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# Novel bis(fluorenyl)benzothiadiazole-cored carbazole dendrimers as highly efficient solution-processed non-doped green emitters for organic light-emitting diodes†

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**Bis(fluorenyl)benzothiadiazole-cored carbazole dendrimers show high thermal and electrochemical stability, and great potential as solution processed hole-transporting non-doped green emitters for OLEDs. A pure green device with CIE coordinates of (0.27, 0.62) and high luminance efficiencies (up to 10.01 cd $A^{-1}$) is achieved, respectively.**

Organic light-emitting diodes (OLEDs) have received enormous attention in the scientific community due to their potential for future flat-panel display and lighting applications.[1] Research on novel luminescent materials has played a key role in developing OLEDs. Both small molecules and polymers have been studied extensively for use in OLEDs. Dendrimers are an alternative class of electroluminescent (EL) materials.[2] Unlike polymers, the beauty of dendrimers is that their light emission can be finely tuned by the selection of the core, solubility can be adjusted by selecting the proper surface groups and the level of intermolecular interactions can be controlled by the type and generation of the dendrons employed, which are vital to performance of OLEDs. Recently, several types of fluorescent[3] and phosphorescent light-emitting dendrimers[4] have been reported to be successfully used in the fabrication of OLEDs by means of a solution process. Obviously the key point of material development is to find out materials emitting pure colors such as red, green and blue with excellent emission efficiency and high stability. So far, there have been several reports on high-efficiency green OLEDs fabricated using a doping method such as 4,4′-*N*,*N*′-(dicarbazole)biphenyl (CBP):tris(2-phenylpyridyl)iridium(III) [$Ir(ppy)_3$] ($\eta$ = 142 cd $A^{-1}$)[5] and tris(8-hydroxyquinolinato)aluminum (Alq3):2,3,6,7-tetrahydro-1,1,7,7,-tetramethyl-1*H*,5*H*,11*H*-10(2-benzothiazolyl)quinolizine-[9,9*a*,1*gh*]coumarin (C545T) ($\eta$ = 49.2 cd $A^{-1}$)[6] systems. However, the complicated fabrication process of the doped OLEDs makes them unsuitable for rapid and mass production. Highly efficient green fluorescent emitters for non-doped OLEDs are in great demand, but unfortunately there are only a few examples reported in the literature such as phenyl-9-[8-(7,10-diphenylfluoranthenyl)]-phenylcarbazole ($\eta$ = 10.1 cd $A^{-1}$),[7] pyrene-substituted ethenes ($\eta$ = 10.2 cd $A^{-1}$)[8] and 9,9-diarylfluorene-terminated 2,1,3-benzothiadiazole ($\eta$ = 12.9 cd $A^{-1}$).[9] These devices however are fabricated by means of the vacuum deposition process and complexes. Recently, we have reported on the synthesis and properties of carbazole dendrimers that prove to be efficient solution processed high $T_g$ amorphous hole-transporting materials for Alq3-based green OLEDs.[10] In this communication, we would like to extend the investigation by using these carbazole dendrons to form new solution-processable hole-transporting non-doped light-emitting dendrimers from which a simple structure non-doped OLED can be fabricated. When bis(fluorenyl)benzothiadiazole is used as a core, the dendrimers will emit in the green region. Herein, we report the detailed synthesis of **G*n*FB**, and their physical and photophysical properties. Investigation of solution processed non-doped OLED device fabrication and performance is also reported.

We began with Ullmann coupling of each carbazole dendron (**G1–G4**) with an excess amount of dibromofluorene **1** catalyzed by CuI/$K_3PO_4$/±*trans*-1,2-diaminocyclohexane in toluene to give the bromo intermediates **2–5** in good yields of 70–75%. Double Suzuki cross-coupling reaction of **2–5** with 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole catalyzed by $Pd(PPh_3)_4$–$Na_2CO_3$(aq) in THF afforded the bis(fluorenyl)benzothiadiazole cored dendrimers (**G*n*FB**) as yellow solids in 55–70% yields (Scheme 1). The structures of the dendrimers were confirmed by MALDI-TOF MS which showed isotopic distributions for each of the molecular ions corresponding to their molecular weights. These dendrimers show high solubility in most organic solvents allowing the thin film of **G*n*FB** to be fabricated by a solution casting process, thus overcoming the high cost of the vacuum deposition process.

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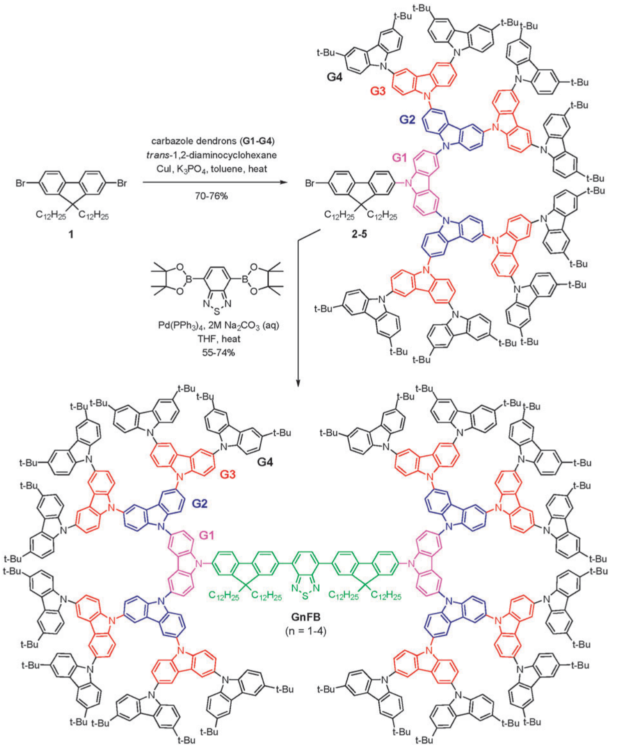
† Electronic supplementary information (ESI) available: Synthesis, characterization and device fabrication, NMR spectra, quantum chemical calculation data, TGA/DSC plots, AFM images, CV plots, data of OLED devices. See DOI: 10.1039/c3cc42931h



**Scheme 1** Molecular structures of the dendrimers **G*n*FB**.

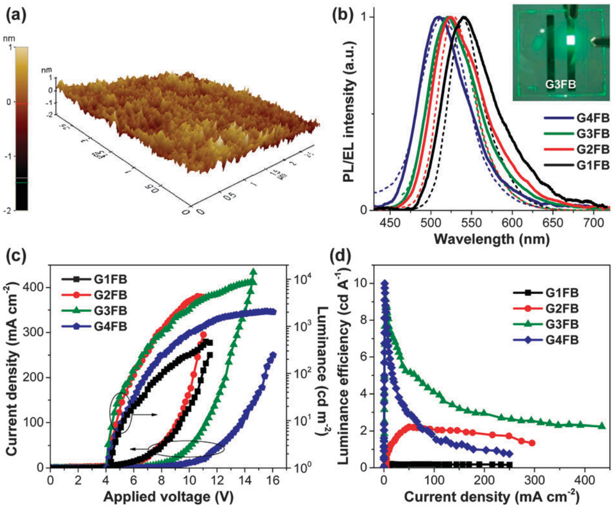


**Fig. 1** (a) AFM image of a spin-coated thin film of **G4FB**. (b) PL spectra of thin films (dot line) and EL spectra (solid line) of the OLEDs. (c) *J–V–L* and (d) *J–η* characteristics of the OLEDs.

The thin films spin-coated from $CHCl_3$:toluene solution upon analysis using AFM show a pretty smooth and pinhole-free surface indicating good film-forming properties (Fig. 1a and ESI†). The geometrical structures of the dendrimers optimized using the PM6 method reveal increasing lysterically hindered structures of the dendrons surrounding the core unit (ESI†). Such structural characteristics can influence some of their electronic and physical properties.[11] In the HOMO, π-electrons are able to delocalize over the fluorene and carbazole moieties, while in the LUMO, the excited electrons localized on the quinoid-like benzothiadiazole plane, creating a donor–acceptor characteristic.

In $CH_2Cl_2$ solution, the absorption spectra of **G*n*FB** show characteristic absorption bands ascribing to the π–π* electron transition of the carbazole and fluorene moieties at 297 and 334 nm, respectively, while the one at longer wavelengths (414–425 nm) belongs to a donor (the end-capped carbazole dendrons) to acceptor (2,1,3-benzothiadiazole core) intramolecular charge transfer (ICT) transition (ESI†). Their solution photoluminescence (PL) spectra exhibit featureless emission bands in the green region ($\lambda_{em}$ = 528–540 nm). Both the emission and ICT peaks are blue-shifted with increasing generation of dendrons, indicating that the donor–acceptor feature in the molecules get weaker and weaker, as supported by the PM6-based calculation results. These dendrimers exhibit green fluorescence with solution quantum yields ($\Phi_F$) in the range of 0.18–0.05. The thin film PL spectra of **G*n*FB** also show featureless emission bands and exhibit slight blue-shifts (∼1–14 nm) of emission maxima relative to their solution spectra (Fig. 1b and ESI†), suggesting that the intermolecular π–π interactions in the solid state of the fluorescent core are well averted by the bulky molecular structure of end-capping dendrons. The electrochemical studies on **G*n*FB** reveal one quasi-reversible wave and well defined multiple quasi-reversible oxidation waves (ESI†). The reduction ascribed to the formation of the anion radical of the electron poor 2,1,3-benzothiadiazole moiety, leading to nearly identical half-wave potentials ($E_{1/2}^{re} = -1.47$ to $-1.45$ V). Whereas the first oxidation ascribed to the removal of electrons from the carbazole dendrons ($E_{1/2}^{ox}$ = 1.12–1.02 V). Multiple CV scans display identical CV curves indicating an electrochemically stable molecule. From these data, the HOMO and LUMO levels of **G*n*FB** were calculated to be −5.49 to −5.39 and −2.95 to −2.78 eV, respectively. The HOMO energy levels of **G*n*FB** match well with the work function of the indium tin oxide (ITO) electrode suggesting that they are hole-transporting green emitters. The results obtained by thermal gravimetric analysis (TGA) reveal that these dendrimers are thermally stable with a 5% weight loss ($T_{5d}$) at a temperature well above 332 °C, while the differential scanning calorimetry (DSC) curves display an endothermic baseline shift owing to glass transition temperatures ($T_g$) ranging from 142 to 364 °C, indicating highly stable amorphous materials (ESI†).

According to the above discussed excellent properties, **G*n*FB** show great potential for use as non-doped hole-transport green emitters in OLEDs. Solution processed double layer devices with the structure of ITO/PEDOT:PSS/**G*n*FB**(spin-coating) (40 nm)/BCP (40 nm)/LiF (0.5 nm):Al (150 nm) were fabricated. The emissive layers (EML) of **G*n*FB** were spin-coated from $CHCl_3$ : toluene (1 : 1) solution with controlled thickness. Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), known to enhance performance of multilayer devices fabricated with a predominantly hole-transporting emitter[12] as a hole-blocking layer, was used to enable synthesis of high-performance devices. The EL characteristics of the devices are shown in Fig. 1b–d and summarized in Table 1. Under applied voltages, all OLEDs exhibit a bright green emission with featureless patterns and peaks centered at ∼509–540 nm (Fig. 1b–d and Table 1). The EL spectra exhibit narrow band width emissions with full width at half maxima (FWHM) of ∼70–72 nm. Particularly, the **G3FB**-based device emits green light with high color purity at about 521 nm and CIE coordinates of (0.27, 0.62) which are very close to the National Television System Committee (NTSC) standard green (0.26, 0.65).[13] This device also emits better green color purity than common Alq3-based devices ($\lambda_{EL}$ = 518; CIE = 0.29, 0.53)[10,14]

**Table 1** Physical data of **G*n*FB** and electroluminescent data of the green OLEDs

| Comp | $\lambda_{em}^{sol}/\lambda_{em}^{film}$ [c] (nm) | $\Phi_F$ [d] | $T_g/T_{5d}$ [e] (°C) | $E_g^{opt}/E_g^{ele}$ [f] (eV) | HOMO/LUMO[g] (eV) | $\lambda_{max}^{EL}$/FWHM (nm) | $V_{on}/V_{100}$ [h] (V) | $L_{max}$ [i] (V) (cd $m^{-2}$, V) | $J_{max}$ [j] (mA $cm^{-2}$) | $\eta_{max}$ [k] (cd $A^{-1}$) | CIE (*x*, *y*) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **G1FB**[a] | 540/539 | 0.18 | 142/332 | 2.54/2.42 | −5.49/−2.95 | 540/72 | 4.2/8.0 | 472/11.2 | 231 | 0.21 | 0.37, 0.59 |
| **G2FB**[a] | 534/529 | 0.13 | 256/360 | 2.58/2.33 | −5.39/−2.81 | 525/71 | 4.1/6.1 | 4328/10.6 | 245 | 2.19 | 0.31, 0.62 |
| **G3FB**[a] | 530/523 | 0.09 | 305/372 | 2.60/2.32 | −5.39/−2.79 | 521/70 | 4.0/6.0 | 8521/14.4 | 391 | 9.12 | 0.27, 0.62 |
| **G4FB**[a] | 528/514 | 0.05 | 364/378 | 2.61/2.30 | −5.39/−2.78 | 509/70 | 4.0/6.9 | 2079/15.6 | 224 | 10.01 | 0.22, 0.56 |
| Alq3[b] | 514/519 | 0.28 | 172/– | 2.7 | −5.8/−3.1 | 518/92 | 2.2/3.4 | 36 122/9.2 | 1631 | 4.32 | 0.28, 0.52 |

[a] ITO/PEDOT:PSS/**G*n*FB**(spin-coating)/BCP/LiF:Al. [b] ITO/PEDOT:PSS/NPB(evaporating)/Alq3/LiF:Al. [c] Measured in $CH_2Cl_2$ and as thin films. [d] Measured in $CH_2Cl_2$ with quinine sulfate as a standard. [e] Obtained from DSC/TGA measured at 10 °C $min^{-1}$ under $N_2$. [f] Calculated from $E_g^{opt} = 1240/\lambda_{onset}$; $E_g^{ele} = E_{onset}^{re} - E_{onset}^{ox}$. [g] Estimated from HOMO = $-(4.44 + E_{onset}^{ox})$; LUMO = $E_g^{opt}$ − HOMO. [h] Turn-on voltages at 1 and 100 cd $m^{-2}$. [i] Maximum luminance at the applied voltage. [j] Current density at maximum luminance. [k] Luminance efficiency.

and CBP:Ir(ppy)$_3$-based phosphorescence devices ($\lambda_{EL}$ = 512, 539sh; CIE = 0.32, 0.61).[15] The EL spectra of all diodes match with their spin-coated thin film PL spectra. No emission shoulder at a longer wavelength due to excimer and exciplex species formed at the interface of the EML and BCP layers, which often occurs in devices fabricated from EMLs with planar molecular structure,[16] is detected. In addition, stable green emissions are obtained from all devices and the EL spectra did not change over the entire driven voltages (ESI†). The **G3–G4FB**-based green OLEDs are the two best performing devices among all these analogues. These devices exhibit maximum brightness ($L_{max}$) up to 8521 cd $m^{-2}$ at 14.4 V, high maximum luminance efficiencies ($\eta_{max}$) of 9.12–10.01 cd $A^{-1}$, and turn-on voltages ($V_{on}$) of 4.0 V. Whereas the **G2FB**-based device shows somewhat lower EL properties with a $L_{max}$ and an $\eta_{max}$ of 4328 cd $m^{-2}$ and 2.19 cd $A^{-1}$ at 50.13 mA $cm^{-2}$, respectively. The efficiencies of **G3–G4FB**-based diodes are far superior to that of the reference evaporated NPB:Alq3-based device ($\eta_{max}$ = 4.32 cd $A^{-1}$). Although the device configuration is yet to be optimized, the performances of the devices based on our new dendrimers are outstanding compared with those of current non-doped green OLEDs[17] and all our reported green OLEDs,[14,18] and also comparable with those of highly efficient vacuum-deposited non-doped green OLEDs reported in recent years.[7–9,19] The EL efficiency of **G3FB** ($\eta_{max}$ = 10.01 cd $A^{-1}$ at 3.93 mA $cm^{-2}$) is much better than that of Alq3,[10,14,18,20] a widely investigated green emitter, clearly indicating the high potential of the present molecules as solid emitters for the construction of efficient EL devices for both display and lighting applications.

In summary, we have demonstrated the synthesis of bis(fluorenyl)-benzothiadiazole-cored carbazole dendrimers (**G*n*FB**) as green emitters for OLEDs. By using carbazole dendrons as the end-caps, we are able to reduce the crystallization and retain the high green emissive ability of a fluorescent core in the solid state, as well as improve the amorphous stability and solubility of the material. A solution processed double-layer OLED using **G*n*FB** as EML emits stable pure green color with high luminance efficiencies (up to 10.01 cd $A^{-1}$) and CIE coordinates of (0.27, 0.62). This report offers a useful strategy to decorate the highly efficient but planar fluorophore to be suitable for applications in solution processed OLEDs and to prepare high $T_g$ amorphous materials for high temperature applications.

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