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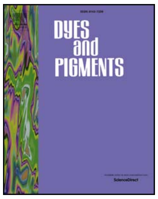

Novel carbazolyl-substituted spiro[acridine-9,9′-fluorene] derivatives as deep-blue emitting materials for OLED applications

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ABSTRACT

Blue organic light-emitting diodes (OLEDs) are of great significance in the fields of flat-panel display and solid-state lighting. Herein, three carbazolyl-substituted blue emitters, namely **SAF-CzB**, **SAF-2CzB**, and **F-2CzB**, were designed and synthesized. Two compounds **SAF-CzB** and **SAF-2CzB** possess a rigid spiro[acridine-9,9′-fluorene] (SAF) central core. The counterpart **F-2CzB**, which contains 9,9-dimethylfluorene as core was, also researched for comparative purpose. The introduction of SAF into fluorene-based materials could simultaneously improve their thermal stability, hole injection and transport ability, as well as prevent the fluorenone defect. The compound **SAF-2CzB** shows a higher decomposition temperature (T_d) of 534 °C compared to that of **F-2CzB** (488 °C). The hole-transporting property of **SAF-2CzB** is also better than that of **F-2CzB** demonstrated by single-carrier devices. The presence of a bulky spiro-annulated triphenylamine moiety at the C9 position of the fluorene might suppress the fluorenone defect. Non-doped OLED based on **SAF-2CzB** as the emitting layer shows the best performance with maximum current efficiency (CE) of $4.07\ \mathrm{cd\ A^{-1}}$ and power efficiency (PE) of $1.83\ \mathrm{lm\ W^{-1}}$, compared with $3.03\ \mathrm{cd\ A^{-1}}$ and $1.08\ \mathrm{lm\ W^{-1}}$ for **SAF-CzB**, $3.14\ \mathrm{cd\ A^{-1}}$ and $1.23\ \mathrm{lm\ W^{-1}}$ for **F-2CzB**. In particular, both **SAF-2CzB**- and **F-2CzB**-based device exhibit good color stability with CIE coordinate of (0.16, 0.11) at the voltage of 7–12 V.

1. Introduction

Efficient blue light-emitting devices (OLEDs) play an important role in both full-color display and solid-state lighting [1–3]. Especially deep-blue emitting materials not only act as the energy-transfer donor for low energy dopant to generate green, red, or white light, but also increase the color gamut and reduce power consumption [4–6]. Recently, phosphorescent [7–9] and thermally activated decayed fluorescence (TADF) [10,11] blue emitting materials have attracted considerable attention. Both kinds of materials can theoretically achieve 100% internal quantum efficiency [12]. Unfortunately, phosphorescent and TADF devices require an appropriate host to reduce aggregation quenching and other functional materials with high triplet energy level for exciton confinement [13,14], and thus result in a complicated device structure. In addition, the phosphorescent emitters suffer from a sharp efficiency roll-off at high brightness due to triplet-triplet annihilation (TTA) and deep-blue emitters remain scarce [9]. Therefore, developing efficient deep-blue fluorescent materials for highly efficient non-doped OLEDs should still to be a concern.

Fluorene has been intensively studied as an attractive building bock due to its high photoluminescence efficiency, high carrier mobility and easy modification [15,16]. Many fluorene-based blue emitters, such as oligomeric fluorenes, polyfluorenes, spiro-bifluorene (SF), and their derivatives have been reported and exhibited impressive device performance [17–20]. However, some deficiencies, including electron-dominated injection/transport property, the longer wavelength emission caused by aggregation and fluorenone defect were observed among them [21,22]. Therefore, efforts have been devoted to address these issues. It was reported that incorporating hole-transporting groups such as triphenylamine (TPA) or carbazole (Cz) into fluorene-based derivatives might promote injection and transport of hole [23]. Meanwhile, the film quality could be also optimized and molecular aggregation would be reduced because of bulky **TPA** or **Cz** unit. Finally, some fluorene-based derivatives were designed with *tert*-buyl, phenyl, or **TPA** group at the C9 position of the fluorene, aiming at preventing the fluorenone defect [24–26]. Although the above-mentioned deficiencies could be addressed by reasonable molecular modification, it will inevitably lead to complicated synthetic processes and an unwanted spectrum red-shift.

Recently, the spiro-acridine-fluorene (SAF) unit has become more

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prominent in recent [27–29]. Compared with the fluorene and spirobifluorene group, the **SAF** contains an electron-donating nitrogen atom and gives rise to its hole-transporting property. On the other hand, the orthogonal spiro configuration could lead to a highly rigid structure, which could reduce the intermolecular interactions and improve the thermal stability of the film [30,31]. What is more, incorporation of a spiro-annulated triphenylamine moiety at the C9 position of the fluorene is conducive to eliminate the fluorenone defect, which is caused by the oxidation of the sp^3 carbon atom.

Herein, taking into account the advantage of **SAF** group, carbazole was integrated with SAF to construct deep-blue emitters, namely **SAF-CzB** and **SAF-2CzB**. The counterpart **F-2CzB**, which contains 9,9-dimethylfluorence as the core, was also synthesized for comparative purpose. The peripheral carbazole group was introduced due to its excellent hole-transporting properties and high triplet energy, guaranteeing a deep-blue emission [32]. All the compounds show good thermal stability with decomposition temperature (T_d) of 429–534 °C. The compound **SAF-2CzB** exhibits good hole-transporting properties, appropriate HOMO energy level and suppressed fluorenone defect. Their molecular structure-property relationships were evaluated by means of theoretical, thermal, photophysical, and electrochemical studies. The non-doped OLED based on **SAF-2CzB** as emitting layer shows the best performance with maximum emission at 440 nm, maximum current efficiency (CE) of 4.07 cd A^{-1} and maximum power efficiency (PE) of 1.83 l m W^{-1}. In particular, both **SAF-2CzB**- and **F-2CzB**-based device exhibit good color stability with the Commission International deL'Eclairage (CIE) coordinate of (0.16, 0.11) at the voltage of 7–12 V.

2. Experimental section

2.1. Materials and reagents

The reagents and solvents for the synthesis and measurements were used without any additional purification. THF was taken from a solvent purification system under N_2 atmosphere using benzophenone as the indicator.

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker ACF400 (400 MHz) spectrometer using $CDCl_3$ or DMSO-d_6 as solvents and tetramethylsilane as the internal reference. High resolution mass spectrometry (HRMS) was received from micrOTOF-Q II 10204. Infrared spectroscopy (IR) was measured using a Thermo Nicolet 380. The elemental analysis data was recorded on a vario MICRO cube elemental analyzer. Thermo Evolution 300 UV–visible spectrometer and HitachiF-4500 fluorescence spectrometer were utilized to record the UV–vis absorption and fluorescence spectra, respectively. The transient photoluminescence (PL) spectrum was measured by FLS980 fluorescence spectrometer. Fluorescence quantum yields (Φ_f) was determined by reference method with quinine sulfate solution in 0.1 M H_2SO_4 ($\Phi_f = 0.54$) as a reference. Thermal gravity analysis (TGA) was undertaken on a METTLER TOLEDOTGA/DSC1 Thermogravimetric Analyzer with the rate of 10 °C min^{-1} from 30 °C to 800 °C under N_2 atmosphere. Differential scanning calorimetry (DSC) was performed on a TA Q20 instrument operated at a heating rate of 10 °C min^{-1} from 25 °C to 400 °C under N_2 atmosphere. Density functional theory (DFT) was utilized to evaluate the molecular geometries and electron density distribution at a B3LYP/6-31G(d.p) level. The cyclic voltammetry was performed using a CHI600E analyzer at a scan rate of 0.1 V s^{-1}. The electrolytic cell is a classic three-electrode cell using Pt wire as working electrode and auxiliary electrode, Ag/$AgNO_3$ as reference electrode, tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4PF_6) as supporting electrolyte and ferrocene (Fc) as internal reference.

2.3. OLED fabrication and measurements

The fabrication of OLEDs was conducted by vacuum deposition process. ITO-coated glasses with a sheet resistance of 30 Ω per square were used as substrate. Before device fabrication, the ITO glass substrates were cleaned by deionized water, ethanol, acetone and ethanol, dried in an oven, and then treated with UV-ozone for 5 min. After these processes, the ITO glass substrates were transferred to a deposition system with the base pressure lower than 7×10^{-4} Pa. Then, all the organic layers were deposited onto the ITO substrates with an evaporation rate of 0.3–1.0 Å s^{-1}. Finally, LiF and Al were sequentially deposited onto the substrate at the deposition rate of approximate 0.2 and 10 Å s^{-1}, respectively. The thicknesses and deposition rates of film were controlled by a quartz crystal thickness monitor. The electroluminescence (EL) spectra, luminance, and Commission International deL'Eclairage (CIE) coordinates were measured with Konicaminolta CS-2000. The current-voltage properties were performed using a Keithley 2400 SourceMeter under ambient atmosphere.

2.4. Synthetic procedures

2.4.1. Preparation of 2′-bromo-10-phenyl-10H-spiro[acridine-9,9′-fluorene] (**Br-SAF**)

A solution of 2-bromotriphenylamine (3.23 g, 10 mmol) in THF (40 mL) was treated with *n*-BuLi (7.5 mL, 1.6 M in hexane, 12 mmol) under argon at −78 °C. The resulting mixture was allowed to stir for 1 h at −78 °C, and then 2-bromo-9*H*-fluoren-9-one (2.84 g, 11 mmol) in THF (20 mL) was added dropwise over a period of 0.5 h. After 1 h reaction at −78 °C, the mixture was gradually warmed up to room temperature overnight. Water (5 mL) was added to the mixture and THF was evaporated under reduced pressure. The resulting solid was dissolved in dichloromethane (100 mL) and washed with water (3 × 50 mL). Then the organic layer was separated, dried over magnesium sulfate, filtered and evaporated, resulting in the crude product, which was directly used in the next reaction without further purification. The crude product was dissolved in acetic acid (50 mL) and hydrochloric acid (36%, 5.0 mL). After refluxed for 4 h, the reaction was cooled to room temperature, filtered and washed with petroleum ether. The resulting solid was further purified by column chromatography using petroleum/CH_2Cl_2 to afford **Br-SAF** (3.64 g, 75%) as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.80 (d, J = 7.5 Hz, 1H), 7.74 (t, J = 7.7 Hz, 2H), 7.68 (d, J = 8.1 Hz, 1H), 7.63–7.57 (m, 2H), 7.52 (ddd, J = 8.1, 2.8, 1.6 Hz, 3H), 7.45–7.39 (m, 2H), 7.32 (td, J = 7.5, 1.2 Hz, 1H), 6.97 (ddd, J = 8.6, 7.1, 1.6 Hz, 2H), 6.61 (td, J = 7.5, 1.2 Hz, 2H), 6.42 (dd, J = 7.9, 1.7 Hz, 2H), 6.39 (dd, J = 8.4, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 158.5, 156.3, 141.3, 141.0, 138.4, 138.1, 131.2, 131.1, 131.0, 129.1, 128.8, 128.6, 127.8, 127.7, 127.5, 126.0, 124.0, 121.9, 121.3, 120.7, 120.0, 57.0.

2.4.2. Preparation of 2′,7′-dibromo-10-phenyl-10H-spiro[acridine-9,9′-fluorene] (**2Br-SAF**)

Following the similar synthetic method for **Br-SAF**, **2Br-SAF** was prepared from 2-bromotriphenylamine (3.23 g, 10 mmol) and 2,7-dibromo-9*H*-fluoren-9-one (3.69 g, 11 mmol). The crude product was purified by column chromatography (silica) to afford **2Br-SAF** (3.82 g, 68%) as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.74 (t, J = 7.7 Hz, 2H), 7.65 (dd, J = 8.0, 0.7 Hz, 2H), 7.61 (td, J = 7.2, 1.3 Hz, 1H), 7.55–7.49 (m, 6H), 6.99 (ddd, J = 8.6, 7.1, 1.6 Hz, 2H), 6.64 (ddd, J = 8.2, 7.2, 1.2 Hz, 2H), 6.42–6.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 158.1, 141.1, 140.7, 137.1, 131.2, 131.1, 131.0, 129.2, 128.7, 127.8, 123.0, 122.4, 121.4, 120.8, 115.0, 57.0.

2.4.3. Preparation of 9-(4-bromophenyl)-3,6-di-tert-butyl-9H-carbazole (**Br-CzB**)

A mixture of 3,6-di-*tert*-butyl-9*H*-carbazole (5.58 g, 20 mmol), 1-bromo-4-iodobenzene (11.75 g, 24 mmol), CuI (0.76 g, 4 mmol), K_2CO_3