



# Novel carbazole dendronized oligofluorenes for solution-processed organic light-emitting diodes



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## ABSTRACT

A group of novel dendrimers containing an oligofluorene core and oligo-carbazole dendrons, were synthesized by a Suzuki cross-coupling reaction. The dendrimers exhibit excellent thermal and amorphous stabilities, and emit deep blue fluorescence with high quantum yields of over 85%. These molecules have non-planar molecular conformations and thus possess excellent solubility and film-forming ability by solution-processing techniques. The dendrimers are used as hole-transporting emitting layers to fabricate organic light-emitting diodes (OLEDs) by a spin coating process. Bright deep blue electroluminescence is obtained with CIE coordinates of ca. (0.16, 0.09), which are quite close to the National Television System Committee (NTSC) standard blue coordinates of (0.14, 0.08). Maximum luminances were in the range of 388–711 cd m<sup>-2</sup> and maximum luminance efficiencies were in the range of 0.91–1.07 cd A<sup>-1</sup> for the derived devices.

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## 1. Introduction

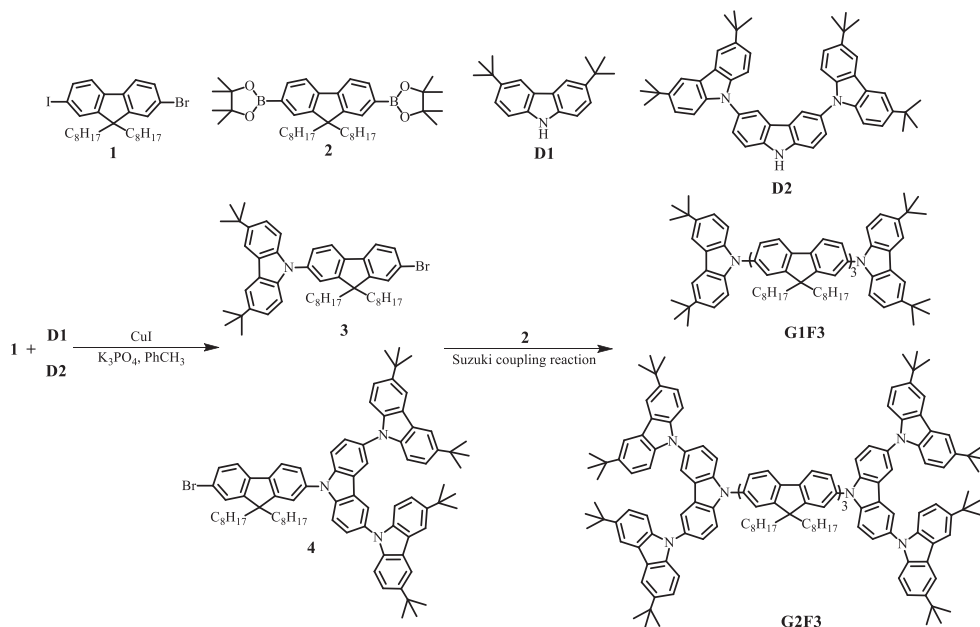
Organic light-emitting diodes (OLEDs) have attracted a great deal of attention because of their practical applications in new-generation flat-panel displays and solid-state lighting [1,2]. Compared to green light-emitting materials, much effort is still needed to further improve the performance of blue light-emitting materials, particularly in terms of luminescent efficiency and color purity [3–5]. Excellent blue emitting materials are more significant, not only as blue emitters, but also as hosts for lower-energy emitters to facilitate efficient white and other color light emission [6,7]. Therefore, continuous efforts have been devoted to high-performance blue light-emitting materials with good stability. Until now, many highly efficient blue OLEDs have been fabricated via the vacuum evaporation technique, which requires a complicated technological procedure and large amount of organic materials, leading to high fabrication costs [8]. It is generally believed that solution-processing techniques, such as spin-coating or ink-jet printing, are low-cost methods for the preparation of large-area OLED products [9,10]. To date, solution-processed blue OLEDs are mainly focused on the polymeric materials such as polyfluorene

derivatives (PFs). However, the long-wavelength emission owing to the formation of ketone defects or excimers/aggregates prevents PFs serving as excellent blue emitters [11–13]. In contrast, conjugated dendrimers have emerged as a new type of light-emitting organic materials for application in OLEDs [14]. They combine the advantages of both small molecules and polymeric materials, for example, repeatable monodispersity and high levels of purity of small molecules, and good solubility and film-formation ability by wet methods of polymers. Although much effort has been dedicated to the development of blue fluorescent dendritic materials and devices, few have demonstrated high stability and pure-blue emission. Therefore, it still remains a challenge to develop an efficient and stable blue-emitting dendrimer with a Commission Internationale de L'Eclairage (CIE) y coordinate value < 0.10.

In this paper, we report the synthesis and luminescent properties of two novel carbazole-based dendrimers, namely **G1F3** and **G2F3** (Scheme 1). The oligofluorene was selected as the core, and the well-known oligo-carbazole dendrons were attached at the termini of the oligo-fluorene core. Furthermore, *tert*-butyl groups are introduced into the dendrimers surface to enhance the solubility and film-forming ability by solution methods of these dendrimers. The dendrimers designed in this way are observed to exhibit excellent thermal and amorphous stability, and to possess relatively shallow highest occupied molecular orbital (HOMO) levels that are favorable for hole injection and transportation. The

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Scheme 1. Synthetic routes of **G1F3** and **G2F3**.

dendrimers **G1F3** and **G2F3** emit bright deep blue fluorescence in both solutions and solid films. They were used as the hole-transporting emitter to fabricate non-doped OLEDs by a spin-coating method and pure blue electroluminescence with CIE coordinate  $y \leq 0.1$  was obtained for both them. A maximum luminance efficiency of  $1.07 \text{ cd A}^{-1}$  with CIE coordinates of (0.16, 0.08) was achieved.

## 2. Experimental

### 2.1. Materials and instruments

Chemicals, reagents and solvents from commercial sources are of analytical or spectroscopy grade and used as received.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Burkert Avance II instrument (500 MHz) and a Varian INOVA instrument (400 or 100 MHz). Mass spectra were recorded on a GC-TOF MS (Micromass, UK) mass spectrometer for TOF-MS-EI and a Micromass micro MX MALDI-TOF mass spectrometer for MALDI-TOF-MS. Elemental analyses were carried out on a Carlo-Eriba 1106 elemental analyzer. Thermogravimetry analyses (TGA) and differential scanning calorimetry (DSC) measurements were carried out using a Perkin–Elmer thermogravimeter (Model TGA7) and a Netzsch DSC 204 at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere, respectively. The fluorescence and UV–vis absorption spectra measurements were performed on a Perkin–Elmer LS55 fluorescence spectrometer and a Perkin–Elmer Lambda 35 UV–Visible spectrophotometer, respectively. The fluorescence quantum yields ( $\Phi$ ) were determined in dilute dichloromethane solutions relative to the quinine sulfate ( $\Phi = 0.55$  in  $0.1 \text{ N H}_2\text{SO}_4$ ) as a standard. Electrochemical measurements were made by using a conventional three-electrode configuration and an electrochemical workstation (BAS100B, USA) at a scan rate of  $100 \text{ mV s}^{-1}$ . A glassy carbon working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) as reference electrode were used. All measurements were made at room temperature on samples dissolved in dichloromethane, with  $0.1 \text{ M}$  tetra-*n*-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) as the electrolyte, ferrocene as the internal standard.

### 2.2. OLEDs fabrication and measurement

The light-emitting devices have a configuration of ITO/**G1F3** or **G2F3** (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). The pre-cleaned ITO glass substrates ( $30 \text{ } \Omega \text{ sq}^{-1}$ ) were treated by UV-Ozone for 20 min. Subsequently the emitting layers were spin-coated on pre-treated ITO substrates from the solution of **G1F3** or **G2F3** in chlorobenzene, the thickness of which was controlled to 40 nm by adjusting the solution concentration and the spin rate. The substrate was transferred into a vacuum chamber to deposit the TPBI (1,3,5-tris[*N*-(phenyl)benzimidazole]-benzene) layer with a base pressure less than  $10^{-6}$  torr. Finally, the device fabrication was completed through thermal deposition of LiF (1 nm) and then capping with Al metal (100 nm) as cathode. The emitting area of each pixel is determined by overlapping of the two electrodes as  $9 \text{ mm}^2$ . The EL spectra, CIE coordinates, and current density–voltage–luminance relationships of devices were measured with computer-controlled Spectrascan PR 705 photometer and a Keithley 236 source-measure-unit. All the measurements were carried out at room temperature.

### 2.3. Compounds synthesis

The intermediates 2-bromo-7-iodo-9,9-dioctylfluorene (**1**), 2,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl)-9,9-dioctylfluorene (**2**) and the carbazole dendrons 3,6-di-*tert*-butyl-9H-carbazole (**D1**), 3,6-bis-(3',6'-di-*tert*-butylcarbazol-9-yl)carbazole (**D2**) were synthesized according to the literature methods [15].

2-Bromo-7-(3,6-di-*tert*-butylcarbazol-9-yl)-9,9-dioctylfluorene (**3**): A mixture of **D1** (500 mg, 1.79 mmol), **1** (1.18 g, 1.99 mmol), CuI (34 mg, 0.179 mmol),  $\text{K}_3\text{PO}_4$  (570 mg, 2.69 mmol) were added to a 100 mL 2-necked flask, and then ( $\pm$ )-*trans*-1,2-cyclohexanediamine (2.2  $\mu\text{l}$ , 0.018 mmol) and toluene (50 mL) were added under a nitrogen atmosphere. After stirring for 18 h at  $110 \text{ }^\circ\text{C}$ , the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure, dichloromethane and water were added. The organic layer was separated and washed with diluted HCl and brine, then dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed

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