Synthesis, characterization, and electroluminescent properties of star shaped donor–acceptor dendrimers with carbazole dendrons as peripheral branches and heterotriangulene as central core

Huaqiang Zhang, Shimin Wang, Yanqin Li, Bin Zhang, Chenxia Du, Xiangjian Wan, Yongsheng Chen

Abstract

Luminescent and redox-active heterotriangulene-based dendrimers (G1 and G2) of first and second generation have been synthesized, and their photophysical properties, oxidation behaviors, and applications in organic light emitting diodes (OLEDs) have been investigated. The dendrimers show efficient aggregation-induced emissions originated from the carbazole dendrons, heterotriangulene core, intramolecular charge-transfer (ICT), and intermolecular aggregation absorptions. Highest-occupied molecular orbital and lowest-unoccupied molecular orbital (HOMO and LUMO) values were acquired using UV–vis spectroscopy and cyclic voltammetry. The OLEDs fabricated with G1 and G2 as non-doping emitters exhibit exclusive aggregation-induced luminescence peaking at 600 and 630 nm, respectively, and demonstrate a good performance with maximum luminance of 1586 cd m−2 at current efficiency of 5.3 cd A−1 for G1 and 827 cd m−2 at current efficiency of 6.9 cd A−1 for G2.

1. Introduction

In the field of molecular electronics and optoelectronics, various OLEDs based on small molecules and polymers have been extensively studied due to their potential applications in flat-panel or flexible display devices. Dendrimers,1 as a very special type of polymers with hyperbranched and perfectly defined structure, have attracted much interest for many years. In order to improve the OLED efficiency, periphery to core energy transfer systems in dendrimer.4 In this regard, it is necessary to further study the structure–property relationship of dendrimers containing new donors and acceptors.

Heterotriangulene A, based on triphenylamine—a moiety that has been widely exploited for its physical and electronic properties, was first synthesized about 30 years ago.5,6 Recently, its solid-state structure and photophysical properties were established by Venkataraman et al.7 The molecule has a planar structure with D_{3h} symmetry and is densely packed into columns in solid state. Its large π-conjugation disc-like structure with three electron-withdrawing carbonyl groups makes itself a good electron-deficient building block for star shaped molecular networks with potential applications for electroluminescent devices.8 Carbazole is a suitable hole carrier and a promising building block for dendritic construction due to its electronic and optical properties.9

By taking advantages of these special properties of A and carbazole, we have now synthesized new star shaped dendrimers of the first and second generations incorporating carbazole dendrons as donor branches and A as an acceptor core. In this series, we report the synthesis, thermal stability, UV absorption, electrochemical behavior, and the unusual photo- and electroluminescent properties of G1 and G2 (Chart 1).
2. Results and discussion

2.1. Synthesis

The synthesis of the core derivative 3 is outlined in Scheme 1. The starting material 1 was synthesized according to the literature.7 Compound 2, obtained using a modified procedure based on literature,10 was hydrolyzed by potassium hydroxide in the mixture of methanol and water.11 It was acylated with thionyl chloride and followed by an Ullmann coupling with the nitro group,10 was hydrolyzed by potassium hydroxide in the mixture of methanol and water.11 It was acylated with thionyl chloride and then through an intramolecular Friedel–Crafts reaction to afford 3.7 The synthesis of dendrimers G1 and G2 is outlined in Scheme 2. G1 was prepared in two steps, a Friedel–Crafts alkylation of carbazole12 followed by an Ullmann coupling with 3.13 Preparation of G2 required a multistep process. Tosylation of carbazole and subsequent iodination afforded species 5.14 Reaction of 4 and 5 followed by a deprotection of the carbazole nitrogen gave trimer 6,15 which was then reacted with 3 to give G2.

2.2. Thermal analysis

Thermal stabilities of A, G1, and G2 were investigated with thermogravimetric analysis (TGA), as shown in Figure 1a. The decomposition temperatures of G1 and G2 are about 510 and 490 °C, respectively, which are higher than those of A (420 °C). Differential scan calorimetric (DSC) (Fig. 1b) analysis of A, G1, and G2 showed no detectable glass transition temperature (Tg) or melting temperature (Tm) before the decomposition temperature, and therefore they are quite thermally stable and can be used for various high-temperature processes in the construction of electronic devices.

2.3. Optical properties

The absorption spectra of 4, 6, G1, and G2 in chloroform show intensive transitions in UV region, with strong absorption bands in the range of 200–300 nm (Fig. 2a, Table 1). The bands at about 250 and 296 nm for these compounds are assigned to carbazole centered transitions.15,16 Overall, the molar absorbance of such bands increases with the number of carbazole units, but not in a manner of good linear relationship. For example, although the molar absorbance of G1 (containing three carbazole units) is about three times of that of 4, the molar absorbance of G2 (containing nine carbazole units) is only about 2.5 times of that of 6 with three carbazole units. While both 6 and G1 have three carbazole units, the molar absorbance of G1 is larger than that of 6. This indicates that the carbazole units in both G2 and 6 strongly perturb one another.17

As indicated by the absorption spectra of 4 and 6, relatively weak absorption bands are presented at wavelength longer than 300 nm; while the absorption features of G1 and G2 at wavelength in 300–370 nm region show moderately strong absorbance (Fig. 2a, Table 1). The band at maximum absorbance around 345 nm can be assigned to the transition of the core part (A) of G1 and G2, but actually of its resonance form A’ (Chart 1) according to literature.5 As already reported for carbazole-phenanthroline compounds,15 intramolecular charge-transfer (ICT) transitions, in which the A core plays the role of acceptor and the carbazole dendrons act as the electron donor, can contribute to the weak bands of G1 and G2 at ~ 370 nm and 420 nm, respectively (inset of Fig. 2a). This is also supported by the solvent dependence of these two bands. For example, the corresponding bands of both G1 and G2 appear in dichloromethane and tetrahydrofuran, but disappear in pentane. In addition, the maximum wavelength of ICT transition of G2 (420 nm) is red-shifted compared to that of G1 (370 nm), suggesting that the extent of ICT process is more intensified in G2 than that in G1. This is obviously due to the stronger electron donating ability of 6 than that of 4.18

Apart from the characteristic absorptions of the branches and core, the solution spectra of G1 and G2 show a new weak broad band...
and a new weak long tail, respectively, at longer wavelength around 500 nm (Fig. 2a and the inset). These absorption features are also presented in the absorption spectra of G1 and G2 films on quartz substrate, but more strongly (Fig. 2b). Thus, the absorption features

![Scheme 2. Synthesis of dendrimers G1 and G2.](image)

![Figure 1. TGA (a) and DSC (b) plots of A, G1, and G2 with a heating rate of 10 °C min⁻¹ under N₂ atmosphere.](image)

![Figure 2. Absorption spectra of 4, 6, G1, and G2 in degassed chloroform (inset is the amplification of partial spectra) (concentrations 4: 1.4×10⁻³ M; 6: 6.0×10⁻⁶ M; G1: 5.0×10⁻⁶ M; G2: 2.4×10⁻⁶ M, different concentrations were used for an optimal absorbance purpose) (a). Absorption spectra of 4, 6, G1, and G2 in thin films spin-coated from chloroform solutions on quartz substrate (b).](image)
of G1 and G2 around 500 nm may be attributed to the aggregation formation resulting from the intermolecular interactions between the molecules at high concentrations or neat films.\(^{19}\)

The photoluminescence (PL) spectra of G1 and G2 excited at 350 nm are shown in Figure 3, from which a prominent difference was observed between the two spectra. G1 and G2 show the same emission bands around 430 nm. These bands, showing common features of concentration quenching, can be assigned to the emission of the locally excited state of the A core.\(^{20}\) Differently, a very broad featureless emission at 613 nm is observed for G1, while no such band could be detected for G2. To explore the origin of the band at 613 nm, we measured the fluorescence of G1 in chloroform with different concentrations. It was found that the emission intensity ratio for band around 430 nm versus band at 613 nm showed apparent concentration dependence. With the increase of concentration of G1, the band intensities at 613 nm increase while those around 430 nm show common features of concentration quenching. Considering the bulky dendrons of G1 and G2, these results illustrated that the band of G1 at 613 nm may originate from the intermolecular J-aggregations where the molecules are arranged in head-to-tail direction rather than the coplanar π–π stacking aggregations.\(^{19,21,22}\) The absence of this band in G2 may be

<table>
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<th>Table 1</th>
<th>Spectroscopic and photophysical data of 4, 6, G1, and G2 in degassed chloroform</th>
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<tr>
<td>Compound</td>
<td>Absorption (\lambda_{\text{max}} ) nm ((c, \text{M}^{-1} \text{cm}^{-1}))</td>
</tr>
<tr>
<td>4</td>
<td>239 (56,928)</td>
</tr>
<tr>
<td></td>
<td>295 (20,051)</td>
</tr>
<tr>
<td>6</td>
<td>245 (148,196)</td>
</tr>
<tr>
<td></td>
<td>269 (90,643)</td>
</tr>
<tr>
<td>G1</td>
<td>250 (175,214)</td>
</tr>
<tr>
<td></td>
<td>295 (113,978)</td>
</tr>
<tr>
<td></td>
<td>344 (120,997)</td>
</tr>
<tr>
<td></td>
<td>370 (12,316)</td>
</tr>
<tr>
<td>G2</td>
<td>250 (333,368)</td>
</tr>
<tr>
<td></td>
<td>274 (278,046)</td>
</tr>
<tr>
<td></td>
<td>296 (242,812)</td>
</tr>
<tr>
<td></td>
<td>337 (119,560)</td>
</tr>
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</table>

Concentrations: 4: 1.4\(\times 10^{-5}\) M; 6: 6.0\(\times 10^{-6}\) M; G1: 5.0\(\times 10^{-6}\) M; G2: 2.4\(\times 10^{-6}\) M. \(^a\) Data were collected in thin films spin-coated from chloroform solutions on quartz substrate.
intermolecular J-aggregation (514 nm) can efficiently transfer to the J-aggregation and sensitize the emission at 613 nm. The fluorescence quantum yields ($\Phi_{\text{FL}}$) of 4, 6, G1, and G2 in dilute solutions in chloroform using quinine sulfate monohydrate as a standard are shown in Table 1.

The thin film emission spectra of G1 and G2 excited at 500 nm are shown in Figure 5. The two strong broad and featureless emission bands around 625 and 660 nm can be assigned to the J-aggregation-induced emissions of G1 and G2, where the molecules are arranged in head-to-tail rather than coplanar $\pi-\pi$ stacking direction in neat films. Compared with the fluorescence in solution, the emission band of G1 in solid film is red-shifted by 12 nm. The red shift can be explained by the fact that in the solid state, the molecules possess a wider distribution of conformations, which gives rise to a lower energy bandgap. When excited at 350 nm, similar PL was observed. This indicates that the excitons produced by direct photoexcitation of the core are likely to migrate readily to the lower energy trapping sites of J-aggregations and sensitize the emissions at 625 and 660 nm, respectively.

### 2.4. Electrochemical properties

Oxidation behavior of 4, 6, G1, and G2 has been investigated in chloroform as shown in Figure 6, and the results are summarized in Table 2. It is reported that a carbazole unit can undergo a reversible one-electron oxidation at relatively mild potentials. This is consistent with what has been observed for 4, which undergoes a reversible oxidation process at +1.12 V versus SCE. However, G1, with four possible redox centers of three carbazole units and one heterotriangulene core, only undergoes a single reversible oxidation process at +1.31 V versus SCE. Structurally, the three carbazole units in G1 are separated rather away and independent of each other. So the single reversible oxidation of G1 can be straightforwardly assigned to simultaneous one-electron oxidation of the three carbazole units as other similar multi-carbazole containing compounds. The oxidation potential of G1 is anode shifted comparing with that of 4, which is due to the electron-withdrawing effect of the core in G1.

The dendrimer G2 contains a large number of redox-active centers, including the branches and the core: six outer carbazole units, three inner carbazole units, and one heterotriangulene core. Its dendron subunit, compound 6, contains three carbazole units with two on outer side and one on inner side. So it is expected that G2 and 6 would show much richer redox behaviors than G1 and 4. But they both undergo only two reversible oxidation processes at

![Figure 6](image)

**Figure 6.** Cyclic voltammograms of 4, 6, G1, and G2 with the concentration of 0.01 M in 0.1 M Bu4NPF6-CHCl3, with a glassy carbon electrode at a scan rate of 100 mV s⁻¹. A platinum wire and an SCE were used as the counter and reference electrode, respectively.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>$E^\text{ox}_0$, V versus SCE</th>
<th>$\lambda_{\text{em}}$, nm</th>
<th>$E^\text{HOMO}$, eV</th>
<th>$E^\text{LUMO}$, eV</th>
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<tbody>
<tr>
<td>4</td>
<td>+1.12 [1]</td>
<td>353</td>
<td>-5.37</td>
<td>-1.86</td>
</tr>
<tr>
<td>6</td>
<td>+0.97 [1]; +1.16 [1]</td>
<td>380</td>
<td>-5.24</td>
<td>-1.98</td>
</tr>
<tr>
<td>G1</td>
<td>+1.31 [3]</td>
<td>555</td>
<td>-5.58</td>
<td>-3.35</td>
</tr>
<tr>
<td>G2</td>
<td>+1.03 [3]; +1.16 [3]</td>
<td>630</td>
<td>-5.37</td>
<td>-3.40</td>
</tr>
</tbody>
</table>

$^a$ The number of exchanged electrons is given in brackets.

$^b$ Estimated from the onset wavelength of optical absorption ($\lambda_{\text{onset}}$) in solid-state film.

$^c$ Calculated using the equation $E^\text{LUMO}=E^\text{HOMO}+E^\text{opt}$. The reference electrode was calibrated with ferrocene (Fc) and $E_{\text{Fc/Fc}}=0.44$ V versus SCE was used.

Table 3: Electrochemical properties of 4, 6, G1, and G2 films.
+0.97, +1.16 V for G6 and +1.03, +1.16 V for G2 versus SCE, respectively. These two compounds are in the series for which the number of reversible oxidation processes is less than the number of carbazole units.\textsuperscript{15} Compound G6 undergoes two successive one-electron reversible oxidation processes, separated by 0.19 V. We can assign such processes to successive oxidation of the two outer carbazole units, as observed for the similar compounds reported by Campagna and Dehaen.\textsuperscript{15,17} The inner carbazole unit cannot be oxidized within the potential window since its HOMO has already been strongly stabilized due to the directly connected two outer oxidized carbazole units. The separation of the two reversible oxidation processes indicates that significant electronic interaction between the two outer carbazole units takes place in G6 under the experimental condition.\textsuperscript{15} Similar results have been observed for the oxidation behavior of G2, which undergoes two successive simultaneous three-electron processes, separated by 0.13 V.\textsuperscript{17,20} The two successive processes are attributed to the two successive oxidations of the six outer carbazole units. And the three inner carbazole units could not be oxidized within the potential window, as in the case of G6. Because now the six outer carbazole units have been oxidized into carbazole cations and this makes the HOMO of G2 strongly stabilized.\textsuperscript{17} In contrast to the situation for G1, the distance between redox-active carbazole units and the electron-withdrawing core in G2 is larger, and the HOMO level of G2 (Table 3) is higher. This explains why the first oxidation potential of G1 is higher than that of G2.

From the thin film absorption spectra (Fig. 2b) and oxidation potentials of G4, G6, G1, and G2, we calculated their absolute values of HOMOs and LUMOs. The HOMO level was obtained from the onset potentials of oxidation by assuming the energy level of ferrocene/ferrocenium (Fc/Fc\textsuperscript{+}) to be −4.8 eV below the vacuum level. The LUMO level was calculated from HOMO value and the optical energy gap (E\textsubscript{opt}) estimated from the edges of the absorption spectra in films on quartz substrate.\textsuperscript{27} Electrochemical data of G4, G6, G1, and G2 are summarized in Table 3. The redox behavior of A could not be obtained due to its low solubility in suitable organic solvents,\textsuperscript{7} therefore its HOMO and LUMO cannot be used for a direct comparison. The HOMO values of G1 and G2 are close to those of G4 and G6, respectively, but slightly negative due to the electron-withdrawing effect of A core. The LUMOs of G1 and G2 come down significantly, causing a much smaller bandgap of G1 and G2 compared to that of G4 and G6, respectively. These results demonstrate that the HOMOs of G1 and G2 should be mainly contributed from the carbazole dendrons and their LUMOs should be mainly contributed from the A core. Thus, in these dendrimers, an intramolecular interaction, where A acts as an electron-acceptor and carbazole dendrons act as the electron donor, is expected as observed in the UV–vis spectra above.

2.5. Electroluminescent (EL) properties

To achieve high performance in organic EL device, it is necessary to attain a hole–electron-transporting balance and effective recombination of holes and electrons in the emitting layer. A three layer device with G1 was fabricated with the following configuration ITO/NPB (30 nm)/G1 (20 nm)/TPBI (30 nm)/LIF (1 nm)/Al (100 nm) by a sequential vacuum thermal deposition. Here, G1 was used as the emitting layer, N’-(di-1-naphthyl)-N,N’-diphenyl-benzidine (NPB) works as the hole-transporting layer, 1,3,5-tris(phenylbenzimidazol-2-yl)benzene (TPBI) as the hole-blocking and electron-transporting layer. G2 cannot be vacuum evaporated due to its high molecular weight, a three layer device with G2 was fabricated using solution process with the following configuration ITO/PEDOT (50 nm)/G2 (100 nm)/TPBI (30 nm)/LIF (1 nm)/Al (100 nm). A polyethylene dioxythiophene) (PEDOT) thin film was deposited on indium tin oxide (ITO) as the anode for facilitating hole injection, and G2 spin-coated on anode was used both as hole-transporting and emitting layer. A thin film of TPBI with thickness of 30 nm was subsequently vapor deposited on the emitting layer as a hole-blocking and electron-transporting material to confine exciton recombination and limit the loss of the faster moving holes to the cathode. (Details of fabrication for these devices are described in the Experimental section. The structure of devices is illustrated in Fig. 8.)
The energy level diagrams provide further insight into the roles of main functional materials played in the devices (Fig. 7). In these configurations, holes and electrons are all restricted in the emission layers. For the device with G1, the differences in ionization potential (ΔI) for ITO/NPB, NPB/G1 are 0.76, 0.12 eV, and electron affinity (ΔEa) for Al/TPBI is 1.58 eV, respectively. Also for the device with G2, the differences in ΔI for ITO/PEDOT, PEDOT/G2 are 0.40, 0.27 eV, and ΔEa for Al/TPBI is 1.58 eV, respectively. The LUMO levels of G1 and G2 are lower than those of TPBI, and therefore there is no electron-injection energy barrier from TPBI to G1 and G2. Although the lower HOMO level of TPBI (−6.20 eV) makes it an efficient hole-blocking layer, but the larger ΔEa for Al/TPBI (1.58 eV) will make the electron injection of the device relatively more difficult than those usually observed in ordinary OLEDs with Alq3 as electron-transporting material, indicating possible high turn-on voltages for these devices.28 Indeed, a high turn-on voltage of 8 V was observed for both devices with G1 and G2. If an electron-transporting and hole-blocking material with a suitable LUMO level is applied to lower the electron-injection energy barrier, the manipulator voltage would be lowered, and consequently the EL performance would be further improved.

Figure 8 shows the electroluminescence spectra of non-doped devices with G1 and G2 as the emission layers. For these two kinds of devices, only red emissions peaking at 600 and 630 nm were observed from G1 and G2, respectively, which closely match the relevant PL spectrum profiles of film samples (Fig. 5). This clearly demonstrates that the emissions from these devices originate from the aggregation-induced emissions of G1 and G2. It should be noted that, compared with the PL spectra of film samples, the EL maximum shows apparent blue shifts of 25 and 30 nm for G1 and G2, respectively. This phenomenon may be attributed to the optical interference of the device structure.29 Under different applied voltages, the emission spectra are very stable (shown in Fig. 8).

The current–voltage and luminescence–voltage curves of two sets of non-doped devices with G1 and G2 are shown in Figure 9. As the voltage increases, the luminescence intensity of G1 and G2 increases in exponential manners. For device with G2, a maximum luminescence of 827 cd m−2 at a current density of 120 mA cm−2 and a current efficiency of 6.9 cd A−1 were acquired at the operation voltage of 14 V. For device with G1, a better performance was obtained with a maximum luminescence of 1586 cd m−2 at a current density of 296 mA cm−2 and a current efficiency of 5.3 cd A−1, when operated at the voltage of 16 V. Furthermore, the current efficiencies decay gently with increasing current densities especially for OLED with G2. Although neither the configurational nor the compositional structure of the present devices is optimized, the two OLEDs show good EL performances compared with those of other dendrimers.30 It is especially interesting to note that there is almost no concentration quenching in OLEDs based on non-doping G1 and G2 owing to their aggregation-induced emission properties. This implies that G1 and G2 are good candidates for efficient non-doped red OLEDs.

3. Conclusions

In summary, we have synthesized two star shaped donor–acceptor dendrimers with carbazole branches and heterotriangulene core using Cu-catalyzed Ullmann coupling reaction and these two compounds show good thermal stabilities. The dendrimers show distinct ground state intramolecular charge-transfer (ICT) transitions between carbazole branches and heterotriangulene core as confirmed by UV–vis spectra and cyclic voltammetric studies. The relative smaller band gaps and the energies of their HOMOs and LUMOs suggest that the dendrimers favor transport of both holes and electrons. The photoluminescence of dendrimers at room temperature shows the characteristics of locally excited emissions in dilute solutions, while aggregation-induced emissions in thin films. The electroluminescent devices with G1 and G2 as non-doping emitters show good EL performances. And there is almost no concentration quenching in OLEDs based on non-doping G1 and G2 owing to their aggregation-induced emission properties. Intensive studies on electroluminescent properties by modifications of donors or acceptors to the structures of these derivative materials are in progress.

4. Experimental

4.1. General materials and methods

Unless stated otherwise, all chemicals and reagents were purchased reagent-grade and used without further purification. Solvents were purified by standard methods. All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques. N,N′-(Di-1-naphthyl)-N,N′-diphenyl-benzidine (NPB), and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) were purified by sublimation prior to use.

1H NMR and 13C NMR spectra were recorded on a Bruker AC-300 Spectrometer. Chemical shifts, δ, were reported in parts per million relative to the internal standard TMS. Mass spectra (MS) were recorded using an LCQ Advantage mass spectrometer. High resolution mass spectra (HRMS) were recorded on a VG ZAB-HS mass spectrometer. FTIR spectra were recorded on Bruker-Tensor 27 spectrometer. Elemental analyses were measured using a Yanaca CDRDER MT-3 instrument. Thermogravimetric analysis (TGA) measurement was performed on a TA instrument SDT-TG Q600 under an atmosphere of N2 at a heating rate of 10 °C min⁻¹. Differential scanning calorimetric (DSC) measurement was recorded on a TA instrument DSC-2910, under an atmosphere of N2 at a heating rate of 10 °C min⁻¹. UV spectra were recorded on a JASCO-V570 spectrometer. Cyclic voltammetry (CV) measurement was performed on an UK98B II Microcomputer-based Electrochemical Analyzer at room temperature with a three-electrode cell in a solution of Bu4NPF6 (0.1 M) in chloroform at a scanning rate of 100 mV s⁻¹. A platinum wire was used as a counter electrode, and an SCE electrode was used as a reference electrode. After
measurement the reference electrode was calibrated with ferrocene (Fc). For steady state luminescence measurements, a JOBIN YVON HORIBA spectrometer was used. Luminescence quantum yields have been calculated by the optically diluted method.24

Fabrication of OLED for G1: ITO coated glass with a sheet resistance of 20 Ω square−1 was used as substrate and anode. Before loading into a deposition chamber, the ITO coated glass was washed with organic solvents, deionized water and finally treated with ultraviolet (UV)–ozone. The organic and metal layers were all deposited in the same vacuum chamber with a base pressure better than 3 × 10−8 Pa without any vacuum break-in among the different deposition processes. The fabrication of OLED for G2 is prepared according to the following standard procedure: ITO coated glass substrates were cleaned via repeated ultrasonic washing and oxygen plasma treating. The buffer layer was spin-coated from 1.2 wt % toluene/chloroform solution. The cathode layer was spin-coated from a 1.2 wt % solution of the specific material. Finally deposited on the organic layers under the same condition. The thickness of the evaporated layers was monitored by an in-situ quartz crystal microbalance. EL spectra and luminance–current–voltage characteristics of the devices were measured with a computer controlled source meter Keithley 236 spectrometer. All device tests were carried out under an ambient atmosphere at room temperature.

4.2. Synthesis of compounds

O,O′,O′′-Amino-trisbenzoic acid-trimethylester (1), 3,6-di-tert-butyl-9H-carbazole (4) (0.32 g, 0.286 × 4 mmol), copper(I) iodide (0.033 g, 0.286 × 0.2 × 3 mmol), 2,2′-bipyridine (0.027 g, 0.286 × 0.2 × 3 mmol), potassium carbonate (0.40 g, 0.286 × 10 mmol), and 3 (0.20 g, 0.286 mmol) were refluxed in o-dichlorobenzene (30 mL) for 24 h. After the mixture was cooled to room temperature, dichloromethane was added and the mixture was filtered. The filtrate was condensed under reduced pressure, and the residue was purified by chromatography on silica gel with a mixture of petroleum ether/dichloromethane (3:1, v/v) as eluent. The G1 product was obtained as a red solid (0.28 g, yield 85%). Mp > 300 °C; 1H NMR (300 MHz, CDCl3, ppm) δ 9.338 (s, 2H), 8.206 (s, 2H), 7.586 (d, J = 8.7 Hz, 2H), 7.544 (dd, J1 = 1.5 Hz, 2H), 1.501 (s, 18H); 13C NMR (75 MHz, CDCl3, ppm) δ 175.5, 144.6, 138.7, 137.1, 131.5, 125.2, 124.5, 116.9, 108.9, 35.1, 32.2; HRMS (MALDI) m/z 1155.7690 [C81H78N4O3] (M + H)+ requires 1155.7612); IR (KBr) ν 2961, 1659, 1473, 1296, 804, 608 cm−1. Elemental analysis calcd for C81H78N4O3: C, 84.19; H, 6.80; N, 4.65%. Found: C, 84.12; H, 6.86; N, 4.90%.

4.2.4. G2

A mixture of 3,6,3′,6′-tetrakis-tert-butyly–9H-[9,3′,6′,9′]-tercarbazole (6) (0.83 g, 0.286 × 4 mmol), copper(I) iodide (0.033 g, 0.286 × 0.2 × 3 mmol), 2,2′-bipyridine (0.027 g, 0.286 × 0.2 × 3 mmol), potassium carbonate (0.40 g, 0.286 × 10 mmol), and 3 (0.20 g, 0.286 mmol) were refluxed in o-dichlorobenzene (25 mL) for 36 h. After the mixture was cooled to room temperature, dichloromethane was added and the mixture was filtered. The filtrate was condensed under reduced pressure, and the residue was purified by chromatography on silica gel with a mixture of petroleum ether/dichloromethane (2:1, v/v) as eluent. The G2 product was obtained as a deep brown solid (0.57 g, yield 80%). Mp > 300 °C; 1H NMR (300 MHz, CDCl3, ppm) δ 9.577 (s, 2H), 8.338 (d, J = 1.8 Hz, 2H), 8.175 (d, J = 1.6 Hz, 4H), 7.852 (d, J = 8.7 Hz, 2H), 7.735 (dd, J1 = 8.7 Hz, J2 = 1.8 Hz, 2H), 7.493 (dd, J1 = 8.7 Hz, J2 = 1.6 Hz, 4H), 7.393 (d, J = 8.6 Hz, 4H), 1.473 (s, 36H); 13C NMR (75 MHz, CDCl3, ppm) δ 175.4, 143.1, 140.2, 139.9, 136.5, 132.7, 132.6, 126.8, 125.7, 125.2, 123.9, 123.5, 119.9, 116.5, 110.8, 109.3, 35.0, 32.3; HRMS (MALDI) m/z 2482.7807 [C177H168N8O3] (M + H)+ requires 2482.3739); IR (KBr) ν 2957, 1724, 1661, 1470, 1364, 1283, 806, 609 cm−1. Elemental analysis calcd for C177H168N8O3: C, 85.61; H, 6.82; N, 5.64%. Found: C, 85.55; H, 6.88; N, 5.72%.

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References and notes