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Covalent Functionalized Conjugated Dendrimers for Organic Light Emitting Diodes: Synthesis, Characterization, and the Deep Blue Electroluminescence

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Two deep blue-emitting dendrimers **11** and **12** with carbazole containing dendrons were developed in this contribution. The carbazole-containing units were introduced to tune the charge-transporting property of the desired dendrimers. The investigation of photophysical properties, electrochemical, and electroluminescence properties demonstrated that the balance between electron and hole transporting was achieved from both dendrimers. The preliminary organic light-emitting diode (OLED) fabrication achieved a pure blue colour with stable CIE chromaticity coordinates (*X*: 0.15–0.16, *Y*: 0.09–0.10) for **11** and **12**. Single layer deep blue emitting diode devices with higher efficiency are achieved without the colour changing. The investigation of OLED performance indicates that dendrimers **11** and **12** are promising light-emitting materials with pure blue colour and good colour stability for OLEDs.

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Although plastic electronics have achieved real applications in past decades,[1] to meet the requirement of commercial high-resolution, full-colour, large size flat-panel displays, organic light-emitting diodes (OLEDs) need further achievements in materials and device fabrication. Pure deep blue-emitting materials with high luminescence efficiency are still a challenge owing to their high energy gap and poor colour stability.[2] Moreover, as the high quality lighting source, white light emitting devices with high luminescence and efficiency were achieved from pure deep blue-emitting materials doped with different recipes.[2] Therefore, continuous efforts have been devoted to blue-emissive materials including small molecules and polymers to improve their colour purity, stability, and device efficiency.

Recently, π-conjugated dendrimers with an intrinsic stiff nature have attracted considerable interest due to their potential applications in optoelectronic devices.[3] In comparison with well known linear oligomers and polymers, π-conjugated dendrimers with large branches exhibit intrinsic two or three-dimensional architectures, which bring new electrical, optical, and morphological properties to the whole molecular structure system. In our previous contribution, we developed several dendrimers with very impressive high bright deep blue light emission to achieve high performance deep blue OLED devices.[2c,4] However, poly(*N*-vinylcarbazole) (PVK) as a hole transport layer is crucial for such dendrimer based OLED devices for balancing the electron and hole injecting and transporting. To simplify the process complexity and to decrease the device fabrication cost, single layer devices, in which no other hole or electron transport layer was needed, were a good solution.[5] To develop new conjugated dendrimers with the balanced electron/hole transporting is still a challenge for achieving the high efficiency single layer emitting devices.[6]

In this contribution, we develop two deep blue emitting dendrimers containing carbazole-functionalized dendrons. In comparison to our previous dendrimers, two different carbazole-functionalized units are introduced to tune the charge transporting property of the desired dendrimer, in which one branch is based on a 9,9′-disubstituted fluorene moiety, and the other is a trialkoxyl substituted benzene unit. The electron/hole transporting is demonstrated to be balanced and single layer deep blue emitting diode devices with higher efficiency are achieved without the colour changing. The preliminary OLEDs fabrication achieves pure blue colour with stable CIE chromaticity coordinates (*X*: 0.15–0.16, *Y*: 0.09–0.10) for **11** and **12**. The investigation of OLEDs indicates that **11** and **12** are promising light-emitting OLED materials with pure blue colour and good colour stability. Such a strategy provides a platform to achieve pure blue-emitting dendrimer materials with high efficiency for OLEDs.

Scheme 1 illustrates the details of the synthetic route to dendrimers **11** and **12**. To a mixture of 2-bromo-9*H*-fluorene and sodium hydroxide in DMSO was successively added 9-(6-bromohexyl)-9*H*-carbazole, to afford compound **1** as a white powder in 95% yield. Followed by a Miyaura reaction, boronic ester **2** was gained in 85% yield.[7] Highly reactive $Pd_2(dba)_3$ and PCy_3 were employed as the catalysts to achieve high yield. A Suzuki cross-coupling reaction between **3**[8] and **2** in the presence of $Pd(PPh_3)_4$ afforded **4** in 72% yield after careful purification. The same Suzuki procedures of readily prepared **5**[9] with 4-methoxyphenylboronic acid in the presence of Pd $(PPh_3)_4$ afforded mono-, di-, and tri-substituted compounds in one pot. After flash column purification, di-substituted compound **6** was obtained in 20% yield. The removal of methyl groups from compound **6** using BBr_3 following by reacting with **9**, afforded **8** in 82% overall yield. The similar Suzuki procedure

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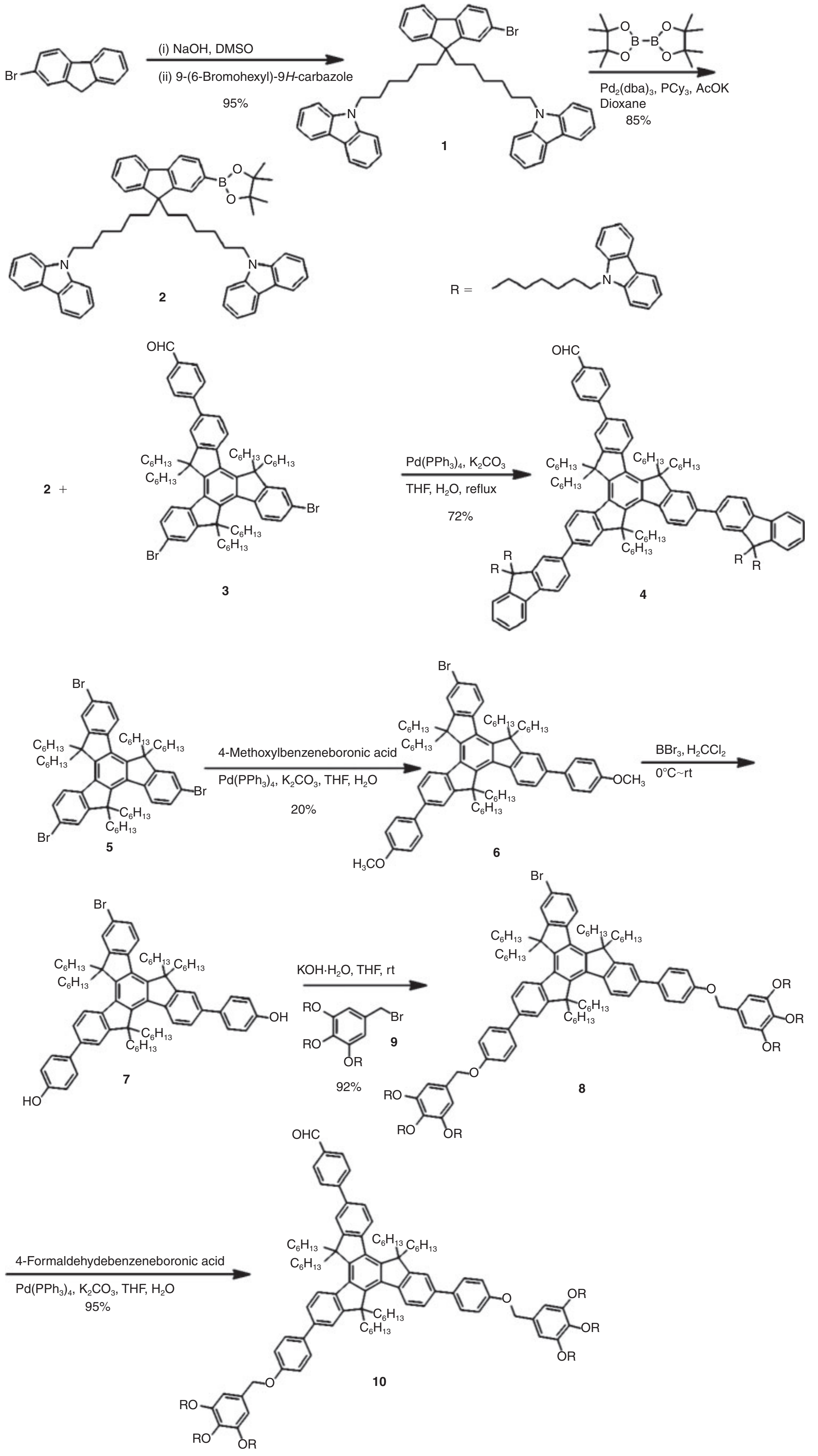
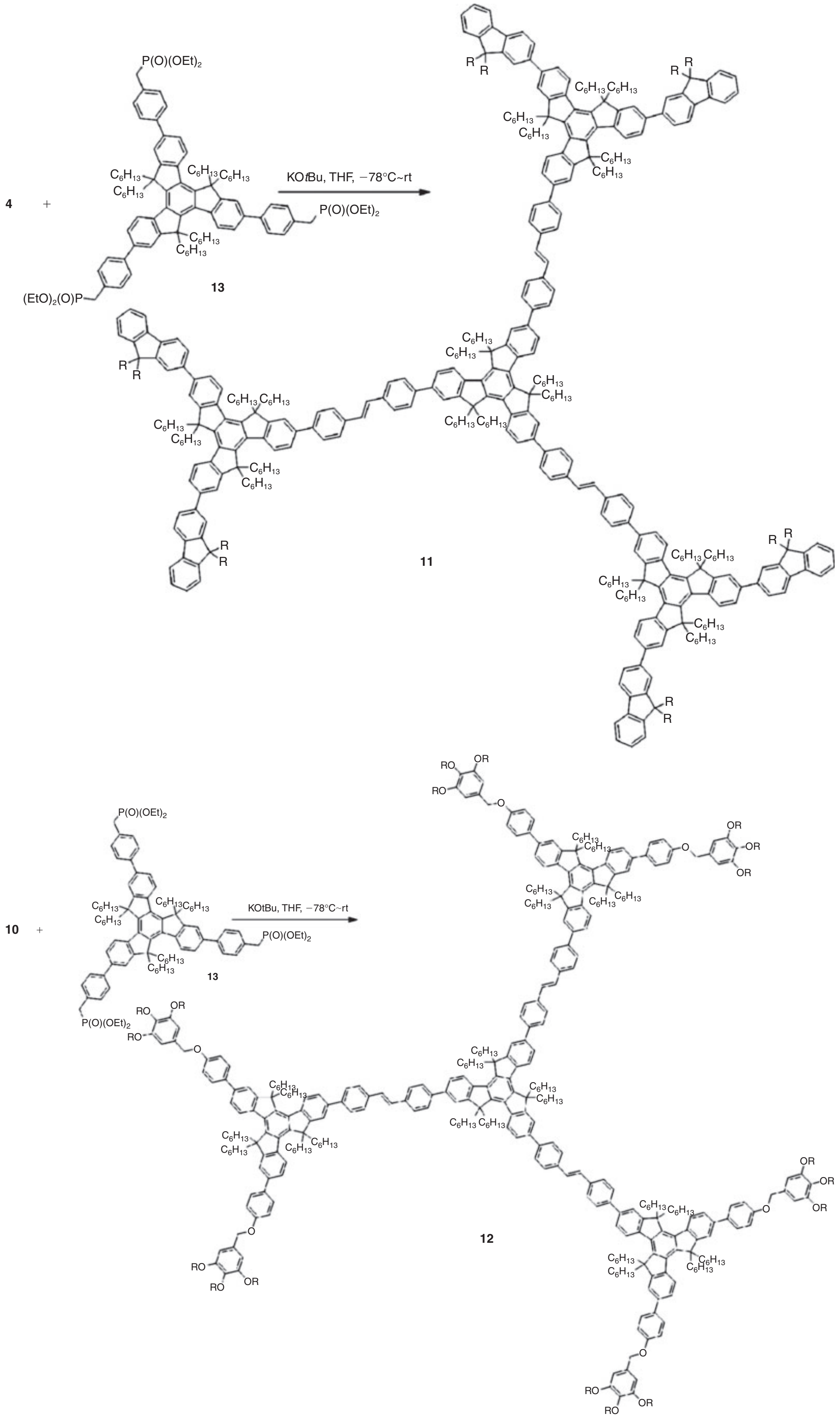


Scheme 1. The synthetic route to carbazole-functionalized dendrimers **11** and **12**.



Scheme 1. (*Continued*)

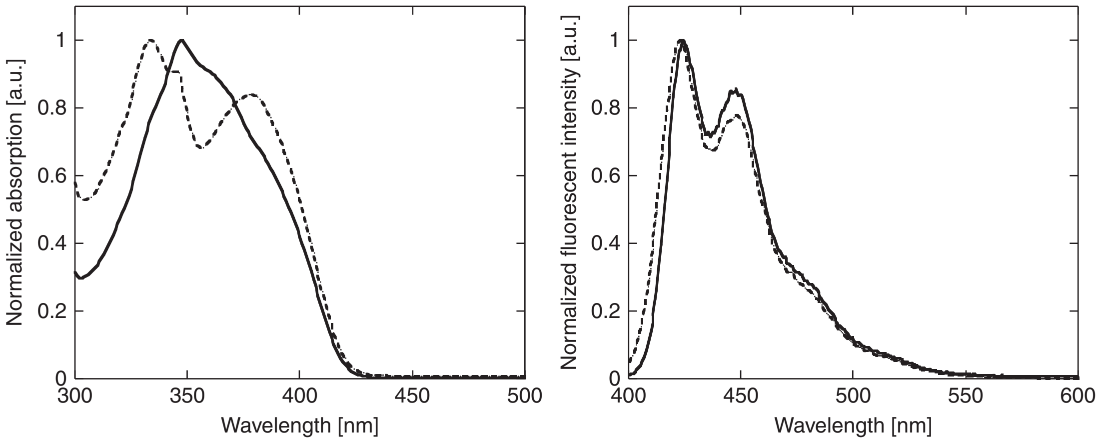


Fig. 1. The absorption (left) and fluorescent (right) spectra for **11** (solid line) and **12** (dotted line) in THF solution with concentration of 10^{-6} M. Emission spectra were obtained upon excitation at the absorption maximum.

of **8** with 4-formylbenzeneboronic acid produced **10** in 95% yield.

Compound **4** as the periphery was reacted with the triphosphate substituted truxene derivative (compound **13**)[4] via a Horner-Wadsworth-Emmons reaction to give dendrimer **11** with 12 carbazole units in 75% yield. The procedure of this reaction was modified to achieve high yield. Because of the instability of the base activated Horner reagent, continuous low temperature was crucial for the reaction. The reaction was kept below −78°C for at least 5 h. Following the same procedure, functionalized dendrimer **12** as a pale yellow powder with 18 carbazole units on the periphery was also obtained, in 71% yield.

Both new dendrimers **11** and **12** showed good solubility in common organic solvents at room temperature. Their structures and the purity were fully characterized and verified by ^{1}H and ^{13}C NMR spectroscopy, and MALDI-TOF MS (see Accessory Publication).

The photophysical properties of both dendrimers were investigated in dilute solutions and in thin films. The concentration of all compounds in THF solutions was approximately 1.0×10^{-6} M. Fig. 1 illustrates the absorption and PL spectra of **11** and **12** in dilute THF solution. For the UV-vis absorption spectra in THF solution as shown in Fig. 1, dendrimer **11** exhibited an absorption maximum $\lambda_{\max}$ at 347 nm with two shoulders at 365 and 384 nm. Dendrimer **12** displayed two absorption bands peaking at 330 nm and 378 nm, which were ascribed to the absorption of the peripheral phenyl-functionalized truxene skeleton, and the stilbene-modified truxene unit, respectively.[10] The absorption at 378 nm was similar to that of some oligo- and poly(*p*-phenylenevinylene) derivatives (∼370–380 nm).[11] The absorption maximum $\lambda_{\max}$ of **11** red-shifted ∼20 nm relative to **12**, which was attributed to the increase of the effective conjugation length from the benzene to fluorene unit. The absorption features of **11** and **12**, with the same onset at 420 nm, indicating that both dendrimers might have the same energy band gaps. The investigation of absorption properties indicated that the modification at the periphery of the dendrimers did not affect the effective conjugation length. For the emission spectra in dilute solution, both **11** and **12** also displayed almost identical features. Two strong emission bands in the visible region were observed for both **11** and **12**. However, in the drop-casting films, the absorption spectra of both **11** and **12** become broad and the vibration band of the emission features was lost (as shown in Fig. A1 in the Accessory Publication available from the Journal's website). Such difference can be explained by the stronger interaction of the molecules in the solid state than in the solution. The photoluminescence (PL) quantum efficiency of dendrimers **11** and **12** both in the diluted solution and in the solid state were determined. In the diluted THF solution, the PL efficiencies were as high as 95% for **11** and 94% for **12**. In the solid state, the PL efficiency was measured to be 21% for **11** and 19% for **12**.

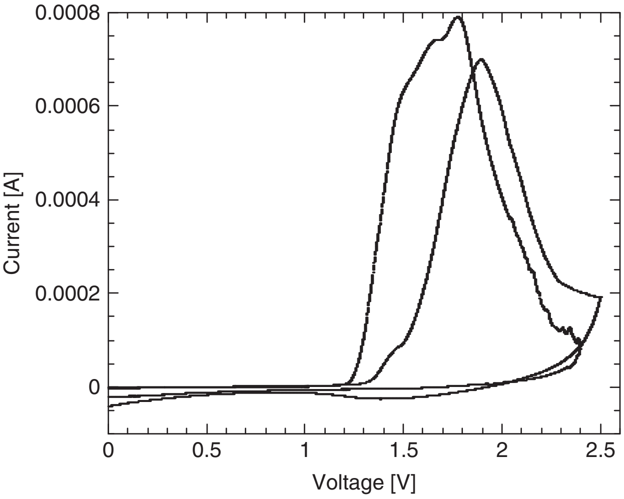


Fig. 2. The cyclic voltammetry spectrums of the drop-casting films. The spot line and the solid line corresponded to compounds **11** and **12**, respectively.

The electrochemical properties of the two dendrimers were also investigated (as shown in Fig. 2). Only one broad oxidation band was observed for each dendrimer. No reduction band was found in the drop-casting film. The onset of the oxidation wave was 1.2 eV for **11** and 1.3 eV for **12**. The HOMO levels, which were estimated by the onset of the oxidation wave, were 5.6 eV for **11** and 5.7 eV for **12**. The LUMO levels, which were estimated by calculation with optical band gap, were 2.6 eV for **11** and 2.7 eV for **12**.

The single layer devices based on the functionalized dendrimers were fabricated. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer was spin-coated onto the ozone plasma treated ITO glass to serve as the hole injection layer and anode. The thickness was ∼40 nm. The Ba/Al layer was served as electron injection layer and cathode. The dendrimer layer was spin-coated onto the PEDOT layer and no other additional layers such as hole transport layer or electron

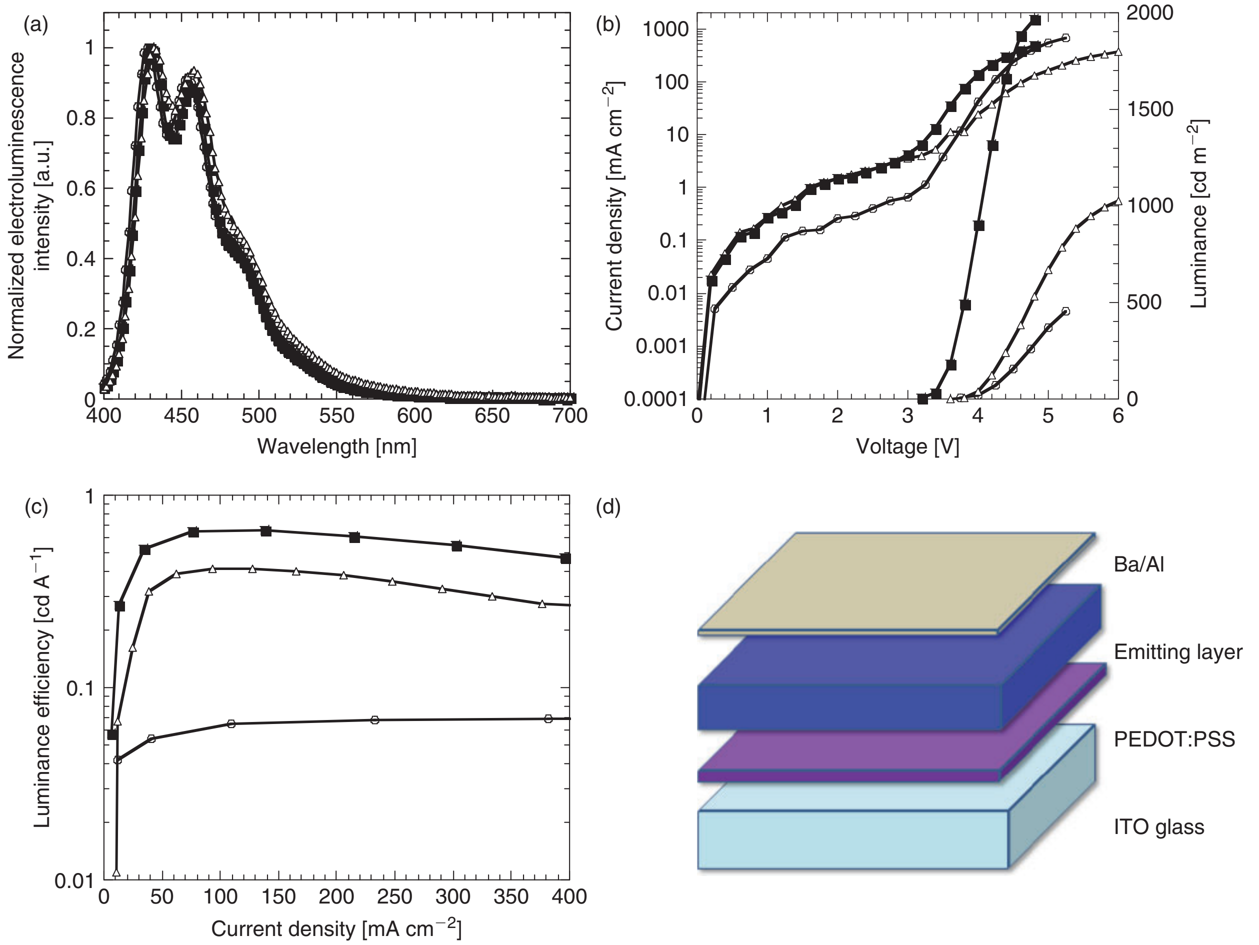


Fig. 3. (a) The electroluminescence spectrum of dendrimers **G0**, **11**, and **12**. (b) The current-voltage-light intensity characteristics for **G0**, **11**, and **12**. (c) The current-luminescence efficiency curve. The circle, triangle, and square are for the **G0**, **11**, and **12**, respectively. (d) The schematic of the device structure.

transport layer were needed (Fig. 3d). As shown in Fig. 3a, the electroluminescence (EL) features of both dendrimers were exactly the same with the non-functionalized dendrimer (**G0**) that we previously studied.[4] The results are very important to show that the functionalization of the dendrimers only changed the charge transportation without changing the backbone energy diagram. Such separated functionalization could enable us to engineer the specific property of the subjects without influencing others. In Fig. 3c, the electroluminescence efficiency enhancement shows that the improvement of the balancing charge transport is very clear. With the same device structure and fabrication conditions, the modified dendrimers showed 2 to 5 times enhancement of the maximum luminescence relative to **G0**. The electroluminescence spectra recorded for the single-layer devices revealed three similar main emission peaks for all emitters, a very sharp peak at ~430 nm and one much broader centred around 460 nm (Fig. 3a). Moreover, the emission maximum λ_{max} was similar to that of their PL spectra. All the devices showed blue light with chromatic coordinates (CIE 1931) in a range of (*X*: 0.15~0.16, *Y*: 0.09~0.10). Importantly, as the operation voltage increasing in a rational range, the electroluminescence intensity of all the devices enhanced but the shape of the emission remained unchanged as well as the chromatic coordinates, which proved the optical spectra stability under electric field. The turn-on voltages were slightly different from 3.2 V to 3.7 V. The electroluminescence efficiencies were increased by 35 times for **11** and 10 times for **12** compared with **G0**.[4] The result indicated that the functionalization via attaching the carbazole units was very efficient to improve the performance of the single layer device. The detailed device optimization and the device physics study is undergoing in our own laboratory.

In conclusion, we have developed two functionalized dendrimers owning both highly pure deep blue emissions and charge transportation balancing. The investigation of their photophysical properties showed that such dendrimer skeletons can be orthogonally modified without affecting the effective conjugation length. The introduction of carbazole units effectively improves the balance of electron and hole transporting in the active layers for OLED devices. The devices performance is enhanced 30 times. We demonstrate an effective way to improve the device efficiency via covalent modification. Future modification and detailed devices physics investigation is undergoing in our group.

Experimental

General Methods

Chemicals were purchased and used as received. All air and water sensitive reactions were performed under a nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled from sodium and benzophenone ketyl. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury plus 300 MHz and Bruker ARX-400 (400 MHz) using $CDCl_3$ as solvent. All chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm), and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm). Absorption spectra were recorded on a

Perkin–Elmer Lambda 705UV-vis Spectrometer. PL spectra were carried out on Perkin–Elmer LS55 Luminescence Spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA, USA) using a 337 nm nitrogen laser with dithranol as matrix. Cyclic voltammetry was performed using a BASI Epsilon workstation and measurements were carried out in acetonitrile containing 0.1 M $n\mathrm{Bu_4NPF_6}$ as the supporting electrolyte. Carbon electrode was used as a working electrode and a platinum wire as a counter electrode. All potentials were recorded versus Ag/AgCl (3 M NaCl (aq.)) as a reference electrode. The photoluminescence efficiencies were determined on the HORIBA JOBIN YVON Nanolog FL3–2iHR spectrometer equipped with F3018 integration sphere.

Device Fabrication and Characterization

OLEDs were fabricated on pre-patterned ITO with sheet resistance 10–20 Ω square^{-1}. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol. Oxygen plasma treatment was performed for 10 min as the final step of substrate cleaning to improve the contact angle just before film coating. Onto the ITO glass was spin-coated a layer of PEDOT:PSS film with a thickness of 40 nm from its aqueous dispersion, aiming to improve the hole injection and to avoid the possibility of leakage. PEDOT:PSS film was dried at 200°C for 10 min. The solution of all materials in *p*-xylene was prepared in a nitrogen-filled drybox and spin-coated on top of the ITO/PEDOT:PSS surface. Typical thickness of the emitting layer was 50–80 nm. Then a thin layer of barium as an electron injection cathode and the subsequent 200 nm thick aluminium protection layers were thermally deposited by vacuum evaporation through a mask at a base pressure below 2×10^{-4} Pa. The deposition rate and the thickness of the barium and aluminium layers were monitored by a thickness/rate meter. The cathode area defines the active area of the device. The typical active area of the devices in this study is 0.15 cm^2. The EL layer spin coating process and the device performance tests were carried out within a glovebox with nitrogen circulation. The luminescence of the device was measured with a calibrated photodiode. External quantum efficiency was verified by the measurement of the integrating sphere, and luminescence was calibrated after the encapsulation of devices with UV-curing epoxy and thin cover glass.

Accessory Publication

Experimental procedures and characterization data, ^{1}H NMR and ^{13}C spectra are available in the Accessory Publication on the Journal's website.

Acknowledgement

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