



# A novel luminophor and host polymer from fluorene-carbazole derivatives for preparing solution-processed non-doped blue and closed-white light devices

Jing Sun<sup>a, b, \*</sup>, Tiaomei Zhang<sup>a, b</sup>, Xiaoqing Liao<sup>c</sup>, Kexiang Wang<sup>a, b</sup>, Minna Hou<sup>a, b</sup>, Dongyu Wu<sup>a, b</sup>, Yanqin Miao<sup>a, b</sup>, Hua Wang<sup>a, b, \*\*</sup>, Bingshe Xu<sup>a, b</sup>

<sup>a</sup> Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan, 030024, PR China

<sup>b</sup> Research Center of Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan, 030024, PR China

<sup>c</sup> Co-innovation Center for Micro/Nano Optoelectronic Materials and Devices, Research Institute for New Materials and Technology, Chongqing University of Arts and Sciences, Chongqing, 402160, PR China

## ARTICLE INFO

### Article history:

Received 9 December 2017

Received in revised form

12 January 2018

Accepted 17 January 2018

Available online 31 January 2018

### Keywords:

Fluorene-carbazole derivatives

Blue luminophor

Host materials

Electroluminescent performance

## ABSTRACT

A novel blue light emitting polymer was designed and synthesized via alternative conjugated 9,9-dioctylfluorene and 9-(6-(9H-carbazol-9-yl)hexyl)-9H-carbazole, named PF2Cz. It exhibited high thermal stability, good film morphology and strong deep-blue emission peaks at 408 and 429 nm in film. The triplet energy level of PF2Cz ( $E_T = 2.30$  eV) was also improved. Non-doped and doped devices were both prepared by solution process to characterize the electroluminescent (EL) properties of PF2Cz. In non-doped devices, PF2Cz acted as blue emitter which exhibited a Commission International de L'Eclairage (CIE) coordinate of (0.164, 0.102) and an external quantum efficiency (EQE) values of 1.28%. Moreover, the doped phosphorescent devices utilized PF2Cz as host material obtained a closed-white light emission with a content of 1 wt% dopant. All these results indicated that the fluorene-carbazole derivatives could be a promising molecular design strategy for the synthesis of blue light and host organic semiconductors.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Polymer light emitting devices (PLEDs) had received great attention owing to their potential in the full-color flat-panel displays and energy-saving solid-state lighting based on the solution process.<sup>1,2</sup> The PLEDs research of three primary colors (red, green, and blue) from conjugated polymer were necessary in their commercial application<sup>3</sup> on the large-scale and flexible displays. To date, red and green light emitting materials had exhibited excellent luminous efficiency and spectra stability, while blue light emitting materials still remained a great challenge<sup>4,5</sup> which also affected the

preparation of high quality white light.<sup>6</sup> Therefore, new type of blue light polymer needed to be designed and synthesized which had a tremendous room for the enhancement of EL performance.

As known that, poly (9,9-dioctylfluorene) (PF) had commendable blue light emission with excellent molecular modification characteristics, high photoluminescent quantum yield (PLQY) and good thermal stability which had a wide application in the PLEDs.<sup>7–9</sup> Recently, A.P. Monkman groups reported two kind of blue fluorene derivatives modified by sulfoxide groups or carbazole groups, respectively, which obtained nice EL performance that fluorene-sulfoxide derivatives exhibited a maximum EQE of 2.7%. However, the CIE coordinates kept away from the pure blue light emission.<sup>10</sup> Subsequently, their group introduced the carbazole groups to fluorene backbone and received a good blue light emission with a CIE coordinate of (0.16, 0.07).<sup>11</sup> It was noted that the maximum luminance ( $L_{max}$ ) and maximum current efficiency ( $CE_{max}$ ) were only 565 cd/m<sup>2</sup> and 0.65 cd/A which was caused by the serious concentration quenching in the single light emitting layer. Based on the above study, fluorene was chosen in the preparation of blue light polymers which could obtain blue light

\* Corresponding author. Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan, 030024, PR China.

\*\* Corresponding author. Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan, 030024, PR China.

E-mail addresses: [sunjing@tyut.edu.cn](mailto:sunjing@tyut.edu.cn) (J. Sun), [wanghua001@tyut.edu.cn](mailto:wanghua001@tyut.edu.cn) (H. Wang).

emission after chemical modification.

In this paper, we designed and synthesized a novel polymer poly(fluorene-(9-(9-(6-hexyl)-carbazole)-carbazole)) (PF2Cz) by introducing carbazole groups<sup>9</sup> to fluorene moiety to realize high-quality blue light emission in the non-doped devices. Furthermore, it could act as blue light and host materials in the doped phosphorescent devices that were in-depth studied demonstrating effective energy transfer carried out from the host to the phosphorescent dopant. All these observations indicating that PF2Cz could be promising candidates for solution processed PLEDs.

## 2. Experimental

### 2.1. Materials

The reagents used in the synthesis and tests were obtained from Energy Chemical and the air-sensitive reagents were performed under dry nitrogen atmosphere. The common solvent of toluene and THF were purified by distilled under nitrogen before use. The raw material of 9-(6-bromohexyl)-carbazole and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene were synthesized according to the literature methods.<sup>12,13</sup>

### 2.2. Synthesis of the monomer and polymer

#### 2.2.1. Synthesis of 9-(9-(6-hexyl)-carbazole)-3,6-dibromocarbazole (**M1**)

Under nitrogen atmosphere, 9-(6-bromohexyl)-carbazole (990 mg, 3 mmol), 3,6-dibromocarbazole (975 mg, 3 mmol) and tertbutyl ammonium bromide (TBAB) (322 mg, 1 mmol) were all added into 50 mL flask with 25 mL toluene solution and stirred for 15 min. Then 5 mL K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M) was added and the mixture was slowly heated to 90 °C for 18 h. The reaction solution was stopped by adding some water, extracted by CH<sub>2</sub>Cl<sub>2</sub> and dried by anhydrous MgSO<sub>4</sub>, and then the organic layer was evaporated to obtain the crude product. Finally, column chromatography on silica gel with the eluent of petroleum ether/CHCl<sub>2</sub> (5:1) was used to purify the crude product. Yield: 1.25 g, 73%. M.P. 110–115 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ(ppm) = 8.11 (d, J = 1.8 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 7.48(dd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 1.8 Hz, 2H), 7.43(ddd, J<sub>1</sub> = 8.4 Hz, J<sub>2</sub> = 7.2 Hz, J<sub>3</sub> = 1.2 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.22 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 9 Hz, 2H), 4.24 (t, J = 6.6 Hz, 2H), 4.12 (t, J = 6.6 Hz, 2H), 1.84–1.78 (m, 2H), 1.77–1.71 (m, 2H), 1.37–1.24 (m, 4H). <sup>13</sup>C NMR: (600 MHz, CDCl<sub>3</sub>): δ(ppm) = 140.4, 139.3, 129.1, 125.7, 123.5, 123.4, 122.9, 120.5, 118.9, 112.1, 110.4, 108.7, 43.1, 42.9, 28.9, 28.7, 27.1, 27.0. Element anal. calcd for C<sub>30</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>2</sub> (%): C, 62.74; H, 4.56; N, 4.88. Found: C, 63.09; H, 4.77; N, 4.65. MALDI-TOF-MS (*m/z*): calcd for C<sub>30</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>2</sub>, 574.35; found, 575.07.

#### 2.2.2. Synthesis of PF2Cz

Under nitrogen atmosphere, **M1** (287 mg, 0.5 mmol) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (321 mg, 0.5 mmol) were dissolved in 15 mL toluene. Subsequently, the catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol%), methyl tri-octyl ammonium chloride (Alicat 336) and 2 mol/L K<sub>2</sub>CO<sub>3</sub> aqueous solution (5 mL) were added to the mixed solution in turn. Then the mixture was heated to 90 °C for 50 h. The end-capped materials of phenyl boronic acid (20 mg) and bromobenzene (0.8 mL) were sequentially added and stirred for another 12 h, respectively. The cooled reaction solution was poured into the stirred methanol and the precipitate was purified by soxhlet extraction utilized acetone and column chromatography on silica gel with the eluent of CHCl<sub>2</sub>. Yield: 245 mg, 61%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.50(1 H, Ar-H), 8.10(1 H, Ar-H), 7.88–7.60(4 H, Ar-H), 7.48–7.28(3 H, Ar-H), 7.23(1 H, Ar-H), 4.28(4 H, CH<sub>2</sub>), 2.14(4 H, CH<sub>2</sub>), 1.87(4 H, CH<sub>2</sub>),

1.44(4 H, CH<sub>2</sub>), 1.23–0.97(10H, CH<sub>2</sub>), 0.95–0.65(5H, CH<sub>2</sub>, CH<sub>3</sub>). Element anal. calcd for C<sub>59</sub>H<sub>68</sub>N<sub>2</sub> (%): C, 88.01; H, 8.51; N, 3.48. Found: C, 88.76; H, 8.19; N, 3.05.

### 2.3. Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DXR 600 MHz spectrometer in deuterated chloroform. Elemental analyses were performed on a Vario EL elemental analyzer. The gel permeation chromatography (GPC) was determined by Waters GPC 2410 using THF as eluent. Thermal gravimetric analyses (TGA) was performed on a Netzsch TG 209 F3 at a heating rate of 10 °C/min and differential scanning calorimetry (DSC) curve was measured on TA Q2000 at a heating rate of 20 °C/min. UV–Vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer and PL spectra were recorded on a Fluoromax-4 spectrophotometer excited at 365 nm. Cyclic voltammetry (CV) curve was obtained on the Autolab/PG STAT302 electrochemical workstation at room temperature. The film morphologies was observed by SPA-300HV atomic force microscope (AFM).

### 2.4. Device fabrication and characterization

The configuration of non-doped devices were ITO/PEDOT:PSS (40 nm)/PF2Cz (70 nm)/TPBi (35 nm)/LiF (1 nm)/Al (100 nm) and the configuration of doped devices were ITO/PEDOT:PSS (40 nm)/PF2Cz:xIr(piq)<sub>3</sub> (x = 1, 3 and 5 wt%) (70 nm)/TPBi (35 nm)/LiF (1 nm)/Al (100 nm) which were prepared by wet process. Firstly, the ITO substrates were cleaned by acetone, isopropyl alcohol, and deionized water consecutively in an ultrasonic bath, and then treated by UV-ozone for 10 min. Secondly, a 40 nm thick PEDOT:PSS layer was spin-coated onto the ITO substrate and then baked at 120 °C for 20 min. Thirdly, PF2Cz with x wt% Ir(piq)<sub>3</sub> (x = 0, 1, 3 and 5) were dissolved in toluene (12 mg/mL) to prepare the non-doped PF2Cz layer and doped PF2Cz layer which were separately spin-coated on the PEDOT:PSS layer and baked at 100 °C for 15 min. Finally, the electron transporting TPBi layer (35 nm) and the composite LiF (1 nm)/Al (100 nm) cathode were evaporated. Scheme 2 showed the schematic of the procedure for fabricating the devices. The current density-voltage-luminance (J-V-L) characteristics were recorded by Keithley 2400 Source Meter and ST-900 M Spot Brightness Meter. The EL spectra and commission internationale de l'Eclairage (CIE) coordinates of the devices were analyzed with a spectra-scan PR655 spectrophotometer. The external quantum efficiency (EQE) values were calculated according to reference<sup>14,15</sup>.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The detailed synthesized route of the intermediate and PF2Cz were shown in Scheme 1. Since carbazole groups had excellent hole-transporting property<sup>16,17</sup> that was usually chosen as host material. Based on this, we utilized flexible hexyl to connect two carbazole groups which were incorporated into fluorene groups. The structure of intermediate was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra and element analysis. There were two bromine on the 3, 6 position of carbazole derivatives that could react with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene by Suzuki coupling reaction to obtain the target product of PF2Cz. The structure of M1 and PF2Cz was characterized by <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR spectra, MALDI-TOF-MS spectra and elemental analysis. The test of GPC gave the number-average molecular weight (*M<sub>n</sub>*) and the weight-average molecular weight (*M<sub>w</sub>*) of PF2Cz (Table 1) that were 5312 and 8942 g/mol, respectively, with a

Download English Version:

<https://daneshyari.com/en/article/7827616>

Download Persian Version:

<https://daneshyari.com/article/7827616>

[Daneshyari.com](https://daneshyari.com)