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tert-Butylated spirobifluorene derivative incorporating triphenylamine groups: a deep-blue emitter with high thermal stability and good hole transport ability for organic light emitting diode applications

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Abstract: A *tert*-butylated spirobifluorene derivative incorporating triphenylamine groups was synthesized starting from the readily available reagent biphenyl. Without any hole-transport layer, an unoptimized double-layer device exhibits excellent electroluminescent performances with a radiance of 3013 cd/m² at 9.8V, a maximum electroluminescent efficiency of 1.71 cd/A, a maximal external quantum efficiency of 2.58% at a brightness of 4.8cd/m², narrow full width at half-maximum (< 54 nm), and blue emission with Commission Internationale de l'Eclairage coordinates of (0.152, 0.103), which is close to the standard for blue. Compared to the reported organic light emitting diodes materials, the molecule displays very high thermal stability. In addition, the bilayer device showed a greatly improved performance as compared to a trilayer device with NPB as hole-transporting layer , which indicated that the molecule possesses good hole transport ability and can be good candidate for hole-transporting layer in organic light emitting diodes.

Keywords: spirobifluorene derivative; electroluminescent property; blue emitter; thermal stability; hole transport

1. Introduction

Organic light emitting diodes (OLEDs) have attracted much attention because of their potential application in

full-color flat-panel displays, solid state lighting sources, and large-area and flexible electronic devices [1-4]. To compete with liquid crystal displays (LCDs) in the display market, OLEDs must have high device performances, good thermal stabilities, excellent color purity, and low production costs [5]. Low molecular weight small molecules are generally vacuum-deposited as thin films in device fabrication. Therefore, film-forming properties and their thermal stability are prerequisite to the performance and longevity of devices. Amorphous materials possessing high glass transition temperatures (T_g) should be propitious to realize high stability OLEDs [6]. A well known class of amorphous materials is the spiro-linked compounds developed by Salbeck's group [7]. Intramolecular bond rotation and vibration in the spiro-linked unit are not possible and an increase in T_g is anticipated. In the past two decades, a lot of satisfactory red and green emitters for OLEDs have been developed; however, efficient and stable non-doped deep blue OLEDs with good CIE coordinates are still rare [1, 5, 8-9], and a host:dopant system is commonly adopted to use the energy transfer from the host to the guest to obtain efficient blue OLEDs. The doping process would increase the complexity and thus the cost of the device fabrication. Besides, potential phase-separation in the host:dopant system was also found to render energy-transfer ineffective [1]. Therefore, to realize commercial full-color displays, high-performance blue emission is a pressing concern. Moreover, developing non-doped deep blue emission, which is defined as having a Commission Internationale de l'Eclairage (CIE) y coordinate value below 0.15 along with an (x + y) value < 0.30[8-12], is of special significance because such an emitter can not only effectively reduce the power consumption of a full-color OLED but also be utilized to generate light of other colors by energy cascading to lower energy fluorescent or phosphorescent dopants [13-19]. The 9,9'-spirobifluorene unit appears to be a very promising building block for the construction of high T_g blue-emitting materials for high performance blue electroluminescent devices [20-24]. L. X. Xiao *et al.* reported a pure blue emitter of 2,7-di(phenanthren-9-yl)- 9,9'-spirobifluorene (**DPSF**) with CIEy \approx 0.08 and T_g = 178°C [25]. However, the high ionization potential of fluorene-based compounds produces a relatively large

hole-injection barrier from the indium tin oxide (ITO) (5.0 eV) or ITO/poly(3,4-ethylenedioxythiophene) (PEDOT) layer (5.2 eV). To overcome this problem, arylamines, such as triphenylamine and carbazole, have been incorporated in fluorene-based derivatives to improve the hole injection and transport abilities and their resulting OLEDs show enhanced device efficiency and stability [5, 8, 26-28]. Such molecular modification can also simplify device structures and reduce the overall cost [1,8].

In this paper, we designed a *tert*-butylated spirobifluorene derivative incorporating triphenylamine groups (**SPF-BP**, Scheme 1). Most spirobifluorene derivatives are synthesized by the use of expensive reagent 2-bromobiphenyl as the starting material, whereas **SPF-BP** can be prepared starting from the readily available reagent biphenyl [29]. The photophysical, electrochemical, thermal properties, and electroluminescent characteristics of **SPF-BP** in unoptimized OLED devices are initially evaluated.

<Scheme1>

2. Experiments

2.1. Reagents and methods

As shown in Scheme 1, triphenylamine groups were directly introduced into the 2', 7'-position of spirobifluorene by the Suzuki coupling method. The intermediate 2,7-di-*tert*-butyl-9,9'-spirobifluorene was prepared according to our previous method [29]. Melting points were determined with an XT-4A apparatus and are uncorrected. Mass spectral studies were carried out using VG12-250 mass spectrometer. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to a Me₄Si standard. Elemental analyses were performed by Atlantic Microlab. Steady-state emission and excitation spectra were recorded on Perkin Elmer LS55 instrument. Visible absorption spectra were determined on Perkin Elmer LGA/DTA measurements were performed at heating rate of 10°C min⁻¹ in the temperature range of 25-800 °C, under nitrogen flow of 10 mL min⁻¹ by instrument Shimadzu DT-40.

Approximately 10 mg of sample were placed in standard aluminium crucible (40 μ L). The cyclic voltammograms were recorded with a computer controlled Zahner IM6e electrochemical workstation (Germany) using polymer films on glassy carbon disks as the working electrodes, Pt wire as the counter electrode, and Ag/Ag⁺ (0.01 M) as the reference. Tetrabutylammonium perchlorate (Bu₄NClO₄) 0.1 M was used as supporting electrolyte in dry CH₂Cl₂.

2.2. Preparation of 2,7-bis-(4-(N,N-diphenylamino)phenyl-2',7'-di-tert-butyl-9,9'-spirobifluorene (SPF-BP)

2,7-dibromo-2',7'-di-tert-butyl-9,9'-spirobifluorene (0.53g, 0.9 А mixture of mmol), 4-(diphenylamino)phenylboronic acid (0.59g, 2 mmol), Pd(OAc)₂ (0.016g, 0.071 mmol), PPh₃ (0.042g, 0.16 mmol) and K₂CO₃ (0.6g, 4.3 mmol) in dry THF (20 ml) were reacted under nitrogen atmosphere. After the mixture was refluxed for 18 h, the mixture was cooled to room temperature. The solvent was evaporated and the residue was subjected to column chromatography on silica gel with CH_2Cl_2 and petroleum ether as eluent (1:30, V/V) to afford white solid (0.45g, 55%). Mp > 250 °C. ¹H NMR (400MHz, CDCl₃) δ (ppm) : 1.17 (s, 18H), 6.75 (s,2H), 6.93 (s, 2H), 7.02 (m, 8H), 7.08 (d, 8H, *J* = 8.0Hz), 7.24 (t, 8H, *J* = 8.0Hz), 7.34 (d, 4H, *J* = 8.0Hz), 7.40 (d, 2H, *J* = 8.0Hz), 7.62 (d, 2H, J = 8.0Hz), 7.74 (d, 2H, J = 8.0Hz), 7.92 (d, 2H, J = 8.0Hz); ¹³C NMR (100MHz, CDCl₃) δ (ppm) : 151.0, 149.2, 147.9, 147.3, 140.5, 139.6, 136.4, 129.5, 128.0, 126.5, 125.2, 124.6, 124.2, 123.1, 122.5, 121.0, 120.4, 119.4, 66.7, 35.1, 35.8. Elemental analysis (%) calcd for C₆₉H₅₈N₂: C 90.55, H 6.39, N3.06. Found: C 91.00, H 6.37, N 3.05. MS(ESI+): 914.5.

2.3 OLED fabrication and characterization

The EL devices were fabricated by vacuum deposition of the materials at a base pressure of 5×10^{-6} Torr onto glass precoated with a layer of indium tin oxide (ITO) with a sheet resistance of 25Ω / square. Before deposition of an organic layer, the clear ITO substrates were treated with oxgen plasma for 5 min. The deposition rate of organic compounds was 0.9-1.1Ås⁻¹. Finally, a cathode composed of cesium pivalate (2nm) and aluminum (100nm) was

sequentially deposited onto the substrate in the vacuum of 10⁻⁵ Torr. The current density (I)-voltage (V)-luminance characteristics of the devices was measured with a Keithley 2400 Source meter and PR655. All measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

3.1 Optical properties

Key photophysical and thermal data are summarized in Table 1. The maximum peak of the UV/vis absorption spectrum of **SPF-BP** was observed at 371 nm on account of the π - π * transition of the conjugated backbone. From Fig. 1, it can be seen that the emission spectra of **SPF-BP** (λ_{ex} =365nm) have large red-shift following the increase of solvent polarity. For example, the maximum emission wavelength of **SPF-BP** is red-shifted by 40 nm from toluene (416 nm) to DMSO (456 nm). The solvatochromic behavior is accompanied by a decrease of the fluorescence quantum yield when the polarity of the solvent increases. The origin of this quenching phenomenon is attributed to the lowered energies of the ICT states but still remains unclear and its amplitude rather unpredictable. The fluorescence quantum yield of **SPF-BP** measured in CH₂Cl₂ solution is 0.76.

The photoluminescence spectrum of **SPF-BP** in thin-solid film presents a maximum peak at 442nm (Fig. 2), which showed obvious red shift than that in CH_2Cl_2 (422 nm) and that in toluene (416nm). The quantum yield of the **SPF-BP** thin film is 0. 65, which was lower than the value measured in solution. The thin film of **SPF-BP** was then gradually heated from rt to 200 °C. As no obvious change in the emission spectra was observed (Fig. 2), the emission color of **SPF-BP** appears to be stable and hence very promising for blue OLED applications [4].

< Table 1>

<Fig. 1>

< Fig. 2>

3.2 Thermal properties

The thermal properties of **SPF-BP** were investigated by DTA and TGA in a nitrogen atmosphere (Fig. 3). A crystallization exothermal peak at 224°C (T_c) was detected. **SPF-BP** showed a small endothermic peak at 266°C, which revealed a high melting point (T_m) [8, 30]. The decomposition temperature of **SPF-BP** was around 466°C, much higher than that of **DPSF** [25]. Although crystallization is adverse for the morphological stability of the **SPF-BP** thin film, the T_c of **SPF-BP** is higher than the T_gs of the reported blue light emitters and hole transport materials and high enough to secure the stability and lifetime performance of **SPF-BP** in OLED devices during repetitive and long-term operations [3, 31]. As expected, incorporation of spirobifluorene is beneficial to raising the thermally stability of the molecule [25].

3.3 Electrochemical Characterization

The electrochemical properties of **SPF-BP** were studied by cyclic voltammetry (CV) experiments at ambient temperature in CH_2Cl_2 (0.1 M *n*-Bu₄NClO₄ as a supporting electrolyte). Fig. 4 shows the cyclic voltammetry of **SPF-BP**. The onset oxidation potential was 0.582 V(vs Ag/Ag⁺). The HOMO energy level of **SPF-BP** was -5.29eV, estimated according to the following expression [32]:

<Fig

HOMO (eV) =-[
$$E_{ox}^{onset}$$
+ 4.71]

The hight-lying HOMO energy level and reversible electrochemical oxidation indicate that hole-injection and transport are favored in **SPF-BP**.

<Fig.4>

3.4 Electroluminescence properties

Two types of OLED devices were fabricated in this study (conditions had not been optimized): ITO/MoO₃(10nm)/NPB(60nm)/ SPF-BP (30nm)/TPBi(35nm)/LiF(1nm)/Al (device 1) and ITO/MoO₃(10nm)/ SPF-BP (75nm)/TPBi(35nm)/LiF(1nm)/Al (device 2). The structures of OLED devices are very similar to those previously reported by Müllen et al. [28]. In these devices, ITO is used as the anode; NPB (1,4-bis[(1-naphthylphenyl)amino]biphenyl) is used as the hole-transporting layer (HTL); TPBi(1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene) is used as the electron-transporting layer ; and LiF/Al is used as the cathode [31, 33]. In type 2, SPF-BP was used as a hole transporting and emitting layer. It is well known that double- and multi-layer OLEDs often show better device performance than single-layer OLEDs, because of better charge confinement [34]. To verify whether better charge carrier balance is needed, a hole-transport layer NPB (60 nm) with HOMO of -5.40eV was inserted in type 1 device. Adding NPB also helps in blocking electrons from reaching the anode. Fig. 5 shows the current density (I)- voltage (V)-luminance characteristics of the devices, and Fig.6 is the P-I (power efficiency vs current density) characteristics. The EL performances of two devices are

Fig.5>

<Fig.6>

excellent and the performance characteristics are summarized in Table 2. In device 1, maximum luminance, maximum current and power efficiencies of respectively 1732 cd/m² (at 11.4 V), 1.60cd/A, 1.19 lm/W were obtained. The device has a onset voltage (defined as the voltage required to obtain a luminance of 1 cd/m²) of 5.7V. Device 2 shows higher maximum efficiencies (maximum current efficiency = 1.71 cd/A; maximum power efficiency = 1.79 lm/W), lower onset voltage of 3.2 V, and higher maximum luminance of 3013 cd/m² (at 9.8V). In addition, the current densities of device 2 are higher than those of device 1. For instance, at a driving voltage of 5 V, the current density of device 2 is 33.5 mA/cm², while that of device 1 is only 3.0 mA/cm². Since the luminescence and efficiency for type 1 device is not increased but decreased, the addition of a hole transporting

layer seems to be unnecessary [28]. The results indicate that **SPF-BP** could function as a hole transporting material used in organic LEDs [28, 34-36].

<Table2>

The EL spectra of device 1 showed a main emission peak at 424 nm with a small shoulder peak at about 447nm (Fig.6) [4]. In device 2, dual band electroluminescent emissions at 429 and 447nm (Fig.7) were observed. It can be found that no long-wavelength emission presented in the thin-film PL spectra (Fig. 2). So the long-wavelength emissions (the shoulder peak in device 1 and the emission peak at 447nm in device 2) in the EL spectra probably result from the excimer or exciplex emission [37-41], which has often been observed in the EL spectra of OLEDs and is mainly attributed to the emission of photons resulting from the direct irradiative recombination of holes and electrons residing in two adjacent molecules [42]. The intensity of the long-wavelength emission became relatively strong in device 2. It may be due to the difference of light extraction came from the two devices with different thickness. The chromatic coordinates calculated from the electroluminescence spectrum in the CIE1931 chromaticity diagram are (0.166, 0.119) for device 1 and (0.151, 0.103) for device 2, both of which are close to the NTSC coordinates for blue of (0.15, 0.07) [8, 43]. Electroluminescence is also characterized by a narrow spectral distribution (spectral half width is 46 nm for device 1 and 54nm for device 2, respectively), which is lower than the typical value [9]. Moreover, the EL spectra show no difference between their performance over a wide range of operation conditions (Fig. 7 and Fig. 8), suggesting good EL stability. It is worthwhile to note that the overall performances for the SPF-BP based devices are very promising in OLEDs application [2, 4, 23].

<Fig.7>

<Fig.8>

4. Conclusions

In summary, we have synthesized a tert-butylated spirobifluorene derivative incorporating triphenylamine

groups by a convenient method and investigated its applications in non-doped OLEDs. The blue-emitting compound was used to fabricate double-layer blue-emitting EL device with very promising performances comparable to those of trilayer blue-emitting device and exhibit hole-transport properties. The concept presented could be extended potentially to further generate a new class of advanced materials for full-color OLED displays or white emitting OLEDs.

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Tables:

- 1. Table 1. Optical, Thermal, and Electrical Properties of SPF-BP.
- 2. Table2. EL Performance of Compound **SPF-BP**.

Table 1. Optical, Thermal, and Electrical Properties of SPF-BP.

$\lambda_{max,Abs}^{a}$	$\lambda_{\max, PL}^{a}$	HOMO (eV)	LUMO ^b (eV)	ΔE_g^{opt} (eV)	T _d (°C)	T _m (°C)
373	416	-5.29	-2.34	2.95	545	266

^a measured in toluene. ^bdeduced from HOMO and ΔE_g^{opt} (ΔE_g^{opt} =1240/ λ_{onset} , λ_{onset} is the onset wavelength of absorption spectra).

Device	ELmax	Brightness	Efficiency	CIE (x, y)
	(nm)	(cd/m^2)	(cd/A)	
1	424	1732	1.60	(0.166,0.119)
2	429, 447	3013	1.71	(0.152,0.103)

Table2. EL Performance of Compound SPF-BP.

Figures' Captions

- **1.** Scheme1. Synthesis of SPF-BP.
- **2.** Fig. 1.One-photon absorption and fluorescence spectra of **SPF-BP** in solvents of different polarity (10⁻⁵ M).
- **3.** Fig. 2. Normalized thin-film emission spectra of **SPF-BP** after annealing, in air, at different temperatures .
- 4. Fig.3. TGA and DTA curve of SPF-BP.
- **5.** Fig.4.CV of **SPF-BP** in CH_2Cl_2 (0.1 M *n*-Bu₄NClO₄ as a supporting electrolyte).
- **6.** Fig.5.The current density (I)-voltage (V)-luminance characteristics of the devices.
- 7. Fig.6.The current density (I)-voltage (V)-luminance characteristics of the devices.

- **8.** Fig.7. EL spectrum of device 1.
- **9.** Fig.8. EL spectrum of device 2.





Fig. 1.One-photon absorption and fluorescence spectra of SPF-BP in solvents of different polarity (10⁻⁵ M).

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Fig. 2. Normalized thin-film emission spectra of SPF-BP after annealing, in air, at different temperatures .

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Fig. 3. TGA and DTA curve of **SPF-BP**.



Fig.4.CV of **SPF-BP** in CH₂Cl₂ (0.1 M *n*-Bu₄NClO₄as a supporting electrolyte).

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Fig.5. The current density (I)-voltage (V)-luminance characteristics of the devices.



Fig.6. The current density (I)-voltage (V)-luminancecharacteristics of the devices.

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Fig.8. EL spectrum of device 2.

Highlight

- ► Quite high thermal stability for organic light emitting diode applications.
- ► Good hole-injection and -transporting ability.
- ► The molecule can be prepared starting from the readily available reagent biphenyl.
- ► The CIE coordinates is close to the standard for blue.
- ► The EL performances are among the best comparing to recently reported blue emitting devices.