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Highly efficient blue light-emitting diodes containing spirofluorene derivatives end-capped with triphenylamine/phenylcarbazole

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ABSTRACT

A series of blue fluorescent emitters based on spirofluorene were synthesized *via* the Horner–Wadsworth–Emmons reaction in moderate yields. Multilayered OLEDs were fabricated with a device structure of ITO/DNTPD (60 nm)/NPB (30 nm)/MADN: Blue dopant materials **1**–**5** (30 nm)/Alq_3 (20 nm)/LiF (1.0 nm)/Al (200 nm). All devices showed efficient blue emission. Among those, device using compound **1** as a dopant material give the best performance with high brightness (2778 cd/m^2 at 8.5 V) and high efficiency (4.9 cd/A, 2.3 lm/W, and 4.0% EQE at 20 mA/cm^2). The peak wavelength of electroluminescence was 473 nm with CIE*x*,*y* coordinates of (0.15, 0.17) at 8.5 V. A deep blue device with CIE*x*,*y* coordinates of (0.15, 0.12) at 8.5 V showed a luminous efficiency of 1.8 cd/A and an external quantum efficiency of 1.9% at 20 mA/cm.

1. Introduction

Small organic molecules used in organic light-emitting diodes (OLEDs) have attracted attention for potential applications in the next generation displays and solid-state lighting sources [1]. Full-color OLEDs display applications require a set of primary red, green and blue emitters [2]. Among the three primary colors, although red and green emitting materials have achieved satisfactory efficiency and color purity, the development of efficient blue-emitting materials is an important issue due to the wide energy band gap (E_g). Therefore, the development of highly efficient deep-blue emitting materials, which is defined as having a Commission Internationale de l'Eclairage (CIE) *y* coordinate value below 0.15 [3], is particularly important for full-color displays. Recently, there has been extensive research into a range of blue-emitting materials [4–9]. Among those, spirobifluorene is considered a promising host and dopant material owing to its specific three-dimensional configuration and excellent thermal stability. For example, Lee et al. reported a spirobifluorene derivative that exhibited high thermal stability (T_g = 193 °C) and high EL efficiency (9720 cd/m^2 and 4.9 cd/A) with an emission peak at 472 nm [10].

In this study, a new class of blue emitters based on spirofluorene derivatives were designed and synthesized. Triphenylamine/phenylcarbazole terminal groups were introduced to enhance the hole injection and transporting properties and improve the charge balance in the emitting layers [11]. In addition, the end-capped group was introduced to either C2- or C4-position of spirobifluorene (compounds **1**–**4**) to test the position effect on the electroluminescent properties. Compound **5** had a dispiro[fluorene-9,9′-anthracene-10′,9″-fluorene] unit on the arylamine group. This paper describes the synthesis and electroluminescent properties of highly efficient blue-emitting materials (**1**–**5**) based on triphenylamine/phenylcarbazole-substituted spirofluorene derivatives for OLED applications.

2. Experimental

2.1. Material preparation and characterization

Unless specified otherwise, all reactions were carried out in a nitrogen atmosphere. Anhydrous tetrahydrofuran was dried using the standard procedure from sodium and benzophenone, and commercially available reagents and solvents were used as received unless otherwise noted. Compounds 9,9′-spirobifluorene-2-carbaldehyde (**6**) [12], 4-bromo-9,9′-spirobifluorene [13], 2′-formyl-dispiro[fluorene-9,9′-anthracene-10′,9″-fluorene] (**8**) [14], diethyl 4-diphenylaminobenzylphosphonate [15] were previously reported.

The ^1H and ^{13}C NMR spectra were recorded on a Varian (Unity Inova 300Nb or Unity Inova 500Nb) spectrometer. The FT-IR spectra were recorded on a Bruker VERTEX70 FT-IR spectrometer. Low- and

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high-resolution mass spectra were measured using a Varian 4000 in EI mode, a Jeol JMS-AX505WA spectrometer in FAB mode or Jeol JMS-600 spectrometer in EI mode.

*4-Formyl-9,9′-spirobifluorene (**7**)*: 2-bromo-9,9′-spirobifluorene (0.95 g, 2.40 mmol) was dissolved in anhydrous THF (55 mL) and stirred under a nitrogen atmosphere for 10 min. The reaction flask was cooled to −78 °C and *n*-BuLi (2.3 mL of a 1.6 M solution in hexane, 3.60 mmol) was added dropwise. The reaction mixture was stirred for 1 h and 0.28 mL (3.60 mmol) of DMF was added dropwise. After stirring for 1 h at −78 °C, the mixture was placed in an ice bath and treated with dilute hydrochloric acid (5.0 mL of 1.0 M). The mixture was then extracted with ethyl acetate. The combined organic layers were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to produce a clear white solid (81% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 10.69 (s, 1H), 8.67 (d, J = 7.9 Hz, 1H), 7.87 (t, J = 7.4 Hz, 3H), 7.42–7.36 (m, 3H), 7.27–7.17 (m, 2H), 7.12 (t, J = 7.5 Hz, 2H), 6.93 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.71 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 192.2, 151.2, 149.8, 148.2, 142.7, 142.1, 140.6, 132.8, 132.3, 129.9, 129.5, 128.4, 128.3, 127.8, 126.2, 124.2, 124.2, 120.4, 65.9; FT-IR (ATR, cm^{-1}): ν = 2924, 1737, 1690, 1449, 1365, 1217, 1206, 1033, 734, 663; FABMS (*m*/*z*): 345 (M^++H).

*(9-(3,5-Di-tert-butylphenyl)-9H-carbazol-3-yl)methanol (**9**)*: Ethanol (20 mL) was added to a mixture of 9-(3,5-di-*tert*-butylphenyl)-9*H*-carbazole-3-carbaldehyde (480 mg, 1.25 mmol) and sodium borohydride (189 mg, 5.00 mmol) in a two-neck round-bottomed flask, and heated under reflux at 78 °C for 2 h. The reaction mixture poured into ice water, extracted with diethyl ether and washed with water. The combined organic layer was dried with anhydrous $MgSO_4$, filtered, evaporated to dryness, and the crude product was purified by silica gel column chromatography using EtOAc/hexane (1/5, v/v) eluent to produce a yellow oil (98% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.13 (d, J = 8.2 Hz, 2H), 7.49 (s, 1H), 7.42–7.37 (m, 6H), 7.30–7.24 (m, 2H), 4.86 (s, 2H), 1.38 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.8, 141.5, 140.8, 137.1, 132.6, 126.2, 125.8, 123.6, 123.3, 121.4, 121.3, 120.5, 120.0, 119.5, 110.3, 110.2, 66.3, 35.3, 31.7; IR (ATR, cm^{-1}): ν = 3015, 2970, 2948, 1549, 1435, 1365, 1229, 1216, 1092, 1032, 1002, 899, 745, 711; MS(EI$^+$) *m*/*z* 385 (M^+).

*Diethyl 9-(3,5-di-tert-butylphenyl)-9H-carbazoylphosphonate (**10**)*: Triethylphosphite (0.36 mL, excess) was added to compound **9** (414 mg, 1.07 mmol) charged with nitrogen. Iodine (272 mg, 1.07 mmol) was then added at once at 0 °C, stirred for 30 min, warmed to room temperature, and stirred for 12 h. The excess triethylphosphite was removed by distillation. The residue was extracted with EtOAc, washed with water, and the combined organic layer was dried with anhydrous $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography using EtOAc/hexane (1/2, v/v) as the eluent to produce a yellow solid (27% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.13 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), 7.49 (t, J = 1.7 Hz, 1H), 7.42 (d, J = 3.7 Hz, 2H), 7.37 (d, J = 1.7 Hz, 4H), 7.30–7.25 (m, 1H), 4.06–4.01 (m, 4H), 3.39 (s, 1H), 3.33 (s, 1H), 1.39 (s, 18H), 1.27–1.24 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.8, 141.4, 140.2 (d, J_{pc} = 2.5 Hz), 137.1, 127.9 (d, J_{pc} = 5.7 Hz), 126.2, 123.4 (d, J_{pc} = 2.7 Hz), 123.2, 122.7, 122.6, 121.6 (d, J_{pc} = 7.3 Hz), 121.4, 121.3, 120.6, 119.9, 110.2, 62.4 (d, J_{pc} = 6.6 Hz), 35.4, 33.9 (d, J_{pc} = 138.8 Hz), 31.7, 16.7 (d, J_{pc} = 6.1 Hz); IR (ATR cm^{-1}): ν = 3000, 2970, 1594, 1483, 1461, 1365, 1229, 1216, 1042, 1022, 943, 822, 749, 713, 646, 613; EIMS (*m*/*z*): 477 (M^+).

General procedure for the Horner–Wadsworth–Emmons reaction: A solution of diethyl 4-diphenylaminobenzylphosphonate (370 mg, 0.94 mmol) and 2-formylspirobifluorene (322 mg, 0.94 mmol) dissolved in THF (20 mL) was stirred. KO*t*-Bu (1.13 mL of a 1.0 M solution in THF, 1.13 mmol) was then added dropwise at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, and then for 1 h at room temperature. The resulting mixture was quenched with water. The solution mixture was extracted with ethyl acetate and washed twice with water. The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford a crude product that was purified by column chromatography with silica gel and subsequent recrystallization from CH_2Cl_2/EtOH.

*2-(4-Diphenylaminostyryl)spirobifluorene (**1**)*: (74% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.85 (d, J = 7.6 Hz, 2H), 7.79 (dd, J = 7.7, 3.7 Hz, 2H), 7.48 (d, J = 7.9 Hz, 1H), 7.38–7.31 (m, 4H), 7.23–7.18 (m, 6H), 7.12–6.93 (m, 11H), 6.88–6.82 (m, 3H), 6.75 (d, J = 7.4 Hz, 2H), 6.69 (d, J = 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 149.5, 149.3, 149.0, 147.7, 147.4, 142.2, 141.7, 141.3, 137.7, 131.6, 129.5, 128.1, 128.0, 127.9, 127.4, 127.0, 126.5, 124.7, 124.4, 124.2, 123.6, 123.2, 121.9, 120.4, 120.2, 120.1, 66.1; FT-IR (ATR, cm^{-1}): ν = 3016, 2970, 2945, 1589, 1508, 1492, 1448, 1366, 1277, 1228, 1216, 1206, 1032, 960, 840, 774, 749, 728; HRMS (EI$^+$) calcd. for $C_{45}H_{32}N$: 586.2534 (M^+), found: 586.2538.

*2-[9-(3,5-Di-tert-butylphenyl)carbazol-3-ylethenyl]spirobifluorene (**2**)*: (73% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.15 (s, 1H), 8.10 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 7.9 Hz, 1H), 7.52–7.47 (m, 3H), 7.40–7.37 (m, 4H), 7.35–7.33 (m, 3H), 7.19 (s, 1H), 7.17 (d, J = 5.2 Hz, 1H), 7.14–7.10 (m, 3H), 7.04 (s, 1H), 6.94 (s, 1H), 6.80 (d, J = 7.5 Hz, 2H), 6.72 (d, J = 7.5 Hz, 1H), 1.37 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.8, 149.6, 149.3, 149.1, 142.0, 141.8, 141.6, 141.1, 140.8, 138.0, 137.0, 129.6, 129.4, 128.1, 128.0, 126.5, 126.4, 126.2, 124.7, 124.4, 124.2, 123.8, 123.4, 121.7, 121.4, 121.3, 120.5, 120.2, 120.1, 118.7, 110.3, 35.3, 31.7. FT-IR (ATR, cm^{-1}): ν = 2964, 2919, 1595, 1461, 1359, 1335, 1319, 1234, 1032, 1004, 959, 821, 749, 668, 620; HRMS (EI$^+$) calcd. for $C_{53}H_{46}N$: 696.3630 (M^+), found: 696.3527.

*4-(4-Diphenylaminostyryl)spirobifluorene (**3**)*: (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.02 (d, J = 7.8 Hz, 1H), 7.90–7.82 (m, 3H), 7.54–7.48 (m, 3H), 7.38–7.26 (m, 6H), 7.18–7.02 (m, 14H), 6.76–6.72 (m, 3H), 6.61 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 149.6, 149.4, 149.2, 147.9, 147.7, 142.5, 142.0, 139.0, 134.5, 131.8, 131.4, 129.9, 129.6, 128.1, 128.0, 127.9, 127.8, 127.6, 126.3, 125.3, 124.8, 124.4, 124.3, 123.8, 123.4, 123.0, 120.4, 65.9. FT-IR (ATR, cm^{-1}): ν = 3031, 2970, 2923, 1586, 1508, 1492, 1446, 1366, 1334, 1281, 1228, 1216, 1032, 970, 814, 744, 728, 693; HRMS (EI$^+$) calcd. for $C_{45}H_{32}N$: 586.2534 (M^+), found: 586.2533.

*4-[9-(3,5-Di-tert-butylphenyl)-carbazol-3-ylethenyl]spirobifluorene (**4**)*: (90% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.39 (s, 1H), 8.24(d, J = 7.6 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 6.0 Hz, 1H), 7.87–7.79 (m, 2H), 7.53–7.30 (m, 12H), 7.21–6.99 (m, 6H), 6.80–6.63 (m, 3H), 1.42 (s, 14H), 1.36 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 152.9, 149.6, 149.4, 149.2, 142.6, 142.0, 141.7, 141.0, 134.8, 132.9, 129.8, 128.1, 128.0, 127.9, 127.6, 126.4, 124.8, 124.3, 124.0, 123.9, 123.4, 122.9, 121.5, 121.3, 121.2, 120.6, 120.2, 119.2, 110.6, 110.4, 66.0, 35.4, 31.7, 31.6. FT-IR (ATR, cm^{-1}): ν = 2964, 1595, 1461, 1360, 1336, 1318, 1233, 1032, 1004, 961, 798, 748, 727, 712, 653; HRMS (EI$^+$) calcd. for $C_{53}H_{46}N$: 696.3630 (M^+), found: 696.3626.

*2-(4-Diphenylaminostyryl)-dispiro(fluorene-9,9′-anthracene-10,9″-fluorene) (**5**)*: (74% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.94–7.91 (m, 4H), 7.46–7.41 (m, 4H), 7.32–7.13 (m, 14H), 7.04–6.89 (m, 9H), 6.78–6.75 (m, 2H), 6.63–6.49 (m, 2H), 6.40–6.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 157.4, 157.3, 147.7, 147.3, 140.7, 136.8, 136.7, 136.4, 136.2, 135.8, 131.7, 129.4, 129.3, 129.0, 128.8, 128.1, 127.9, 127.8, 127.4, 127.0, 125.8, 125.7, 124.5, 123.8, 123.7, 123.1, 120.3, 58.1; FT-IR (ATR, cm^{-1}): ν = 3016, 2970, 2945, 1590, 1507, 1492, 1446, 1366, 1279, 1228, 1216, 1032, 951, 821, 745, 725, 692; HRMS (EI$^+$) calcd. for $C_{58}H_{40}N$: 750.3160 (M^+), found: 750.3161.