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White organic light emitting diodes based on fluorene-carbazole dendrimers

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ABSTRACT

In this paper, we report on the Prod. Type: FTP fabrication and characterization of blue and white light emitting devices based on two fluorene-carbazole containing dendrimers and para-sexiphenyl (6P) oligomers. Blue light emitting diodes were fabricated using 9′,9″-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis-9′H-9,3′:6′,9″-tercarbazole (OFC-G2) and 9′,9″-(9,9′-spirobi[fluorene]-2,7-diyl)bis-9′H-9,3′:6′,9″-tercarbazole (SBFC-G2) dendrimers as a hole transport and emissive layer (EML) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as an electron transport layer. White light emitting diodes were fabricated using 6P and these two dendrimers as an EML. OLED device with the structure of ITO/PEDOT:PSS (50 nm)/OFC-G2 (40 nm)/6P (20 nm)/LiF:Al (0.5:100 nm) shows maximum luminance of nearly 1400 cd/m^2 and a Commission Internationale de l'Eclairage chromaticity coordinates of (0.27, 0.30) at 12 V.

1. Introduction

White organic light-emitting diodes (WOLEDs) have attracted much attention because of their potential use in display backlights, full color display applications, and solid-state lighting purposes [1–5]. There have been many ways to develop the white-light emission at OLEDs, such as a single layer polymer blends with white emission material [6–8], multilayer device with RGB (red/green/blue) emission layers [9–12], a doped device with a host material [13–15], fluorescent or/and phosphorescent dyes [16,17].

During last decade, the intensive research has been carried out to generate the material with high light emitting efficiencies, high thermal stability, and good amorphous film formation property [18,19]. Carbazole-based compounds demonstrate high thermal, morphological and photochemical stability [20]. These compounds have been extensively studied in many applications such as electrochromic devices, organic light-emitting diodes, organic field-effect transistors and photovoltaic cells, exploiting their intrinsic photophysical and redox properties [21–24]. Carbazole molecules can easily be functionalized at its 3,6-, 2,7- or *N* positions [25–27] and then covalently linked into polymeric systems, both as building blocks in the main chain [28] and pending groups in the side chain [29]. It is known that fluorene derivatives are important materials for OLEDs because of their high quantum yield of photoluminescence (PL) and electroluminescence (EL) efficiencies and high thermal stabilities. Spiro-functionalization at the bridge position of fluorene (C-9) having a specific steric configuration has been attracting much attention as organic functional material in terms of its specific physical properties [30].

Para-sexiphenyl (6P) consists of 6 phenyl rings connected with single bonds and it has blue photo and electroluminescence emission [31]. A number of OLED [32], organic field effect transistor (OFET) [33], photovoltaic [34] and non-linear optics [35] applications of 6P have been reported so far. The optical properties of 6P thin film depend on the orientation of the molecules relative to the surface of the substrate. OLEDs based on 6P are able to emit light over the whole visible part of white light [36] or polarized light [37].

In our previous work we reported the hole transporting and emissive layer properties of a serial of dendrimeric carbazole derivatives with Alq3 based OLEDs. However, in this work, two of those dendrimeric carbazole molecules 9′,9″-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis-9′H-9,3′:6′,9″-tercarbazole (OFC-G2) and 9′,9″-(9,9′-spirobi[fluorene]-2,7-diyl)bis-9′H-9,3′:6′,9″-tercarbazole (SBFC-G2) used as hole transporting materials (HTMs) and emissive layer (EML) with 6P and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) to produce while light emitting OLED (WOLED) devices. Multilayer OLED devices having the structure ITO/PEDOT:PSS/OFC-G2 or SBFC-G2/BCP/LiF:Al and ITO/PEDOT:PSS/OFC-G2 or SBFC-G2/6P/LiF:Al were fabricated and characterized.

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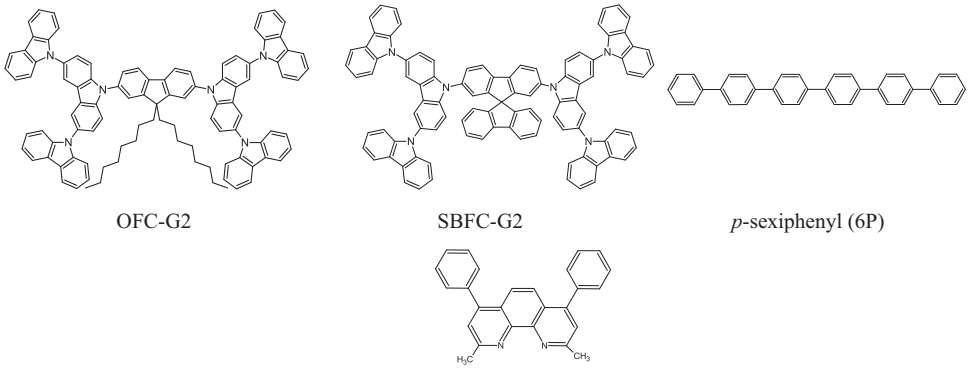

Fig. 1. Chemical structure of OFC-G2, SBFC-G2, 6P and BCP.

Table 1
Physical data for compounds OFC-G2 and SBFC-G2 [39].

Compound	T_g[a] (°C)	T_d[b] (°C)	λ_{max}[c] (nm)	λ_{em}[c] (nm)	E_g[d]	E_{ox}[e] (eV)	HOMO/LUMO[f] (eV)
OFC-G2	253	505	342	388	3.24	0.99	5.38/2.14
SBFC-G2	–	650	343	387	3.24	1.07	5.45/2.21

[a] Obtained from DSC measurements.
[b] Obtained from TGA measurements.
[c] Solvent $CHCl_3$.
[d] Optical band gap.
[e] Onset potentials.
[f] HOMO/LUMO energy levels were calculated with reference to ferrocene (4.8 eV) according to onset potentials. LUMO energy level was derived from the relation, E_g=HOMO–LUMO (where the band gap was derived from the observed optical edge).

2. Experimental section

2.1. Chemicals

The molecular structures of the compounds used in the experiments are illustrated in Fig. 1. The synthesis, characterization, thermal, photophysical and electrochemical properties of OFC-G2 and SBFC-G2 were reported by our group [38]. Physical data for OFC-G2 and SBFC-G2 adapted from previous paper are shown in Table 1.

All the reagents and solvents used for the synthesis of dendrimers were purchased from Aldrich and used without further purification. BCP, 6P and PEDOT:PSS for EL device fabrication were purchased from Aldrich, TCI America and H.C. Starck, respectively.

2.2. Device fabrication

Electroluminescent devices fabricated in this work have the following configurations:

ITO/PEDOT:PSS (50 nm)/OFC-G2 (40 nm)/BCP (10 nm)/LiF:Al (0.5:100 nm) (**device 1**), ITO/PEDOT:PSS (50 nm)/SBFC-G2 (40 nm)/BCP (10 nm)/LiF:Al (0.5:100 nm) (**device 2**), ITO/PEDOT:PSS (50 nm)/OFC-G2 (40 nm)/6P (20 nm)/LiF:Al (0.5:100 nm) (**device 3**), ITO/PEDOT:PSS (50 nm)/SBFC-G2 (40 nm)/6P (20 nm)/LiF:Al (0.5:100 nm) (**device 4**). OFC-G2 and SBFC-G2 were used as hole transporting layer (HTL) and EML, BCP was used as an electron-transporting layer (ETL) and 6P was used as an EML. Fig. 2a and b shows the scheme of OLED devices and energy diagrams of materials respectively.

The ITO substrates are patterned by a conventional wet-etching process using an acid mixture of HCl and H_2SO_4 as etching agent. Patterned ITO glass substrates with a sheet resistance between 10 and 12 square^{-1} are cleaned sequentially with acetone and iso-propanol by ultrasonic bath for 15 min, then dried in an oven and finally treated in an UV/O_3 cleaner. PEDOT–PSS (~50 nm) is spin casted at 4000 rpm for 30 s on ITO glass, then dried at 120 °C for 30 min under vacuum. Dendrimers in chlorobenzene (1.5 w/v%) solutions were spin casted at 3000 rpm for 30 s onto PEDOT:PSS layer to get 40 nm film thickness. Then BCP or 6P were evaporated onto dendrimer layer with a film thickness about 10 and 20 nm. Finally LiF (0.5 nm) Al cathode (100 nm) is deposited by thermal evaporation through a shadow mask. All device fabrication and characterization process are carried out under nitrogen atmosphere in a glove box system (MBRAUN-Germany) integrated with device fabrication and characterization units. *I–V* characteristics were measured with a Keithley sourcemeter (236 and 2400 model). Electroluminescence measurements were performed with Spectrasan PR-655 spectroradiometer, Oceanoptics Q65000 fiber optic spectrometer and Admesy–Bronthes colorimeter. Film thicknesses were determined with a Digital Instrument 3100 AFM.

3. Results and discussion

EL spectra of all devices are shown in Fig. 3. Device 1 and 2, including BCP as ETL, give blue emission with peak at 448 nm. The photoluminescence spectra of thin films of dendrimers are in good agreement with electroluminescence of device 1 and 2 (see Figs. 3 and 4). It shows that electroluminescence solely responsible for dendrimers and BCP does not have any influence on emission bands. On the other hand the case is vice versa on device 3 and 4. When 6P used instead of BCP, electroluminescence shows a wide and broadened band that covers most of visible region and definable as a white light. That is why in case device 3 and 4 emissive layer is 6P while dendrimers act as HTL. However, the solid state photoluminescence and electroluminescence of 6P is not in good agreement (see Figs. 3 and 4). To better understand this issue, *a* mixture of dendrimer and 6P prepared and cast onto glass substrates to measure solid state photoluminescence. We have to notice that since the interaction between dendrimer and 6P is stronger in homogenous mixture than that of layer by layer. That is why, the interaction occurs only at interface in bilayer film. However, in homogenous mixture, both molecules can interact easily and it is possible to detect it with reflection from surface. The excitation wavelength was 380 nm during measurements. Fig. 4 shows photoluminescence of pristine and mixture of materials. It is clear from Fig. 4, strong interaction leading to broadened emission band occurs between dendrimer and 6P. Especially SBFC-G2 dendrimer shows much stronger interaction than OFC-G2. This interaction may lead to formation of excimers or exciplex which results in broadened electroluminescence spectrum. On the other hand the shape and broadness of emission peaks depends on the excimer