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Efficient tuning of electroluminescence from sky-blue to deep-blue by changing the constitution of spirobenzofluorene derivatives

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ABSTRACT

Two novel benzimidazole-attached spiro[benzofluorene] derivatives, 2,2′-(spiro[benzo[*c*]fluorine-7,9′-fluorene]-5,9-diylbis(4,1-phenylene))bis(1-phenyl-1*H*-benzo[*d*]imidazole) and 2,2′-(spiro[benzo-[*de*]anthracene-7,9′-fluorene]-2′,3-diylbis(4,1-phenylene))bis(1-phenyl-1*H*-benzo[*d*]imidazole), were prepared by a Suzuki coupling reaction. Their photophysical and photochemical properties were studied systemically. The fluorescent organic light-emitting diodes were fabricated by using them as the emitters, all of them showed strong blue emission. Interestingly, from the benzoanthracene derived compound a high color purity was found with Commission de L'Eclairage 1931 chromaticity coordinates of (0.15, 0.10) and an efficiency of 1.96 cd/A. To the best of our knowledge, this is the first time to obtain a deep-blue emission with spiro[benzofluorene] derivative in a nondoped device.

1. Introduction

Blue organic light-emitting diodes (OLEDs) have been attracting great scientific and commercial attention for their potential applications in both full-color display and solid-state lighting [1–4]. Much significant progress has been demonstrated and the external quantum efficiencies (EQE) over 20% have been accessible for phosphorescent OLEDs (PhOLEDs) and more than 10% for fluorescence. However, it is still particularly difficult to generate a deep-blue emission with Commission Internationale de l'Eclairage (CIE) coordinates in the range of ($CIE_x < 0.15$, $CIE_y < 0.15$) due to the intrinsic wide band gap nature of deep-blue emitters [5–7]. Although great effort has been made to develop deep-blue fluorescent emitters in the past decade, there is still a clear need to improve the color purity and stability of deep-blue OLEDs.

Spirofluorene and their derivatives as important intermediates have attracted great interest due to their special structures and properties. In 2008, Gong et al. introduced asymmetric spirobenzofluorenes containing naphthalene groups into OLEDs, the results indicated good stabilities, high carrier mobilities and high fluorescence quantum yields [8]. Subsequently, Huang et al. reported series of novel spirobenzofluorene/pyrene derivatives as dopant materials and obtained deep-blue emission [9]. Recently, Gong et al. demonstrated one of spirobenzofluorene dimers as host materials and the maximum efficiency was up to 7.44 cd A^{-1} with deep-blue emission [10]. However, the reported results based on spirofluorene derivatives showed that most examples were used as host or dopant materials. It is well-known that the electroluminescent properties are extremely sensitive to the dopant concentration and very difficult to control by using co-deposition methods [11–13]. Furthermore, the energy transformation may be ineffective because of the potential phase separation in host-dopant system [14]. Therefore, to develop the nondoped, highly efficient, deep-blue emitters based on spirobenzofluorene derivatives is attractive.

In this study, we designed and synthesized two novel blue emitting materials, 2,2′-(spiro[benzo[*c*]fluorine-7,9′-fluorene]-5,9-diylbis(4,1-phenylene))bis(1-phenyl-1-*H*-benzo[*d*]imidazole) (SBFBI) and 2,2′-(spiro[benzo[*de*]anthracene-7,9′-fluorene]-2′,3-diylbis(4,1-phenylene))bis(1-phenyl-1*H*-benzo[*d*]imidazole) (SAFBI), integrating spirobenzofluorene and benzoimidazole

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moieties. It is particularly intriguing to compare the electroluminescent properties of SBFBI and SAFBI, both have the same molecular constructing units. We only changed the constitution of spirobenzofluorene core between two benzoimidazole units, the emission was found to be changed from sky-blue to deep-blue. Our results provide a way to design and synthesize deep-blue materials based on spirofluorene derivatives. The thermal properties and energy levels were fully investigated. The OLEDs based on SAFBI as the emitting layer achieved a current efficiency of 1.96 cd A^{-1} and a deep-blue CIE(x,y) of (0.15, 0.10), which was the first time to obtain a deep-blue emitter with spirobenzofluorene derivative in a non-doped system to our knowledge.

2. Experimental

2.1. Materials and measurements

Manipulations involving air-sensitive reagents were performed under an inert atmosphere of dry nitrogen. Commercially available reagents were used without further purification unless otherwise stated. Naphthalene-1,8-diamine, phenylboronic acid, 2-bromo-9*H*-fluoren-9-one, 9*H*-fluoren-9-one, naphthalen-1-ylboronic acid, 1-bromo-2-iodobenzene, 2-(4-bromophenyl)-1-phenyl-1*H*-benzo[*d*]imidazole were purchased from TCI co. and used as received. 1,8-diiodonaphthalene [15], 1-iodo-8-phenylnaphthalene [16], 3-bromospiro[benzo[*de*]-anthracene-7,9′-fluorene] [17], 1-(2-bromophenyl)naphthalene, spiro[fluorene-7,9′-benzofluorene], 5-bromospiro-[benzo[*c*]fluorene-7,9′-fluorene] [8], and 1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-benzo[*d*]imidazole [18] were synthesized according to the methods of the reported literature. Melting points were obtained with Shanghai YiCe WRX-4 melting-point apparatus. Fourier transform-infrared (FTIR) spectra were performed using Thermo Nicolet 6700 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured on a Bruker DRX-400 spectrometer with chemical shifts reported as ppm (in CDCl$_3$ or Acetone-d$_6$, TMS as internal standard). High-resolution mass spectra were obtained from Bruker Esquire LC/Ion Trap Mass Spectrometer and JEOL/HX-110. Elemental analyses were performed with a Perkin–Elmer 2400 II elemental analyzer. UV–vis absorption spectra (UV) were recorded on a Perkin–Elmer Lambda 950 spectrophotometer. Fluorescence (PL) measurements were carried out with a FLSP920 spectrophotometer in a solution of 10^{-6} mol/L and solid state, respectively. Differential scanning calorimetry (DSC) curves were obtained with Metler Toledo DSC822 instrument at 20 °C min^{-1} under nitrogen flushing. Thermogravimetric analyses (TGA) were carried out using a Perkin–Elmer Pyris thermogravimeter under a dry nitrogen gas flow at a heating rate of 10 °C min^{-1}. The electrochemical properties of derivatives was studied through cyclic voltammetry (CV) on a CHI 660D analyzer with a three electrode configuration with a Pt disk as the working electrode of 0.01 cm^2, a Pt wire as the counter electrode, and an Ag/AgCl as the reference electrode, and in a dichloromethane solution containing 0.1 M of tetrabutylammonium hexafluorophosphate as supporting electrolyte.

2.2. Preparation of 5,9-dibromospiro[benzo[c]fluorene-7,9′-fluorene] (5,9-dBr-SBFF)

5-Bromospiro[benzo[*c*]fluorene-7,9′-fluorene] (4.01 g, 9.0 mmol) was dissolved in trichloromethane (50 mL) in a two-necked flask; bromine (2.16 g, 13.5 mmol) was then added slowly in a dropwise fashion over a period of 20 min. The mixture was stirred at room temperature, then the reaction mixture was extracted with dichloromethane and water. After the organic layer was evaporated with a rotary evaporator, the resulting powdery product was purified by column chromatography to give a yellow solid. Yield, 93%. ^{1}H NMR (400 MHz, Acetone-d$_6$) δ 9.01 (d, 1H, $J = 8.32$ Hz), 8.59 (d, 1H, $J = 8.32$ Hz), 8.35 (d, 1H, $J = 8.32$ Hz), 8.08 (d, 2H, $J = 7.39$ Hz), 7.91 (t, 1H, $J = 7.39$ Hz), 7.81 (t, 1H, $J = 7.86$ Hz), 7.72 (d, 1H, $J = 8.32$ Hz), 7.49 (t, 2H, $J = 7.39$ Hz), 7.20 (t, 2H, $J = 7.86$ Hz), 7.10 (s, 1H), 6.91 (s, 1H), 6.78 (d, 2H, $J = 7.39$ Hz).

2.3. Preparation of 2′,3-dibromospiro[benzo[de]anthracene-7,9′-fluorene] (2′,3-dBr-SBAF)

Using a similar approach for 5,9-dBr-SBFF, yellow powder was finally obtained. Yield, 98%. Mp 231 °C. FTIR (KBr, cm^{-1}) 3053, 3023, 739, 765 (aromatic C–H), 1587, 1489, 1463, 1440 (aromatic C=C), 753 (aromatic C–Br). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, 1H, $J = 7.86$ Hz), 8.16–8.10 (m, 2H), 7.95 (d, 1H, $J = 8.06$ Hz), 7.81 (d, 1H, $J = 7.67$ Hz), 7.70 (d, 1H, $J = 8.06$ Hz), 7.49 (dd, 1H, $J_1 = 8.15$ Hz, $J_2 = 1.75$ Hz), 7.38 (td, 1H, $J_1 = 7.57$ Hz, $J_2 = 0.78$ Hz), 7.35–7.30 (m, 2H), 7.17 (td, 1H, $J_1 = 7.57$ Hz, $J_2 = 0.97$ Hz), 7.05–7.01 (m, 2H), 6.94 (d, 1H, $J = 7.67$ Hz), 6.68 (d, 1H, $J = 7.28$ Hz), 6.51 (dd, 1H, $J_1 = 8.01$ Hz, $J_2 = 0.58$ Hz). HRMS (m/z): cacld for (M$^+$+H) $C_{29}H_{17}Br_2$ (524.9598), found 524.9582.

2.4. Synthesis of 2,2′-(spiro[benzo[c]fluorene-7,9′-fluorene]-5,9-diylbis(4,1-phenylene))bis (1-phenyl-1H-benzo[d]imidazole) (SBFBI)

1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)-1*H*-benzo[*d*]imidazole (1.75 g, 4.4 mmol), 5,9-dBr-SBFF (1.0 g, 2.0 mmol), bis(triphenyl phosphine)palladium(II)chloride (0.20 g, 0.28 mmol) and toluene (100 mL) were stirred in a three-necked flask for 30 min. To the above solution was added potassium carbonate (2 M, 20 mL) and anhydrous ethanol (30 mL). The resulting solution was refluxed 2 days at 105 °C. The reaction mixture was extracted with dichloromethane and water. After the organic layer was evaporated with a rotary evaporator, the resulting powdery product was purified by column chromatography to give a white solid. Yield, 45%. Mp 385 °C. FTIR (KBr, cm^{-1}) 3064, 3053, 3038, 818, 756, 742 (aromatic C–H), 1597, 1499, 1450, 1406 (aromatic C=C), 1476 (C=N), 1260 (C–N). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.95 (d, 1H, $J = 8.51$ Hz), 8.53 (d, 1H, $J = 8.19$ Hz), 8.00–7.94 (m, 3H), 7.89 (d, 2H, $J = 7.53$ Hz), 7.79–7.73 (m, 2H), 7.66–7.23 (m, 27H), 7.13 (td, 2H, $J_1 = 7.61$ Hz, $J_2 = 0.74$ Hz), 7.00 (d, 1H, $J = 1.64$ Hz), 6.79 (d, 2H, $J = 7.53$ Hz), 6.75 (s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 151.4, 151.3, 151.2, 150.7, 147.7, 147.3, 142.4, 142.3, 142.3, 142.2, 142.1, 140.0, 138.6, 136.9, 136.7, 136.4, 136.3, 135.9, 132.0, 130.3, 130.2, 130.1, 129.9, 129.8, 129.2, 129.1, 128.0, 127.4, 127.4, 127.3, 127.1, 127.0, 126.9, 125.9, 124.2, 124.1, 124.0, 123.9, 123.8, 123.7, 123.4, 122.8, 122.3, 120.2, 119.3, 119.2, 110.7. ESI-MS (m/z): 904.5 (M$^+$+H). HRMS (m/z): cacld for (M$^+$+H) $C_{67}H_{43}N_4$ (903.3409), found 903.3417. Anal. Calcd for $C_{67}H_{42}N_4$: C, 89.11; H, 4.69; N, 6.20; Found: C, 89.03; H, 4.63; N, 6.21.

2.5. Synthesis of 2,2′-(spiro[benzo[de]anthracene-7,9′-fluorene]-2′,3-diylbis(4,1-phenylene))bis(1-phenyl-1H-benzo[d]imidazole) (SAFBI)

The synthesis of SAFBI is similar to that of SBFBI by a Suzuki coupling reaction, white powder was finally obtained. Yield, 87%. Mp > 300 °C. FTIR (KBr, cm^{-1}) 3060, 3034, 831, 762, 748 (aromatic C–H), 1598, 1499, 1449, 1402 (aromatic C=C), 1478 (C=N), 1262 (C–N). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, 1H, $J = 7.85$ Hz), 8.26 (d, 1H, $J = 7.91$ Hz), 8.02 (d, 1H, $J = 8.01$ Hz), 7.97 (d, 1H, $J = 7.91$ Hz), 7.92 (d, 1H, $J = 8.01$ Hz), 7.86 (d, 1H, $J = 7.56$ Hz), 7.77 (d, 2H, $J = 8.11$ Hz), 7.74 (dd, 1H, $J_1 = 8.42$ Hz, $J_2 = 0.82$ Hz), 7.65 (dd, 1H, $J_1 = 7.91$ Hz, $J_2 = 1.54$ Hz), 7.62–7.54 (m, 8H), 7.52–7.39 (m, 9H),