantum yield and good thermal stability [8–13]. However, their EL efficiencies and color purities are not sufficient for the practical applications. Therefore, the suitable strategies to improve their EL performances were required. Among those are the substitutions of anthracene core with the various functional groups. Particularly, the introduction of the various aromatics into C-9 and C-10 positions of anthracene has provided many materials with the efficient EL properties [14–17].

In this paper, we have designed and synthesized two blue emitting materials based on fluorene substituted phenyl anthracene derivatives, 10-(9,9′-dimethyl-2-(10-phenylanthracen-9-yl)-9*H*-fluoren-7-yl)-phenylanthracene (**1**), and 2′,7′-di-(10-phenylanthracen-9-yl)-9,9′-spirobi[9*H*-fluorene] (**2**). In these compounds, phenylanthracene moiety was linked by dimethylfluorene and spirofluorene. Fluorene moieties such as alkylated fluorene and spirobifluorene are expected to be good EL building units for OLED materials, due to their excellent fluorescent properties and good morphological, thermal, and electrochemical stabilities [18,19]. However, only a few systematic studies have investigated the EL properties of blue-emitting materials based on fluorene derivatives [20]. To investigate the EL properties of these materials **1** and **2**, multilayered OLEDs were fabricated using these materials as the emitting layer. Moreover, to inquire into possibility of white OLED application, we fabricated another device using one of these materials with the combination of well-known red-phosphorescent iridium complex [21,22].

2. Experimental details

2.1. Synthesis and characterization

All reagents and solvents were obtained from commercial suppliers (Aldrich and TCI, both in Seoul, Korea) and were used without further purification.

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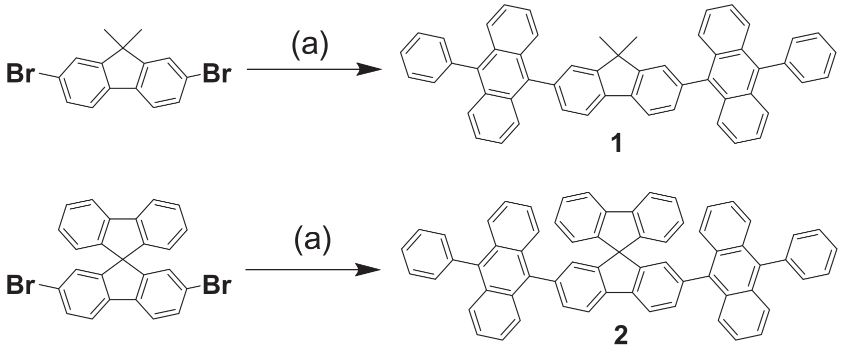

Scheme 1. Structures and Synthetic routes of **1** and **2**. (a) 9-Phenylanthracen-10-yl boronic acid, $Pd(PPh_3)_4$, 2 M Na_2CO_3, toluene, ethanol.

10-(9,9′-dimethyl-2-(10-phenylanthracen-9-yl)-9*H*-fluoren-7-yl)-phenylanthracene (**1**). 9-Phenylanthracen-10-yl-boronic acid (2.4 mol) and the corresponding aryl bromides such as 2,7-dibromo-dimethylfluorene (1.0 mol), $Pd(PPh_3)_4$ (0.04 mol), aqueous 2.0 M Na_2CO_3 (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 by recrystallization from CH_2Cl_2/EtOH. Yield: 65%. ^{1}H-NMR ($CDCl_3$, 500 MHz, δ): 8.09 (d, $J = 7.6$ Hz, 2H), 7.86–7.85 (m, 4H), 7.74–7.72 (m, 4H), 7.64–7.61 (m, 6H), 7.58 (d, $J = 7.0$ Hz, 2H), 7.56–7.49 (m, 6H), 7.40–7.35 (m, 8H), 1.65 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 154.2, 139.1, 138.4, 138.2, 137.6, 137.2, 131.4, 130.4, 130.4, 130.1, 130.0, 128.5, 127.5, 127.1, 126.0, 125.1, 125.1, 120.1, 120.0, 27.4 FT-IR (ATR): ν 2927, 2856, 1634, 1509, 1465, 808, 767, 702 cm^{-1}. MS (APCI$^+$) (*m/z*): 698 [M$^+$]. calcd for $C_{55}H_{38}$: C, 94.52; H, 5.48. Found: C, 93.54; H, 5.43.

2′,7′-di-(10-phenylanthracen-9-yl)-9,9′-spirobi[9*H*-fluorene] (**2**). Synthetic route of this compound was identical to that of compound **1**, except 2,7-dibromo-dimethylfluorene was changed with 2,7-dibromo-9,9′-spirobi[9*H*-fluorene]. Yield: 78%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ): 8.20 (d, $J = 7.7$ Hz, 2H), 7.69–7.67 (m, 4H), 7.64–7.58 (m, 10H), 7.56 (dd, $J = 8.0$ Hz, 2H), 7.54–7.52 (m, 3H), 7.46 (d, $J = 7.4$ Hz, 2H), 7.34 (d, $J = 7.0$ Hz, 2H), 7.30–7.27 (m, 8H), 7.24 (s, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.18 (dd, $J = 7.5$ Hz, 3H), 7.12 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, δ): 141.2, 140.1, 137.1, 135.4, 135.0, 131.3, 131.2, 129.8, 129.8, 128.4, 128.4, 127.8, 127.8, 127.6, 127.4, 126.9, 126.8, 125.0, 124.9 FT-IR (ATR): ν 2972, 2867, 1740, 1442, 1377, 819, 765, 734, 701 cm^{-1}. MS (APCI$^+$) (*m/z*): 821 [M$^+$]. calcd for $C_{65}H_{40}$: C, 95.09; H, 4.91. Found: C, 93.62; H, 5.03.

2.2. Physical measurements

^{1}H- and ^{13}C NMR were 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. The UV–Vis absorption and photoluminescence 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 ($\Phi_{DPA} = 0.90$) [9]. The photoluminescence spectra in solid films were measured by the following methods; 0.05 ml of compounds **1** and **2** (0.02 M in dichloromethane) was dropped on quartz and then solvent was dried at the room temperature and under the atmospheric pressure. The photoluminescence spectra were measured using AMINCO-Bowman series 2 luminescence spectrometer. 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 photoluminescence 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.

Table 1
Physical properties of compounds **1** and **2**.

Compound	UV λ_{max} (nm)[a]	PL λ_{max} (nm)[a,b]	FWHM (nm)[a,b]	HOMO/LUMO (eV)[c]	E_g (eV)[d]	Φ_f [e]	T_d (°C)
1	398	426/439	50/49	−5.85/−2.83	3.02	0.83	439
2	398	426/449	50/31	−5.84/−2.82	3.02	0.99	422

[a] In CH_2Cl_2 (ca. 1×10^{-5} M).
[b] Solid thin film on quartz plates.
[c] HOMO energy level was determined by low-energy photoelectron spectrometer (Riken-Keiki, AC-2) and LUMO = HOMO + ΔE.
[d] ΔE is the band-gap energy estimated from the intersection of the absorption and photoluminescence spectra.
[e] Using DPA as a standard; $\lambda_{ex} = 360$ nm ($\Phi = 0.90$ in CH_2Cl_2).

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 cleaned in an ultrasonic bath by the following sequences: in acetone, methyl alcohol, distilled water and kept in isopropyl alcohol for 48 h and dried by N_2 gas gun. The substrates were treated by O_2 plasma treatment with the conditions of 2×10^{-2} Torr at 125 W for 2 min. All organic materials and metal were deposited under high vacuum (5×10^{-7} Torr). All of the properties of the OLEDs such as current density (*J*), luminance (*L*), luminous efficiency (LE), and the CIE chromaticity coordinates of OLEDs were measured with Keithly 2400, Chroma meter CS-1000A. Electroluminescence was measured using Roper Scientific Pro 300i.

3. Results and discussion

Synthetic route of **1** and **2** is shown in Scheme 1. Compounds **1** and **2** were synthesized by Pd-catalyzed Suzuki-cross coupling reaction between the (10-phenylanthracen-9-yl)boronic acid and the corresponding aryl bromide with moderate yields (65% and 78%). All the compounds were characterized by ^{1}H NMR, ^{13}C