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Synthesis and Characterization of Carbazole Dendrimers as Solution-Processed High T_g Amorphous Hole-Transporting Materials for Electroluminescent Devices

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We report on an efficient and facile synthesis of up to 4th generation carbazole dendrons by using a mild Ullmann coupling reaction. The dendrimers, namely **GnC** (n = 1-4), are thermally stable amorphous materials with high glass transition temperatures ($T_{\rm g}$) up to 347 °C and exhibit chemically stable redox properties. The compounds show great potential to work as solution-processed hole-transporting materials for electroluminescent devices. Double-layer Alq3-based organic light-emitting diodes employing these dendrimers as the hole-transporting layers with the device configuration of

Introduction

Organic light-emitting diodes (OLEDs) have received enormous attention from the scientific community due to their potential use in flat-panel displays and lighting applications.^[1] In the past decade, great progress has been made in both device fabrication techniques and materials development.^[2] One of the key developments is the use of holetransporting layers (HTLs) for hole injection from the anode into the emitting layer, providing significant improvement in the performance of the device.^[3] 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), provide many attractive

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ITO/PEDOT: PSS/**GnC**(spin-coating)(40 nm)/Alq3(50 nm)/ LiF(0.5 nm):Al(150 nm) emit a bright green color ($\lambda_{\rm em} = 514$ nm) from the Alq3 layer, with maximum luminance, maximum current efficiency, and turn-on voltage of 29,262 cd m⁻², 5.11 cd A⁻¹, and 3.0 V, respectively. The abilities of **GnC** to act as hole-transporting materials in terms of thermal property and device performance are superior to common hole-transporters, *N*,*N'*-diphenyl-*N*,*N'*-bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) and *N*,*N'*-bis(3methylphenyl)-*N*,*N'*-bis(phenyl)benzidine (TPD).

properties such as high charge carrier mobility and ease of sublimation. However, their low T_g (65 °C for TPD and 100 °C for NPB), ease of crystallization, and low morphological stability usually lead to degradation and short life-time of the devices.^[4] Recently, many arylamine- and carbazole-based AHTMs with high T_g such as carbazole end-capped molecules,^[5] 9,9-bis{4-[bis(4-carbazol-*N*-yl-biphenyl-4-yl)amino]phenyl} fluorenes,^[6] binaphthalene derivatives,^[7] triarylamine-based starburst molecules,^[8] and carbazole dendronised triphenylamines^[9] have been reported.

It is known that suppression of crystallization and improvements in the morphological stability of the molecule can be achieved by forming a bulky structure, in particular the structure of a dendrimer.^[5,10] Dendrimers have several unique characteristics that arise from their spherical shape, giving them properties that are very different from both polymers and small molecules. Because of their precise structure, they can be characterized like any small molecules. Unlike polymers, they have distribution size that can lead to slight variations their properties. However, as macromolecules, they can form amorphous films, and have high melting temperature (T_m) and high T_g , and are therefore much less likely to crystallize. Recent progress in organic synthesis has enabled dendritic molecules to be constructed with well-designed building blocks in the core, branching points, and on the surface.^[10b,11] Many kinds of dendrons and dendrimers have been synthesized and considered for several applications including electroactive materials for OLEDs such as stilbene and phenylacetylene den-

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drimers as emitting materials,^[12] and arylamine and oxadiazole dendrimers as hole- and electron-transporting layers.^[13]

Owing to its excellent hole-transporting ability, high charge carrier mobility, high thermal, morphological and photochemical stability, and the ease of functionality at the 3-, 6-, or N-positions, carbazole has been used as a building block to form many HTMs.^[5,14] Certainly, it is very attractive to explore and develop high generation carbazole dendrons and their dendrimers, which meet the requirements as AHTMs for OLEDs and can be synthesized by using simple and low-cost methods. To this end, we wanted to incorporate all the required aspects for efficient AHTMs in the chosen dendrimers (GnC; Scheme 1). Use of carbazole as both the branching unit and the core offers perfect holetransporting ability with high charge carrier mobility and high $T_{\rm g}$. The strongly twisted carbazole unit in the dendron and the presence of tert-butyl groups at the surface leads to bulky dendrimers with high solubility,^[5] and thereby delivers electrochemically and thermally stable amorphous

thin films that could be deposited by straightforward solution processes. In terms of device fabrication, solution-processed OLEDs fabricated by using small molecules have great advantages, because the materials used are easy to synthesize and to purify, and the fabricating method is convenient, low cost and can be adapted to large-scale synthesis with less material waste.^[15] Herein, we report a detailed synthesis of carbazole dendrimers up to 4th generation. An investigation of their physical and photophysical properties, and green OLED fabrication and characterization are also reported.

Results and Discussion

Synthesis and Characterization

The synthetic route to carbazole dendrimers (GnC) is outlined in Scheme 1. Dendrimers up to the 4th generation were synthesized by using a combination of convergent and divergent approaches. In the former method, the dendrimer



Scheme 1. Synthetic route to the carbazole dendrimers (GnC).

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is assembled from the outside or the surface groups and then built inwards through the branching groups towards the core, whereas in the latter method, the dendrimer grows outwards from the core, diverging into space. tert-Butyl substituents on the 3- and 6-positions of the peripheral carbazole ring were chosen as the surface groups to provide solubility and add to the electrochemical stability of the dendrimer. The key reaction in the synthesis was the Ullmann coupling reaction involving a coupling of carbazole with aryl halides under a mild catalytic system of CuI as catalyst, (\pm) -trans-1,2-diaminocyclohexane as co-catalyst, and K₃PO₄ as base in toluene at reflux. From available 3,6-dibromo-N-dodecylcabazole (2),^[16] the tetrabromo intermediate, 3,6-bis(3',6'-dibromocarbazol-N'-yl)-N-dodecylcarbazole (7) was prepared. Ullmann coupling of 2 with carbazole (1) followed by bromination of the resultant compound 5 with N-bromosuccinimide (NBS) in tetrahydrofuran (THF) gave tetrabromo compound 6 in a total yield of 80%.

3,6-bis(3',6'-di-tert-butylcarbazol-N'-yl)carbazole The (8) intermediate was prepared from available 3,6-di-tert-butylcarbazole (4).^[17] First, tosyl-protected amine, 3,6-diiodo-N-tosylcabazole (3), was synthesized from carbazole (1) by iodination with KI/KIO₃ in AcOH followed by N-tosylation with TsCl in the presence of KOH in acetone. Coupling of 3 with 4 under the Ullmann coupling conditions followed by detosylation of the resultant compound 7 with KOH in a mixture of THF/dimethyl sulfoxide (DMSO)/ H₂O afforded 8 in 75% yield over two steps. The 1st generation carbazole dendrimer G1C was formed by alkylation of 4 with dodecylbromide in the presence of NaH in N,Ndimethylformamide (DMF) and obtained as a colorless oil in 96% yield. To form the 2nd and 3rd generation dendrimers G2C and G3C, respectively, intermediate 2 was coupled with either carbazoles 4 or 8 under the Ullmann coupling conditions to give G2C and G3C as white solids in good yields of 77 and 71%, respectively. The Ullmann coupling of intermediate 6 with 8 under the same conditions afforded the 4th generation dendrimer G4C as a white solid in 69% yield. The structures of GnC were characterized unambiguously by FTIR, ¹H NMR, and ¹³C NMR spectroscopy as well as by MALDI-TOF mass spectrometry, which confirmed that all dendrimers were monodisperse, with their molecular weights being identical to the calculated masses. These dendrimers showed good solubility in most organic solvents, allowing thin films of GnC to be fabricated by a solution casting process, thus overcoming the high cost of the vacuum deposition process.

Theoretical Calculations and Optical Properties

The geometrical structures of the dendrimers **GnC** optimized by using the TDDFT/B3LYP/6-31G (d,p) method^[18] are shown in Figure 1 (see also the Supporting Information). The results showed that each new generation of the dendrimers introduced further bulk to the structure. As the generation number increased, the number of repeating branching units got exponentially larger, while the volume available increased as the cube of the generation number. The dendrimers therefore become increasingly sterically hindered structures, which are pushed into a sphere with the core at the center and the outer face covered by the surface groups. Apart from the differences in the size, the conformations of all dendrimers are very similar. In the HOMO, π -electrons are able to delocalize over the bis(carbazol-N'-yl)carbazole moieties, while in the LUMO, the excited electrons localize on the N-dodecylcarbazole core.

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Figure 1. The HOMO and LUMO orbitals of G4C calculated by using the TDDFT/B3LYP/6-31G (d,p) method in CH_2Cl_2 .

The optical properties of GnC were investigated by UV/ Vis and photoluminescence (PL) spectroscopy in both dilute CH₂Cl₂ solution and thin-film spin-coated from CHCl₃/toluene (1:1) solution on quart substrates. The results are shown in Figure 2 and summarized in Table 1. The solution absorption spectra of these dendrimers showed similar absorption features, which were characterized by strong absorption bands at around 289 nm assigned to the π - π * local electron transition of each carbazole unit, and less intense absorption bands at longer wavelength (ca. 300 nm) related to the π - π * electron transition of the conjugated bis(carbazol-N'-yl)carbazole segments. The absorption edge of G1C slightly red-shifted (ca. 5 nm) relative to those of G2–4C, suggesting that the generation number of the dendrons has little effect on electronic properties of the dendrimers. The energy band gaps (E_{σ}) of G2–4C, estimated from the absorption edge, were nearly identical (3.69-

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Figure 2. UV/Vis absorption and PL spectra of dendrimers measured in CH₂Cl₂ and as thin-film spin-coated on quartz substrates.

3.60 eV), indicating similar π -conjugation length despite their large differences in molecular size. This can be explained by an out-of-plane twisting of each carbazole unit in the dendron, which limits π -interaction between the carbazoles. However, the lone electron pair of the nitrogen of the carbazole allows π -electron delocalization between the carbazoles in the bis(carbazol-N'-yl)carbazole moiety as observed in the calculated HOMO orbitals of G2-4C (Figure 1). The solution photoluminescence (PL) spectra of **GnC** showed emission bands in the purple-blue region (363–402 nm). PL spectra of G2–4C were featureless, nearly the same, and redshifted (39 nm) compared with that of G1C. Fluorescence quantum yields ($\Phi_{\rm F}$) of GnC, determined in CH₂Cl₂ using quinine sulfate as a standard, gradually decreased from 0.42 to 0.11 as the generation number of the dendrimer increased. The thin-film PL spectra of G2-4C also showed featureless emission bands and exhibited slight shifts of emission maxima relative to their solution spectra, suggesting that the intermolecular π - π interactions of these dendrimers in the solid state were highly hindered by their bulky molecular structures.

Electrochemical Properties

To analyze the redox properties of these dendrimers, cyclic voltammetry (CV) was carried out by using a threeelectrode cell setup with $0.1 \text{ M} n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte in CH₂Cl₂ under an argon atmosphere; the results are shown in Figure 3 and tabulated in Table 1. G1C displayed one quasireversible oxidation process at 1.09 V. whereas G2-4C exhibited well-separated multiple quasireversible oxidation processes. The first oxidation waves of G2–4C occurred at nearly the same potentials (0.99–1.02 V) and were lower than that of G1C indicating that there is π electron delocalization between the carbazoles. Their multiple CV scans revealed identical CV curves with no additional peak at lower potential on the cathodic scan (E_{pc}) being observed, indicating no oxidative coupling at the 3or 6-positions of the peripheral carbazole leading to electropolymerization. The present of 3,6-di-tert-butyl groups could prevent this type of electrochemical coupling reaction, which is usually detected in carbazole derivatives with unsubstituted 3,6-positions.^[19] The results suggested that these dendrimers were electrochemically stable molecules. Moreover, under these measurement conditions, no distinct reduction process was detected in any of the samples. The HOMO energy levels of the dendrimers were calculated from the onset of the oxidation. The HOMO level of G1C (-5.47 eV) was somewhat lower than those of G2-4C (-5.35 to 5.38 eV). The LUMO energy levels of these materials were calculated by subtracting the energy band gaps (E_{g}) from HOMO levels and were foud to lie between -1.98 and -2.05 eV (Table 1). With their HOMO energy levels match-



Figure 3. CV curves of the dendrimers measured in CH₂Cl₂/ nBu_4NPF_6 at a scan rate of 50 mV s⁻¹.

Table 1. Optical, thermal, electrochemical and electronic properties of the dendrimers.

Compd.	$\lambda_{abs} (\log \epsilon)^{[a]}$ [nm (M ⁻¹ cm ⁻¹)]	λ _{em} ^[a] [nm]	λ _e ^[b] [nm]	$\Phi_{\mathrm{F}}^{\mathrm{[c]}}$	Stokes shift ^[d] [nm]	$T_{\rm g}/T_{\rm 5d}^{\rm [e]}$ [°C]	$E_{1/2}$ vs. Ag/Ag ^{+[f]} [V]	E ^{ox} onset ^[f] [V]	$E_{\rm g}^{\rm [g]}$ [eV]	HOMO ^[h] [eV]	LUMO ^[h] [eV]
G1C	353 (4.17)	363, 378	366sh, 376	0.42	25	-/250	1.09	1.03	3.41	-5.47	-2.05
G2C	349 (4.09)	402	397, 412sh	0.30	53	114/369	0.99, 1.17	0.91	3.69	-5.35	-1.98
G3C	349 (1.05)	402	401	0.25	53	257/370	1.00, 1.17, 1.45	0.93	3.60	-5.37	-2.01
G4C	349 (3.92)	402	403	0.11	53	347/420	1.02, 1.18, 1.49	0.94	3.60	-5.38	-2.02

[a] Measured in CH₂Cl₂. [b] Measured in thin-film on quartz substrate. [c] Measured in CH₂Cl₂ with quinine sulfate as a standard. [d] Calculated from the difference of λ_{abs}^{max} and λ_{em}^{max} . [e] Measured by DSC/TGA at a heating rate of 10 °C min⁻¹. [f] Obtained from CV at a scan rate of 50 mV s⁻¹. [g] Estimated from the optical absorption edge, $E_g = 1240/\lambda_{onset}$. [h] Calculated by HOMO = -(4.44 + E^{ox}_{onset}); LUMO = HOMO - E_g , where E^{ox}_{onset} is the onset potential of the oxidation.

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ing well with the work functions of indium tin oxide (ITO) electrode and their stable electrochemical properties, these dendrimers have great potential for hole-injection and transport in OLEDs.^[20]

Thermal and Morphological Properties

For OLED applications, the thermal stability of organic materials is crucial for device stability and lifetime. Thermal instability or low T_{g} of the amorphous organic layer may result in the degradation of organic devices due to morphological changes. The thermal properties of G2-4C were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the results are shown in Figure 4 and summarized in Table 1. The results suggested that all the dendrimers tested were thermally stable materials with decomposition temperature at 5% weight loss (T_{5d}) over 369 °C in TGA measurements. The phase transition properties of these dendrimers analyzed by DSC revealed amorphous phases. In both 1st and 2nd heating scans of G2-4C, the DSC curves displayed an endothermic baseline shift owing to glass transition (T_g) , with no crystallization or melting being detected at higher temperatures in either scans. These results indicated that the tested dendrimers were stable amorphous materials with T_{g} values higher than those of commonly used HTMs such as NPB $(T_g = 100 \text{ °C})$ and TPD $(T_g = 63 \text{ °C})$, and many reported carbazole and triphenylamine derivatives.^[4–8] It was noticed that as the size of the dendrimers increased, the T_{g} values of these materials increased from 114 °C for G2C, 257 °C for G3C and 347 °C for G4C, because of the rigid and highly twisted structure of the carbazole branching unit. The results indicate that the dendritic carbazole backbone



Figure 4. (a) DSC and (b) TGA thermograms of the dendrimers measured at a heating rate of 10 °C min⁻¹ under N_2 .



Figure 5. (a) Tapping mode AFM image of a spin-coated film of **G4C**. (b) Powder XRD patterns of the dendrimers on silicon wafer substrate.

can reduce the degree of crystallization and improve the amorphous stability of the materials, which, in turn, could enhance the morphological stability of the thin film and improve the lifetime of the device.^[21] Moreover, the ability of GnC to form a molecular glass and dissolve well in organic solvents offer the possibility of preparing good thin films by solution casting processes, which are highly desirable for applications in electroluminescent devices. The amorphous characteristics of GnC were further characterized by powder X-ray diffraction (XRD) using silicon wafer as a substrate. The GnC bulk powders were scattered on top of the substrate. The XRD patterns are shown in Figure 5 (b). For G2C, a series of peaks were recorded at 2 theta of 15, 17 and 19° (the corresponding d-spacing values being 5.93, 5.21 and 4.67 Å), which were attributed to π - π stacking of carbazole segments. In higher generation dendrimers G3-4C, these peaks became broad amorphous peaks at the same positions. The morphologies of the dendrimers were also analyzed by atomic force microscope (AFM) by using the standard tapping mode. The thin films were spin-coated from CHCl₃/toluene solution on a glass substrate and then heated at 60 °C for 30 min to remove the solvents. As depicted in Figure 5 (a) (see also the Supporting Information), the films of GnC showed a relatively smooth surface, indicating their good film-formation abilities.

OLED Studies

According to the excellent properties of the dendrimers discussed above, the abilities of **GnC** as a hole-transporting

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Figure 6. (a) Schematic structure and (b) EL spectra of the OLEDs.

layer (HTL) in OLEDs were investigated. Alq3-based green OLEDs with the structure ITO/PEDOT:PSS/GnC (spincoating) (40 nm)/Alq3 (50 nm)/LiF (0.5 nm):Al (200 nm) were fabricated, in which Alq3 is the green light-emitting and electron-transporting layer (EML) (Figure 6, a). The GnC layers as HTL were spin-coated from CHCl₃/toluene (1:1) solution with a controlled thickness. To evaluate the effect of the interfacial layer and to compare hole-transporting abilities of the synthesized dendrimers GnC with commercial HTM, reference devices I, V-VII of the same structure with and without commercial 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) as HTL were made. Because the devices were fabricated in an identical manner, any changes between them should indicate differences due to the new material or device structure. The optical and electrical characteristics of all fabricated OLED devices are illustrated in Figure 6 (b), Figure 7 (see also the Supporting Information) and all parameters are summarized in Table 2. From our study and other reports,^[22] it was found that incorporation of the conductive polymer poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) in the de-



Figure 7. (a) *J-V-L* characteristics and (b) variation in luminance efficiency with current density of the OLEDs.

vice as a hole injection layer not only increased the maximum luminance (L_{max}) from 9043 cd m⁻² [luminance efficiency (η) of 1.03 cd A⁻¹] in device I to 24548 cd m⁻² (η of 4.11 cd A^{-1}) in device II, but also significantly decreased the turn-on voltages (Von) from 6.1 to 3.2 V. Moreover, their EL spectra were almost identical. It has been pointed out that the lower operating voltage of PEDOT:PSS-based devices can be attributed to the rough and porous surface of the spin-coated PEDOT:PSS polymer layer, which increases the contact area to enhance hole injection and lowers the barrier at the organic-organic interface by relocating the barrier to the more conductive PEDOT:PSS layer.^[23] To enable high-performance devices, therefore, PEDOT:PSS as hole injection layer was integrated into the devices. Under applied voltage, all GnC-based devices II-IV exhibited a bright-green emission with peaks centered at 514 nm and CIE coordinates of (0.27, 0.51) (Figure 6, b). The electroluminescence (EL) spectra of these diodes were identical, and matched with the PL spectrum of Alq3, the EL of the refer-

Table 2. Device characteristics of the fabricated OLEDs.

Device	HTL	$\lambda_{\rm EL} \ [nm]^{[c]}$	$V_{\rm on}/V_{100} [V]^{[d]}$	$L_{\rm max}$ [V] $(cd m^{-2}/V)^{[e]}$	$J_{\rm max} ({\rm mA cm^{-2}})^{[{\rm f}]}$	$\eta (\mathrm{cd}\mathrm{A}^{-1})^{[\mathrm{g}]}$	EQE (%)[h]	CIE $(x, y)^{[i]}$
I ^[a]	G2C	515	6.1/7.0	9043 (12.0)	1036	1.03	0.09	0.28, 0.51
II ^[b]	G2C	514	3.2/4.5	24548 (10.8)	1196	4.11	0.20	0.27, 0.50
III ^[b]	G3C	514	3.0/4.4	29262 (11.6)	1114	5.11	0.25	0.26, 0.51
IV ^[b]	G4C	514	3.0/5.6	28450 (12.8)	944	5.01	0.24	0.27, 0.51
$V^{[b]}$	NPB	519	2.5/3.6	31857 (9.4)	1599	4.45	0.22	0.30, 0.53
VI ^[b]	TPD	519	2.5/3.7	22539 (8.8)	1296	4.05	0.20	0.29, 0.53
VII ^[b]	_	518	4.2/5.4	4961 (10.0)	693	0.91	0.07	0.30, 0.54

[a] ITO/HTL(spin-coating)/Alq3/LiF:Al. [b] ITO/PEDOT:PSS/HTL(spin-coating)/Alq3/LiF:Al. [c] Emission maximum. [d] Turn-on voltages at 1 and 100 cd m⁻². [e] Maximum luminance at applied voltage. [f] Current density at maximum luminance. [g] Luminance efficiency. [h] External quantum efficiency. [i] CIE coordinates.

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ence devices V-VII, and also other reported EL spectra of Alq3-based devices.^[5,24] No emission at the longer wavelength owing to exciplex species formed at the interface of HTL and ETL materials, which often occurs in devices fabricated from HTL with planar molecular structure, was detected.^[25] In our case, the formation of exciplex species could be prevented by the bulky nature of the dendritic carbazole backbone. From these results, and in view of the fact that a barrier for electron-migration at the Alq3/HTL interface (ca. 1.00 eV) is about twice as high as those for hole-migration at the HTL/Alq3 interface (ca. 0.44 eV), the present device configuration of ITO/PEDOT:PSS/GnC/ Alq3/LiF:Al, GnC would act only as HTM, and Alq3 would act preferably as an electron blocker more than as a hole blocker and charge recombination would thus be confined to the Alq3 layer. More importantly, a stable emission was obtained from all diodes II-IV and the EL spectra and CIE coordinates did not change over the entire applied voltage range (see the Supporting Information).

The light turn-on voltages for all devices II-IV were in the range of 3.2-3.0 V and the operating voltages at 100 cd m^{-2} (V₁₀₀) were in the range of 4.5–5.6 V, indicating good performance is achieved for all devices. By comparison with the reference device VII, it was found that the incorporation of GnC in the device as HTL not only increased L_{max} from 4961 to 24548–29262 cd m⁻², but also significantly decreased the $V_{\rm on}$ from 4.2 to 3.0 V. Furthermore, their EL spectra were nearly identical. Moreover, the device characteristics in terms of maximum luminous efficiency clearly demonstrated that the hole-transporting abilities of G3-4C were greater than those of the most commonly used HTMs, NPB (device V) and TPD (device VI). Device III, having dendrimer G3C as HTL, exhibited the best performance with a high $L_{\rm max}$ of 29262 cd m⁻² for green OLED at 11.6 V, a low V_{on} of 3.0 V, a maximum η of 5.11 cd A^{-1} , and a maximum external quantum efficiency of 0.25%. Comparable device performance was observed from device IV (with G4C as HTL) (Table 2), however, the device using G2C as HTL showed lower device performance. Although, many HTMs have been reported, in terms of the amorphous morphology, significantly high $T_{\rm g}$, solution processability, and device efficiency, these dendrimers G3-4C are among the best HTMs reported. They are therefore highly promising as an alternative hole-transport material to NPB and TPD.

Conclusions

We have presented a facile and efficient synthesis of rigid carbazole dendrimers up to the 4th generation by using simple Ullmann coupling and detosylation reactions. These dendrimers showed chemically stable redox and thermally stable amorphous properties with high glass transition temperatures (T_g) up to 347 °C. Alq3-based green OLEDs using these materials as the hole-transporting layer (HTL) with the device configuration of ITO/PEDOT:PSS/HTL/ Alq3/LiF:Al emit brightly ($\lambda_{em} = 514$ nm) from the Alq3 layer with a maximum luminance, maximum efficiency, and low turn-on voltage of 29262 cd m⁻², 5.11 cd A⁻¹, and 3.0 V, respectively. The suitability of these dendrimers to act as solution-processed HTLs for green OLEDs in terms of device performance and thermal properties were better than commonly used hole-transporters NPB and TPD. 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 to form dendritic structures with other fluorescent or nonfluorescent core units might be an effective way to prepare high T_g amorphous materials for various applications.

Experimental Section

Materials and Instruments: All reagents were purchased from Aldrich, Acros or Fluka, and used without further purification. All solvents were supplied by Thai companies and used without further distillation. THF was heated to reflux with sodium and benzophenone, and distilled prior to use. CH2Cl2 for electrochemical measurements was washed with concentrated H₂SO₄ and distilled twice from calcium hydride. Chromatographic separations were carried out on Merck silica gel 60 (0.0630–0.200 mm). ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer with TMS as the internal reference by using CDCl₃ as solvent in all cases. Infrared (IR) spectra were measured as KBr discs with a Perkin-Elmer FTIR RXI spectrometer. UV/Vis spectra were recorded as dilute solutions in CH2Cl2 with a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra were recorded as dilute solutions in CH₂Cl₂ and thin films spin-coated from CHCl₃/toluene (1:1) solution with a Perkin-Elmer LS 50B Luminescence Spectrometer. DSC and TGA were performed with a Mettler DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, under nitrogen with heating rates of 10 °C min⁻¹. CV was carried out with an Autolab potentiostat PGSTAT 12 with a three-electrode system (platinum counter electrode, glassy carbon working electrode and Ag/Ag+ reference electrode) at a scan rate of 50 mV s⁻¹ in the presence of nBu_4NPF_6 as a supporting electrolyte in CH₂Cl₂ under argon. Melting points were measured with an Electrothermal IA 9100 series digital melting point instrument and are uncorrected. MALDI-TOF mass spectra were recorded with a Bruker Daltonics (Bremen, Germany) Autoflex II Matrix-Assisted Laser Desoprtion/Ionization-Time of Flight Mass Spectrometer (BIFEX) using a-cyano-4-hydroxycinnamic acid as matrix. Atomic force microscopy (AFM) analysis was performed with a SPA 4000 STM/AFM system using standard tipping mode with resonance of 222.223 kHz, force constant of 6.1 N m⁻¹ ($\pm 20\%$), cantilever length of (87 \pm 5) µm, cantilever width of $(32\pm5) \mu m$), scan area of 3–5 μm and scan speed of 1 Hz. Powder X-ray diffraction (XRD) was analyzed with a PHILIPS X'Pert-MDP X-ray diffractometer using Cu- K_{α} radiation (λ = 1.5418 Å) at 1,400 W, 40 kV and 35 mA in the scanning angle (2 theta) of 10-40° with resolution of 0.04° at a counting step of 1 s/step. The samples in powder form were placed on silicon wafer substrate.

Quantum Chemical Calculations: Ground-state geometries were fully optimized by using a DFT level with the B3LYP hybrid functional. All optimizations were calculated without any symmetry constraints using the 6-31G(d,p) basis set on the Gaussian09 software package.^[18]

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Fabrication and Characterization of OLEDs: Alq3-based green OLED devices using GnC, TPD and NPB as HTL with configuration of ITO/PEDOT:PSS/HTL(40 nm)/Alq3(50 nm)/ LiF(0.5 nm):Al(150 nm) were fabricated and characterized as followed. Patterned indium tin oxide (ITO) glass substrate with a sheet resistance 14 ohm sq⁻¹ (purchased from Kintec Company) was thoroughly cleaned by successive ultrasonic treatment in detergent, deionized water, 2-propanol, and acetone, and then dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS hole injection layer was spin-coated on top of ITO from a 0.75 wt.-% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C for 15 min under vacuum. Thin films of GnC layers as THL were cast on top of the PEDOT:PSS layer by spin-coating a CHCl₃/ toluene solution of GnC (1.5% w/v) at a spin speed of 3000 rpm for 30 second to obtain a 40 nm thick layer. The film thickness was measured by using a Tencor a-Step 500 surface profiler. Alq3 was then deposited onto the surface of the HTL film as light-emitting (EML) and electron-transporting layer (ETL) with a thickness of 50 nm by evaporation from resistively heated alumina crucibles at an evaporation rate of 0.5–1.0 nm s⁻¹ by vacuum evaporator deposition (ES280, ANS Technology) under a base pressure of ca. 10⁻⁵ mbar. The film thickness was monitored and recorded with a quartz oscillator thickness meter (TM-350, MAXTEK). The chamber was vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick LiF and a 150 nm thick aluminum layer were subsequently deposited through a shadow mask on the top of EML film without braking vacuum, to from active diode areas of 4 mm². The measurement of device efficiency was performed according to M. E. Thomson's protocol and the external quantum efficiencies of the device was calculated by using a previously reported procedure.^[26] Current density-voltage-luminescence (J-V-L) characteristics were measured simultaneous by the use of a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired by an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature.

3,6-Diiodo-N-tosylcarbazole (3): A mixture of 1 (20.0 g, 59.80 mmol), KI (25.80 g, 77.75 mmol), and KIO₃ (25.58 g, 59.81 mmol) in acetic acid (334 mL) was stirred and heated to reflux under N_2 for 30 min. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂ $(3 \times 150 \text{ mL})$. The combined organic phases were washed with water (2×150 mL), brine (100 mL), dried with anhydrous Na₂SO₄, filtered, and the solvent was remove in vacuo to dryness. The residue was purified by recrystallization with a mixture of CH₂Cl₂ and hexane to give 3,6-diiodocarbazole (23.04 g, 92%) as a white powder. To a solution of 3,6-diiodocarbazole (10.0 g, 23.87 mmol) and KOH (6.11 g, 109.15 mmol) in acetone (150 mL) under an N₂ atmosphere was added slowly p-toluenesulfonylchloride (20.07 g, 109.15 mmol). The reaction mixture was then heated at reflux for 15 min, then the reaction solution was poured into water (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with water $(2 \times 100 \text{ mL})$, brine (100 mL), dried with anhydrous Na₂SO₄, filtered, and the solvent was remove in vacuo to dryness. Purification by recrystallization (CH₂Cl₂/hexane) gave the product (12.31 g, 90%) as a yellow solid (m.p. > 250 °C). FTIR (KBr): v = 2958, 1594, 1465, 1423, 1362 (S=O), 1207, 1188, 1169 (S=O), 1130, 1090, 1020, 967, 819, 711 cm⁻¹. ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 2.30 \text{ (s, 3 H)}, 7.15 \text{ (d, } J = 8.4 \text{ Hz}, 2 \text{ H)},$ 7.66 (d, J = 8.4 Hz, 2 H), 7.79 (dd, J = 9, 1.5 Hz, 2 H), 8.09 (d, J = 9 Hz, 2 H), 8.17 (s, 2 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 21.55, 32.02, 87.96, 116.97, 126.46, 127.17, 129.15, 129.90, 134.45,

136.54, 137.81, 145.48 ppm. MALDI-TOF: m/z calcd. for C₁₉H₁₃I₂NO₂S [M⁺] 572.875; found 572.280.

3,6-Bis(carbazol-N'-yl)-N-dodecylcarbazole (5): A mixture of 2 (2.00 g, 4.04 mmol), 1 (1.49 g, 8.89 mmol), CuI (0.38 g, 2.02 mmol), K₃PO₄ (2.14 g, 10.10 mmol), and (±)-trans-1,2-diaminocyclohexane (0.23 g, 2.10 mmol) in toluene (50 mL) was stirred and heated to reflux under N₂ for 24 h. After cooling to room temperature, water (30 mL) was added and the mixture was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic phases were washed with water $(2 \times 30 \text{ mL})$, brine (50 mL), dried with anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel (CH₂Cl₂/hexane, 1:4) followed by recrystallization (CH₂Cl₂/methanol) afforded the product (2.18 g, 81%) as a colorless solid (m.p. 232 °C). ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 8.26$ (s, 2 H), 8.21 (d, J = 7.80 Hz, 4 H), 7.68 (s, 4 H), 7.47–7.41 (m, 8 H), 7.36–7.28 (m, 4 H), 4.49 (t, J = 7.20 Hz, 2 H), 2.06 (t, J = 6.90 Hz, 2 H), 1.56–1.33 (m, 18 H), 0.93 (t, J = 6.30 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): $\delta =$ 141.91, 129.35, 125.98, 125.87, 123.15, 120.29, 119.86, 110.13, 109.77, 43.15, 31.94, 29.67, 29.61, 29.51, 29.38, 29.21, 27.46, 22.86, 14.29 ppm. MALDI-TOF: *m*/*z* calcd. for C₄₈H₄₇N₃ [M⁺] 665.377; found 665.412.

3,6-Bis(3',6'-dibromocarbazol-N'-yl)-N-dodecylcarbazole (6): To a stirred solution of 5 (1.00 g, 1.50 mmol) in THF (60 mL) in the dark, was added NBS (1.10 g, 6.16 mmol) in small portions. The mixture was stirred at room temperature for 5 h, then water (15 mL) was added and the mixture was extracted with CH₂Cl₂ $(2 \times 30 \text{ mL})$. The combined organic phases were dried with anhydrous Na₂SO₄, filtered, and the solvent was removed in vacuo to dryness. Purification by column chromatography over silica gel (CH₂Cl₂/hexane, 1:3) followed by recrystallization (CH₂Cl₂/methanol) gave the product (1.45 g, 99%) as a white solid (m.p. 150 °C). ¹H NMR (300 MHz, CDCl₃): δ = 8.21 (s, 4 H), 8.16 (s, 2 H), 7.68 (d, J = 8.70 Hz, 2 H), 7.57 (d, J = 8.70 Hz, 2 H), 7.48 (d, J =8.55 Hz, 4 H), 7.22 (d, J = 8.70 Hz, 4 H), 4.49 (t, J = 7.20 Hz, 2 H), 2.04 (t, J = 6.90 Hz, 2 H), 1.57–1.27 (m, 18 H), 0.87 (t, J =6.30 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 140.82, 140.45, 129.33, 128.46, 126. 61, 125.78, 123.32, 123.21, 119.72, 112.85, 111.48, 110.45, 43.78, 31.92, 29.64, 29.58, 29.46, 29.35, 29.17, 27.41, 22.69, 14.12 ppm. MALDI-TOF: m/z calcd. for $C_{48}H_{43}Br_4N_3$ [M⁺] 977.019; found 977.107.

3,6-Bis(3',6'-di-*tert***-butylcarbazol**-*N'***-yl**)-*N***-tosylcarbazole** (7): Compound 7 (4.77 g, 78%) was synthesized from 3 and 4 in a manner similar to that for 5 and obtained as a white solid (m.p. 222–224 °C). FTIR (KBr): $\tilde{v} = 2949$, 1614, 1453, 1374 (S=O), 1362, 1325, 1295, 1261, 1235, 1179, 1169 (S=O), 1132, 1092, 1033, 973, 875, 807, 740 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.48$ (s, 36 H), 2.42 (s, 3 H), 7.28–7.37 (m, 6 H), 7.47 (dd, J = 9.0, 1.5 Hz, 4 H), 7.76 (dd, J = 9.0, 1.8 Hz, 2 H), 7.94 (d, J = 8.1 Hz, 2 H), 8.07 (d, J = 1.8 Hz, 2 H), 8.16 (s, 2 H), 8.17 (s, 2 H), 8.58 (s, 1 H), 8.61 (s, 1 H) ppm. ¹³C NMR (300 MHz, CDCl₃): $\delta = 21.70, 32.04, 32.08, 34.77, 109.01, 109.14, 116.20, 116.34, 118.53, 123.43, 123.57, 123.73, 126.79, 127.13, 130.10, 134.58, 135.06, 137.41, 139.55, 145.51 ppm. MALDI-TOF:$ *m/z*calcd. for C₅₉H₆₁N₃O₂S [M⁺] 875.448; found 874.919.

3,6-Bis(3',6'-di-*tert***-butylcarbazol**-*N'***-yl)carbazole (8):** A mixture of 7 (1.0 g, 1.14 mmol), KOH (0.13 g, 2.32 mmol), DMSO (6 mL), THF (12 mL) and water (2 mL) was stirred and heated at reflux under an N₂ atmosphere for 25 min. After cooling to room temperature, 10% HCl (20 mL) was added followed by water (10 mL) and methanol (5 mL). The precipitate was collected by filtration and washed with water several times followed by recrystallization



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(CH₂Cl₂/methanol) to give the product (0.78 g, 95%) as a white solid (m.p. 246–248 °C). FTIR (KBr): $\tilde{v} = 3450$ (NH), 2958, 1627, 1363, 1325, 1292, 1262, 1236, 1168, 1033, 875, 809, 741 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): $\delta = 1.48$ (s, 36 H), 7.33 (d, J = 8.4 Hz, 4 H), 7.47 (d, J = 8.4 Hz, 4 H), 7.59 (d, J = 6.9 Hz, 4 H), 8.18 (s, 6 H), 8.45 (s, 1 H) ppm. ¹³C NMR (300 MHz, CDCl₃): $\delta = 30.93$, 32.06, 34.74, 109.14, 111.89, 116.19, 119.40, 123.09, 123.56, 124.09, 125.93, 130.44, 139.04, 140.22, 142.53 ppm. MALDI-TOF: *m*/*z* calcd. for C₅₂H₅₅N₃ [M⁺] 721.439; found 720.876.

3,6-Di-tert-butyl-N-dodecylcarbazole (G1C): To a stirred ice-cooled solution of 4 (0.50 g, 1.79 mmol) in N,N-dimethylformamide (15 mL) was added sodium hydride (0.10 g, 4.47 mmol) followed by 1-bromododecane (0.62 g, 2.51 mmol). The reaction mixture was stirred at 70 °C for 24 h. After cooling to room temperature, water (30 mL) was added and the mixture was extracted with CH₂Cl₂ $(2 \times 30 \text{ mL})$. The combined organic phases were washed with dilute HCl $(2 \times 30 \text{ mL})$, water (30 mL), and brine (30 mL), dried with anhydrous Na₂SO₄, filtered, and the solvents were removed to dryness. Purification by column chromatography over silica gel (hexane) gave the product (0.80 g, 92%) as a pale-yellow oil. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3): \delta = 8.39 \text{ (s, 2 H)}, 7.74 \text{ (d, } J = 8.70 \text{ Hz}, 2 \text{ H)},$ 7.51 (d, J = 8.20 Hz, 2 H), 4.41 (t, J = 7.20 Hz, 2 H), 2.06 (t, J = 6.90 Hz, 2 H), 1.28–1.51 (m, 18 H), 0.91 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 141.55, 139.25, 123.40, 122.97, 116.44, 108.25, 43.31, 34.31, 34.86, 32.35, 32.20, 29.88, 29.76, 29.70, 29.62, 29.36, 27.57, 22.97, 14.40 ppm. MALDI-TOF: m/z calcd. for C₃₂H₅₀N [MH⁺] 448.394; found 448.391.

3,6-Bis(3',6'-di-*tert***-butylcarbazol**-*N***'-yl**)-*N***-dodecylcarbazole** (**G2C**): Synthesized from **2** and **4** in a manner similar to that for **5** and obtained as a white solid, yield 0.30 g (77%); m.p. 166–167 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.20 (s, 2 H), 8.18 (s, 2 H), 7.65 (s, 4 H), 7.46 (d, *J* = 8.40 Hz, 4 H), 7.33 (d, *J* = 8.70 Hz, 4 H), 4.48 (t, *J* = 7.20 Hz, 2 H), 2.06 (t, *J* = 6.90 Hz, 2 H), 1.29–1.56 (m, 18 H), 0.89 (t, *J* = 6.90 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 142.46, 140.29, 139.98, 129.83, 125.69, 123.51, 123.40, 123.07, 119.45, 116.17, 109.93, 109.14, 43.71, 34.73, 32.06, 31.93, 29.67, 29.65, 29.59, 29.48, 29.37, 29.21, 27.45, 22.70, 14.12 ppm. MALDI-TOF: *m*/*z* calcd. for C₆₄H₈₀N₃ [MH⁺] 890.635; found 890.646.

3,6-Bis[3',6'-bis(3'',6''-di-*tert*-butylcarbazol-N''-yl)carbazol-N'yl]-N-dodecylcarbazole (G3C): Synthesized from 2 and 8 in a manner similar to that for 5 and obtained as a white solid, yield 0.36 g (71%); m.p. > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.48 (s, 2 H), 8.28 (s, 2 H), 8.16 (s, 8 H), 7.85 (q, 4 H), 7.61 (s, 8 H), 7.56 (d, J = 8.40 Hz, 8 H), 7.34 (d, J = 8.10 Hz, 8 H), 4.59 (t, J = 7.20 Hz, 2 H), 2.14 (t, J = 6.90 Hz, 2 H), 1.28–1.57 (m, 18 H), 0.87 (t, J = 6.90 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 142.51, 141.46, 140.22, 130.67, 128.98, 125.97, 123.72, 123.61, 123.53, 123.10, 120.08, 119.37, 116.18, 111.10, 110.54, 109.11, 43.90, 34.71, 32.04, 31.90, 30.89, 29.64, 29.60, 29.50, 29.34, 29.25, 27.48, 22.67, 14.09 ppm. MALDI-TOF: *m/z* calcd. for C₁₂₈H₁₄₀N₇ [MH⁺] 1775.117; found 1775.182.

3.6-Bis{3',6'-bis[3'',6''-bis(3''',6'''-di-*tert***-butylcarbazol**-*N'''***-yl]-carbazol**-*N''***-yl]-N-dodecylcarbazole (G4C):** Synthesized from **6** and **8** in a manner similar to that for **5** and obtained as a white solid, yield 0.56 g (69%); m.p. > 250 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.64 (s, 2 H), 8.58 (s, 4 H), 8.27 (s, 8 H), 8.15 (s, 16 H), 7.69 (d, *J* = 2.40 Hz, 8 H), 7.81 (q, 8 H), 7.62 (q, 16 H), 7.43 (d, *J* = 7.20 Hz, 16 H), 7.33 (d, *J* = 8.4 Hz, 16 H), 4.68 (t, *J* = 7.20 Hz, 2 H), 2.18 (t, *J* = 6.90 Hz, 2 H), 1.29–1.65 (m, 18 H), 0.88 (t, *J* = 6.30 Hz, 3 H) ppm. ¹³C NMR (300 MHz, CDCl₃): δ = 142.52, 142.18, 141.39, 140.19, 130.74, 129.87, 128.74, 126.01,

123.91, 123.77, 123.53, 123.10, 120.08, 119.41, 116.18, 111.69, 111.05, 109.09, 34.70, 32.03, 31.92, 30.92, 29.66, 29.55, 29.36, 27.53, 22.39, 14.12 ppm. MALDI-TOF: m/z calcd. for C₂₅₆H₂₆₀N₁₅ [MH⁺] 3544.081; found 3544.091.

Supporting Information (see footnote on the first page of this article): Quantum chemical calculation results, AFM images, OLED device data, and ¹H and ¹³C NMR spectra.

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Carbazole Dendrimers for Electroluminescent Devices



Dendrimers



Carbazole dendrimers have high glass transition temperatures and have amorphous and stable electrochemical properties. Their abilities to act as solution-processed holetransporting layers in Alq3-based green OLEDs are superior to common hole-transporters such as NBP and TPD.

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Synthesis and Characterization of Carbazole Dendrimers as Solution-Processed High $T_{\rm g}$ Amorphous Hole-Transporting Materials for Electroluminescent Devices

Keywords: Dendrimers / Thin films / Glasses / Solid-state structures / Organic light-emitting diodes