

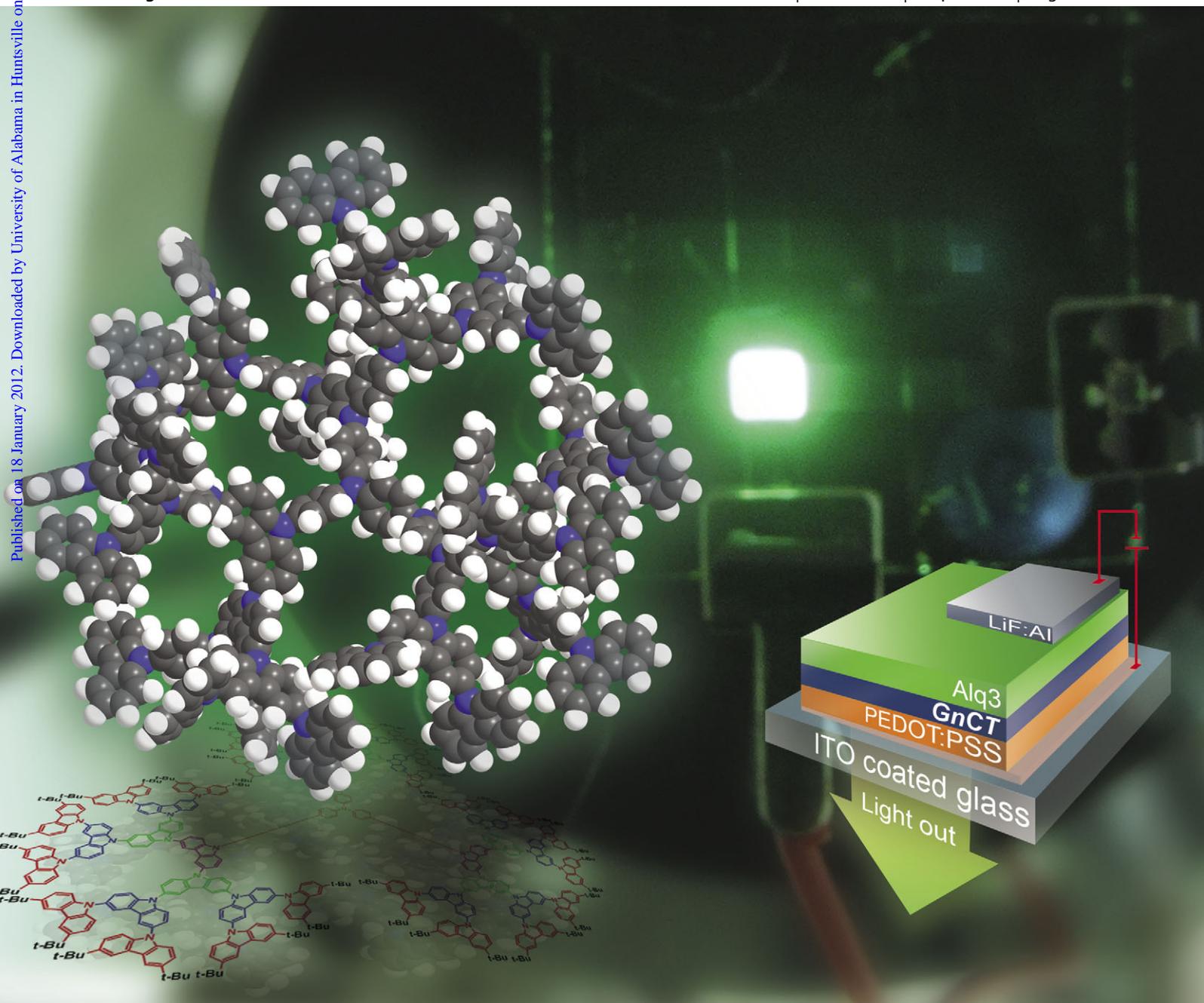
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## COMMUNICATION

**Carbazole dendronised triphenylamines as solution processed high  $T_g$  amorphous hole-transporting materials for organic electroluminescent devices†**

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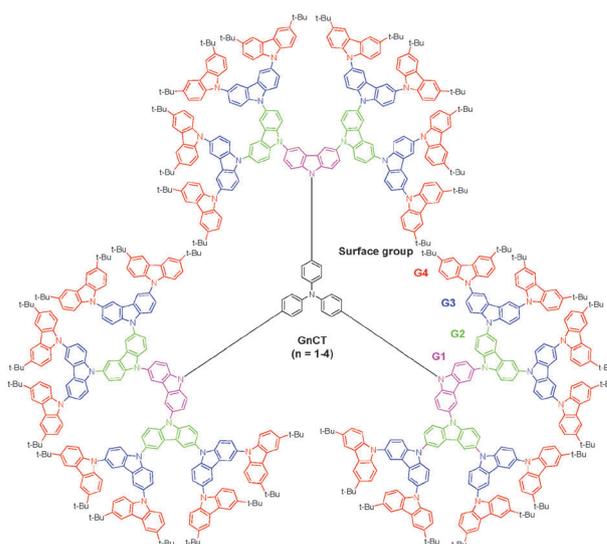
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**Carbazole dendrimers up to 4th generation were synthesized. They showed significantly high  $T_g$ , amorphous and stable electrochemical properties, and great potential as solution processed hole-transporting materials for OLEDs. Alq3-based green devices exhibited high luminance efficiency and CIE coordinates of  $4.45 \text{ cd A}^{-1}$  and (0.29, 0.53), respectively.**

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention due to their applications such as full-color flat panel displays and general illumination.<sup>1</sup> The past decade has seen great progress in both material development and device fabrication techniques.<sup>2–5</sup> One of the key developments is the use of hole-transporting layers (HTLs) for hole injection from the anode into the emitting layer providing significant improvement in the performance of the device.<sup>6</sup> In general, high glass transition temperature ( $T_g$ ) amorphous hole-transporting materials (AHTMs) are needed for highly efficient and long lifetime OLED devices. The most commonly used HTMs, *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) and *N,N'*-bis(3-methylphenyl)-*N,N'*-bis(phenyl)benzidine (TPD), exhibit many attractive properties such as high charge carrier mobility and ease of sublimation. However, their low  $T_g$  ( $65^\circ\text{C}$  for TPD and  $100^\circ\text{C}$  for NPB), ease of crystallization and low morphological stability usually lead to degradation and short lifetime of the devices.<sup>7</sup> Although many arylamine- and carbazole-based AHTMs with high  $T_g$  such as carbazole end-capped molecules,<sup>8,9</sup> 9,9-bis(4[bis(4-carbazol-9-yl-biphenyl-4-yl)-amino]phenyl)fluorenes,<sup>10</sup> and triarylamine-based starburst molecules<sup>11–13</sup> have been reported, solution-processed analogues remain rare and largely unexplored in OLEDs. It is known that a suppressing crystallization formation and improvement in morphological stability of the molecule can be achieved by

forming a bulky structure, in particular dendrimer structure.<sup>9,14,15</sup> Recent progress in organic synthesis provides the build-up of dendritic molecules bearing well designed building blocks in the core, branching point and on the surface.<sup>15,16</sup> Owing to its excellent hole-transporting ability, high charge carrier mobility, high thermal, morphological and photochemical stability, and easy functionalization at the 3,6 or N-positions, carbazole has been used as a building block to form many HTMs.<sup>9–12,17</sup> Therefore, we herein implemented all required aspects in the chosen dendrimers (**GnCT**, Fig. 1). Carbazole as the branching unit and triphenylamine as the core offer a perfect hole-transporting ability with high charge carrier mobility. The strongly twisted carbazole unit in the dendron and the presence of *tert*-butyl groups as the surface offer bulky dendrimers with high solubility, and thereby yield electrochemically and thermally stable amorphous thin film with high glass transition temperatures.<sup>9</sup>

The convergent synthetic routes toward carbazole dendrons (**Gn-H**,  $n = 1–4$ ) and their triphenylamine dendrimers (**GnCT**,  $n = 1–4$ ) are described in the ESI.† The dendrons up to 4th generation were synthesized in good yields using an iterative



**Fig. 1** Molecular structures of **GnCT**.

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† Electronic supplementary information (ESI) available: Synthetic details and characterization, NMR spectra, optimized geometrical structures, optical spectra, TGA/DSC plots, XRD patterns, AFM images, CV plots, OLED device data. See DOI: 10.1039/c2cc16878b

**Table 1** Physical data and device performance of the dendrimers

Compd	Device	Solution		Film		HOMO/LUMO <sup>a</sup> (eV)	$V_{\text{on}}^b$ /V	$L_{\text{max}}$ /cd m <sup>-2</sup>	$\eta$ /cd A <sup>-1</sup>	CIE(x, y)
		$\lambda_{\text{em}}$ /nm	$\Phi_{\text{F}}$	$\lambda_{\text{em}}$ /nm	$T_{\text{g}}$ /°C					
<b>G1CT</b>	I	389	0.37	395	215	-5.21/-1.81	3.13	1835	3.75	0.29, 0.53
<b>G2CT</b>	II	402	0.30	402	321	-5.36/-1.96	2.96	24 165	4.20	0.29, 0.53
<b>G3CT</b>	III	403	0.29	404	368	-5.38/-2.00	2.92	25 390	4.47	0.29, 0.53
<b>G4CT</b>	IV	403	0.12	404	401	-5.38/-2.01	2.88	25 397	4.32	0.29, 0.53
<b>NPB</b>	V	450	0.45	440	100	-5.40/-2.40	2.90	20 373	3.22	0.29, 0.53

<sup>a</sup> Calculated from HOMO = -(4.44 +  $E_{\text{onset}}$ ) and LUMO = HOMO +  $E_{\text{g}}$ . <sup>b</sup> Turn-on voltage at luminance of 1 cd m<sup>-2</sup>.

cycle of two orthogonal reactions namely Ullmann coupling and detosylation reactions. Ullmann coupling of each **Gn-H** with tri(*p*-iodophenyl)amine **3** afforded **GnCT** as white solids in reasonable good yields of 75–78%. The structures of all dendrons and dendrimers were characterized unambiguously with FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopy and MALDI-TOF mass spectrometry (ESI<sup>†</sup>). These dendrimers show good solubility in most organic solvents. As a result, uniform and stable amorphous thin films of these dendrimers can be obtained from a solution spin coating process. The geometrical structures of the dendrimers optimized using the HF/6-31G (d,p) method revealed increasingly sterically hindered structures which are pushed towards a sphere with the core at the center and the outer face covered by the surface groups (ESI<sup>†</sup>). Such structural characteristics can influence some of their electronic and physical properties.

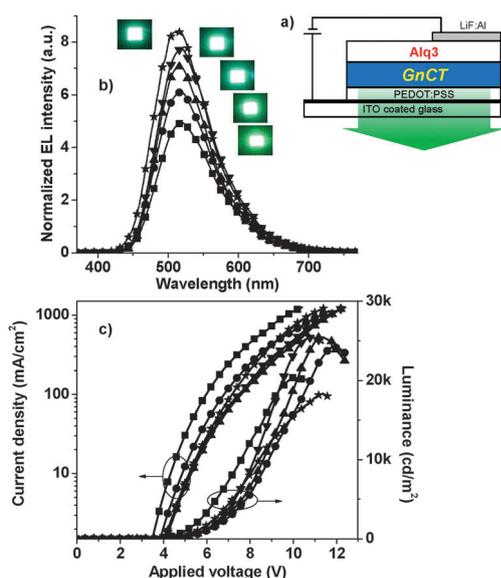
The optical properties of **GnCT** were investigated in both solution and solid state (Table 1 and ESI<sup>†</sup>). The solution and solid state absorption spectra of these dendrimers show characteristic absorption features of both carbazole and triphenylamine. The absorption edges slightly red-shifted from **G1CT** to **G4CT**, suggesting that the generation number of the dendrons has little effect on electronic properties of the dendrimers. The energy band gaps ( $E_{\text{g}}$ ) of the dendrimers deduced from the absorption edge were nearly identical (3.40–3.37 eV), despite the somewhat different molecular sizes. The solution photoluminescence (PL) spectra of **GnCT** showed an emission band in the blue purple region with a featureless pattern. PL spectra of **G2CT–G4CT** were nearly the same and red shifted (15 nm) as compared to the PL of **G1CT**. Fluorescence quantum yields ( $\Phi_{\text{F}}$ ) of **GnCT** determined in CH<sub>2</sub>Cl<sub>2</sub> gradually decreased from 0.37 to 0.12 as the generation number of the dendrimer increased. In thin film, a slight red shift (6 nm) in PL spectra of **G1CT** from its solution PL was observed, while those of **G2CT–G4CT** were identical to their corresponding solution PL, indicating weak intermolecular electronic interactions in the less bulky **G1CT** dendrimer.

To gain insight into the thermal and morphological properties of these dendrimers differential scanning calorimetry (DSC) was carried out (ESI<sup>†</sup>). The results suggested that they were thermally stable amorphous materials with glass transition temperature ( $T_{\text{g}}$ ) increasing from 215 °C (**G1CT**) to 401 °C (**G4CT**) as the generation number of the dendron increased because of the rigid structure of the carbazole dendron (Table 1 and ESI<sup>†</sup>). These  $T_{\text{g}}$  values were substantially higher than those of the commonly used HTMs (NPB, TPD), and many reported carbazole and triphenylamine derivatives.<sup>8–12,17</sup> To our knowledge, **G4CT** is among one of the highest  $T_{\text{g}}$  AHTMs that have been

reported so far. The amorphous characteristics of **GnCT** were further studied by powder X-ray diffraction (XRD) using silicon wafer as a substrate (ESI<sup>†</sup>). For **G1CT**, a series of sharp peaks were recorded at  $2\theta$  of 17°, 18° and 21° (the corresponding  $d$  values are 5.2, 4.9 and 4.3 Å) which were attributed to the  $\pi$ - $\pi$  stacking of carbazole segments. In higher generation dendrimers, these peaks became broad amorphous peaks at the same positions. The morphologies of the dendrimers were also characterized by atomic force microscopy (AFM). The films of all dendrimers spin-coated with chloroform : toluene (1 : 1) solution showed quite smooth surface, indicating their good film formation abilities (ESI<sup>†</sup>). For **G1CT**, a few pinholes were observed. The presence of pinholes in the film might cause large leakage of current.<sup>18</sup> We believe that small molecular size and crystallization ability of **G1CT** cause the pinhole formation in the film.

Cyclic and differential pulse voltammetry (CV and DPV) studies on these materials revealed quasireversible oxidation processes with no distinct reduction process being detected in all samples (ESI<sup>†</sup>). Multiple CV scans displayed identical CV curves with no additional peak at lower potential on the cathodic scan ( $E_{\text{pc}}$ ) being observed, indicating electrochemically stable molecules. The HOMO level of **G1CT** (5.21 eV) calculated from the onset of the oxidation was slightly higher than those of higher generation dendrimers (5.36–5.38 eV). Besides, the LUMO energy levels of these materials were calculated to be between 1.81 and 2.01 eV by subtracting the energy band gaps from HOMO levels (Table 1).

To investigate HTM abilities of **GnCT**, green OLEDs were fabricated using these dendrimers as hole-transporting layers (HTL); indium tin oxide (ITO)/PEDOT:PSS/HTL(50 nm)/Alq3(40 nm)/LiF(0.5 nm):Al(150 nm), with tris(8-hydroxyquinoline)aluminium (Alq3) as the green light-emitting (EML) and electron-transporting layers (ETL) (Fig. 2a). The HTL was spin-coated using chloroform : toluene (1 : 1) solution with controlled thickness. Under applied voltage, all devices exhibited a bright green emission with peaks centered at 518 nm and CIE coordinates of (0.29, 0.53). The electroluminescence (EL) spectra of these diodes were identical, and matched with the PL spectrum of Alq3, the EL of the reference device (device V) and also other reported EL spectra of Alq3-based devices (Fig. 2b).<sup>8–13,17</sup> No emission at the longer wavelength owing to exciplex species occurred at the interface of HTL and ETL materials, which is often observed in the devices fabricated from HTL with planar molecular structure, was detected.<sup>19</sup> In our case, the formation of exciplex species could be prevented by the bulky nature of the carbazole dendron. From these results and in view of the fact that the barrier for electron migration at the Alq3/HTL



**Fig. 2** (a) Structure, (b) EL spectra and (c) voltage–current–luminance ( $J$ – $V$ – $L$ ) characteristics of the OLEDs; device I (■), device II (●), device III (▲), device IV (▼) and device V (★).

interface ( $\sim 1.00$  eV) is nearly five times higher than those for hole migration at the HTL/Alq3 interface ( $\sim 0.21$  eV), under the present device configuration **GnCT** would act only as HTM, and Alq3 would act preferably as an electron blocker more than as a hole blocker and charge recombination thus confined to the Alq3 layer. More importantly, a stable emission was obtained from all diodes with the EL spectra and CIE coordinates did not change over the entire applied voltages (ESI†). The light turn-on voltage at  $1 \text{ cd m}^{-2}$  for all devices was in the range of 2.88–3.13 V and the operating voltage at  $100 \text{ cd m}^{-2}$  was in the range of 3.80–4.40 V, indicating that good performance is achieved for all the devices (Fig. 2c and Table 1).

The device characteristics in terms of maximum brightness ( $L_{\text{max}}$ ), turn on voltage and maximum luminous efficiency ( $\eta$ ) clearly demonstrated that the hole-transporting abilities of **G2CT**–**G4CT** were greater than NPB-based device (device V). Device III having compound **G3CT** as HTL exhibited the best performance with a high maximum brightness of  $25390 \text{ cd m}^{-2}$  for green OLED at 10.80 V, a low turn on voltage of 2.92 V, a maximum luminous efficiency of  $4.47 \text{ cd A}^{-1}$  and a maximum external quantum efficiency of 0.21% (Fig. 2c and ESI†). In order to explain the different efficiencies of the OLED devices, analysis of band energy diagrams of all devices was performed and it revealed that the injection barriers for the gathered holes to transfer from the HTL to Alq3 are 0.59 eV (device I) and  $\sim 0.42$  eV (devices II–IV) (ESI†). Accordingly, migration of a hole from the HTL to Alq3 layers is more effective in devices II–IV compared to device I, resulting in efficient charge recombination in the Alq3 emitting layer and better device performance. It has been demonstrated that the efficiency of an OLED depends both on the balance of electrons and holes and the  $\Phi_{\text{F}}$  of the emitter.<sup>20</sup> Although many HTMs have been reported, in terms of the amorphous morphology, significantly high  $T_{\text{g}}$ , solution processability and device efficiency, these dendrimers are among good HTMs reported.

In conclusion, we have presented a facile and efficient synthesis of rigid carbazole dendrons up to 4th generation using simple Ullmann coupling and detosylation reactions. Their triphenylamine dendrimers showed chemically stable redox and thermally stable amorphous properties with substantially high glass transition temperatures ( $T_{\text{g}}$ ) up to  $401^\circ\text{C}$ . The abilities of these dendrimers as solution-processed HTLs for green OLEDs in terms of device performance and thermal property were greater than those of a common hole-transporter NPB. These dendrimers may also be promising materials for long lifetime device applications, especially for high temperature applications in OLEDs or other organic optoelectronic devices. The use of these carbazole dendrons by forming dendritic structures with other fluorescent or nonfluorescent core units might be an effective way to prepare high  $T_{\text{g}}$  amorphous materials for device applications.

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