Dendrimers

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Polytriphenylene Dendrimers: A Unique Design for Blue-Light-Emitting Materials**

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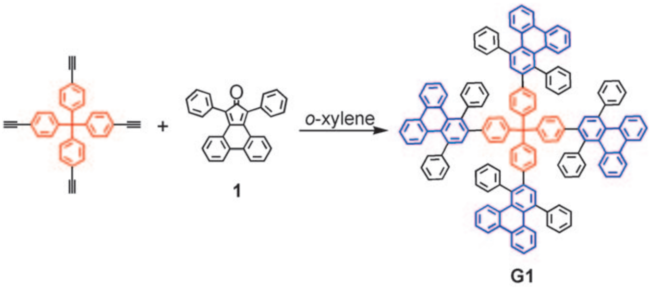
In the past decade, light-emitting dendritic materials have attracted much interest, owing to their application as emissive layers in organic light-emitting diodes (OLEDs).[1] This class of materials allows the advantages of small molecules, such as anthracene, phenanthrene, or pyrene[2] to be combined with those of conjugated polymers, such as polyfluorenes[3] or poly(*para*-phenylene vinylene)s.[4] To date, the most promising design for dendrimer light-emitting-diode (DLED) materials has comprised a fluorescent[5] or a phosphorescent[6] core and a conjugated, but non-emissive, dendron shell to keep the emissive units separated, thus avoiding excimer formation and quenching effects. The utilization of conjugated dendrons facilitates sufficient charge transport, which is a necessary premise for efficient devices. One of the biggest advantages of using dendritic molecules is the variety of possible combinations of cores, dendrons, and surface groups.[7]

The attractive properties of multichromophoric dendrimers[8] suggested a new approach towards blue-light-emitting materials with the following characteristics: a) blue-light emission is brought about by the presence of electronically decoupled polycyclic aromatic hydrocarbon units; b) the units are incorporated into a rigid dendritic polyphenylene scaffold; they thus adopt sterically defined positions and avoid intradendrimer chromophore–chromophore interactions; c) amorphous films are obtained as a result of the lack of intermolecular interactions, and d) the amount of extraneous substituents and coupling units is kept at a minimum.

Triphenylene derivatives have been extensively studied with regard to their discotic liquid crystallinity[9] and optoelectronic applications in OLEDs, field-effect transistors, and photovoltaic cells.[10] However, to date, although a number of triphenylene-based small molecules and polymers have been designed and investigated, the high tendency towards self-association of triphenylene often leads to a dramatic decrease in fluorescence intensity, owing to their strong π–π stacking interactions.[11] To our knowledge, dendrimers based exclusively on interlinked triphenylene units have not been realized, probably as a result of the challenges associated with functionalized triphenylene derivatives serving as branching reagents in dendrimer and hyperbranched polymer synthesis. In this study, triphenylene is incorporated as a building block for the dendritic systems **G1** (Scheme 1), **G2**, and **G3** (Scheme 2). Though bearing a higher risk of intramolecular (triphenylene–triphenylene) chromophore interactions,[12] the use of triphenylene allows for a higher density of emitting units in the active layer. Therefore, the amount of electro-inactive material contained in dendrimer films can be kept at a minimum. Chemical, photophysical, and optoelectronic characterizations show that the new triphenylene-based dendritic materials are promising candidates for blue-light-emitting devices.



Scheme 1. Synthesis of the polytriphenylene dendrimer **G1** (CO is also released during the reaction). The blue sections indicate the triphenylene units which are the blue-emitting chromphores.

The first-generation dendrimer **G1** (Scheme 1), with four triphenylene units, was synthesized by heating the commercially available "phencyclone" **1** and an *o*-xylene solution of tetra(4-ethynylphenyl)methane at reflux in a microwave reactor for 2 h. After the removal of the excess of **1** by repeated precipitation in methanol, the first-generation dendrimer **G1** was recrystallized from a mixture of tetrachloroethane and hexane.

The synthesis of the higher-generation polytriphenylene dendrimers **G2** and **G3** was carried out following a divergent synthetic protocol.[13] The key step is the utilization of a novel AB_2-type compound, that is, diphenylcyclopentaphenanthre-

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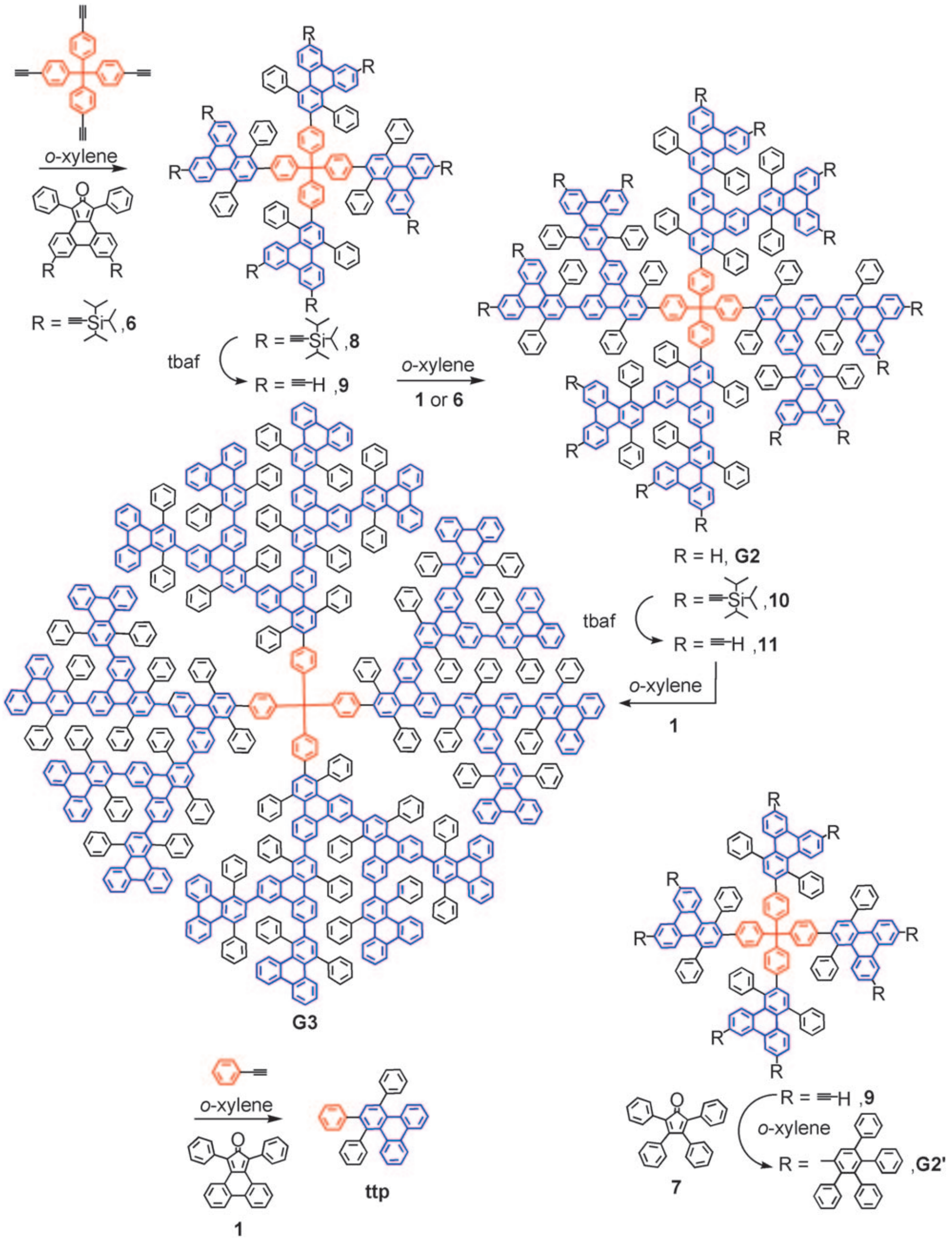
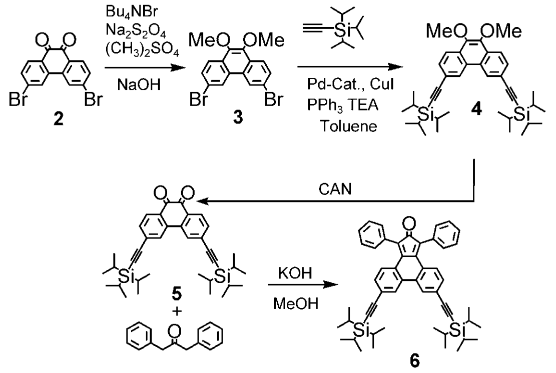


Scheme 2. Synthesis of polytriphenylene dendrimer **G2**, **G3**, **G2′**, and the model compound 1,2,4-triphenyltriphenylene (ttp).

none derivative **6** (Scheme 3), which combines a diene function and two protected ethynyl functions in the same molecule. Compared to the tetraphenylcyclopentadienone derivatives used in the synthesis of known polyphenylene dendrimers,[13] compound **6** contains an additional bond between two neighboring phenyl rings, a Diels–Alder [4+2] reaction leads to triphenylene units. The synthesis of the key intermediate compound **6** began with the reaction of commercially available phenanthrene-9,10-dione with bromine in nitrobenzene, according to standard methods, to give 3,6-dibromophenanthrene-9,10-dione (**2**, Scheme 3), and the subsequent protection of the dione group in **2** by reductive methylation, to form 3,6-dibromo-9,10-dimethoxyphenanthrene (**3**). The bromo groups in compound **3** were then substituted using ethynyltriisopropylsilane under Sonogashira–Hagihara conditions, to afford 9,10-dimethoxy-3,6-bis((triisopropylsilyl)ethynyl)phenanthrene (**4**). Upon oxidation with cerium ammonium nitrate (CAN), the methoxy groups in **4** were cleaved and 3,6-bis((triisopropylsilyl)ethynyl)phenanthrene-9,10-dione (**5**) was obtained. The final step, by Knoevenagel condensation of **5** with 1,3-diphenylacetone, gave the central building block 3,6-bis((triisopropylsilyl)ethynyl)phencyclone **6** (Scheme 3).

Dendrimers **G2**, with 12 triphenylene units, and **G3**, with 28 triphenylene units, were synthesized from building block **6** by Diels–Alder [4+2] addition (Scheme 2). The triisopropylsilyl (tips) groups in dendrimers were deprotected with tetrabutylammonium fluoride (tbaf) and the resulting ethynyl groups were further treated with either building block **1** to obtain **G2**, or with **6**, continuing the divergent synthetic method, to furnish **G3**. For comparison, a model compound 1,2,4-triphenyltriphenylene (ttp; Scheme 2) containing the triphenylene repeating unit, and another polyphenylene derivative, dendrimer **G2′** (Scheme 2) with a pentaphenyl shell, were also prepared by Diels–Alder reactions. The structures of dendrimers **G1**, **G2**, and **G3** were elucidated by NMR spec-



Scheme 3. Synthesis of diphenylcyclopentaphenanthrenone **6**. CAN = cerium ammonium nitrate, TEA = triethylamine.

troscopy and MALDI-TOF mass spectrometry. The MALDI-TOF mass spectra each revealed a single intense signal corresponding to the calculated mass of dendrimers **G1**, **G2**, and **G3** (Figure 1).

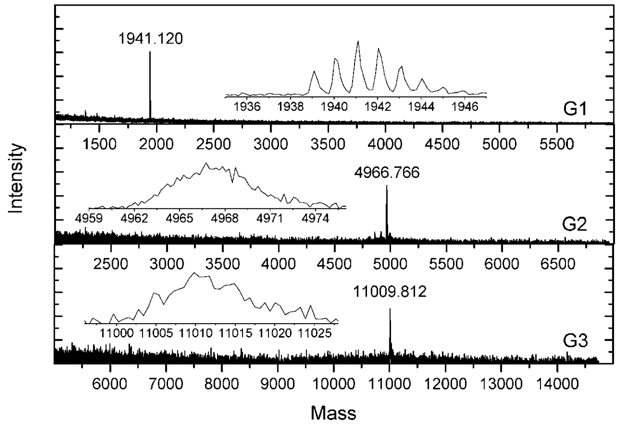


Figure 1. MALDI-Mass spectra for **G1**, **G2**, and **G3**.

To investigate the spatial arrangements of polytriphenylene dendrimers and their optimum tetrahedral geometry, single-crystal X-ray analysis of **G1** was performed to provide the most direct description of the molecular structural features.[14] The single crystal of dendrimer **G1** (see Supporting Information, Figure S1) was obtained as colorless, tiny, needle-shaped crystals, by slow evaporation of a solution in a 1:1 mixture of tetrachloroethane and hexane at room temperature (see Supporting Information, Table S1, monoclinic, cell parameters: $a=17.46$, $b=10.81$, $c=35.86$ Å, and $\beta=91.0°$).[15] In the single crystal, each triphenylene unit is twisted out of the plane, as a result of the attached phenyl rings. Furthermore, the phenyl substitution reduces the π–π stacking tendency. In one molecule, the four triphenylene units are separated by a tetraphenylmethane core, breaking the conjugation. The molecules are packed in such a way that the triphenylene branches of neighboring dendrimers are aligned orthogonal to each other, and the shortest distance between adjacent triphenylene units is 3.73 Å (see Supporting Information, Figure S2). Therefore, the triphenylene units are not in a π-stacked arrangement, which would quench fluorescence.

The dendrimers **G1**–**G3** are readily soluble in common solvents, such as chloroform, toluene, and tetrahydrofuran (THF). Their UV/Vis absorption and photoluminescence (PL) properties were investigated in toluene solutions (10^{-3} g L^{-1}) and spin-coated films (Table 1). Compounds ttp and dendrimer **G1** demonstrate identical absorption and photoluminescence maxima as, since the four ttp units in **G1** are connected through a sp3 carbon, they have the same chromophores (Figure 2a). With the elongation of the longest conjugated oligotriphenylene segments, the absorption and photoluminescence maxima of dendrimers **G2** and **G3** are slightly bathochromically shifted as a consequence of the increasing number of neighboring ttp units on each branch of the molecule, in which some π-orbital overlap occurs between the ttp units. The intermolecular interactions and aggregations of dendrimers **G1**, **G2**, and **G3** were investigated by measuring the absorption and photoluminescence spectra of their toluene solutions at different concentrations. Over three orders of magnitude (10^{-4}, 10^{-3}, and 10^{-2} g L^{-1}) no bathochromic-shift and excimer emissions could be observed (see Supporting Information, Figure S3). This concentration independence suggests that the dendritic branches in each dendrimer effectively suppress the intermolecular interactions and prevent aggregation.[16] Absence of aggregation is also evidenced by the rather high photoluminescence quantum yield (QY) of these dendrimers. With quinine sulfate as a standard,[17] the quantum yields of dendrimers **G1**, **G2**, and **G3** in dilute toluene solutions (10^{-6} M) were measured as 6.6, 27.0, and 35.2 %, respectively. These values reveal an increasing quantum yield scaling with the size of the molecules. This increase could be ascribed to the reduced branch rotation in higher generations which decreases the vibrational relaxation and the intersystem crossing in the excited state. Another plausible explanation for the higher quantum yield in higher generations could invoke the

Table 1: Optical data for dendrimers and model compound.

Sample	λ_{max}^{Abs} [nm] Solution	Thin film	λ_{max}^{PL} [nm] Solution	Thin film	Quantum yield [%][a]
ttp	289	298	401	402	3.8
G1	283	293	400	406	6.6
G2	304	312	414	431	27.0
G3	299	313	424	442	35.2
G2′	312	317	408	418	14.8

[a] relative to quinine sulfate dehydrate.[16]

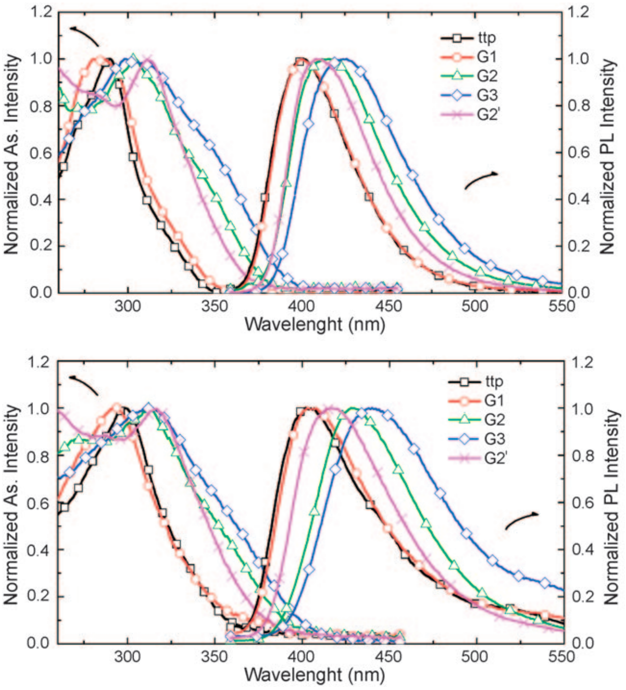


Figure 2. UV/Vis absorption and photoluminescence (PL) spectra ($\lambda_{ex}=300$ nm) of dendrimers and the model compound in toluene solution (a) and in the solid state (b).

interactions between the chromophores and environment: With increasing dendritic generation, the central chromophores in the larger molecules are more effectively shielded, which suppresses interactions among the chromophores themselves or between the chromophores and solvent molecules, which would otherwise result in fluorescence quenching.

Figure 2b shows the absorption and photoluminescence spectra of dendrimers **G1**, **G2**, and **G3** in solid states. In the photoluminescence spectra of ttp and **G1**, bathochromic shifts of 1 nm and 6 nm, respectively, were observed compared to those of the solutions. However, dendrimers **G2** and **G3** display a more pronounced bathochromic shift of 17–18 nm, respectively, compared to their corresponding solution spectra. We attribute this bathochromic shift to the solid-state packing which leads to increased coupling of individual ttp units with increasing generations. It is notable that the absorption happens mainly from $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$,[11,18] because $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ are symmetry forbidden in isolated triphenylene molecules and only unresolved shoulder peaks can be observed around 350 nm for these transitions.[11] The broadening of the high-wavelength flank of absorption peaks could be due to reduced symmetry[19] caused by the nonplanarity, attached phenyl rings, and neighboring triphenylene units, thus increasing the oscillator strength of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions.

The thermal properties of dendrimers **G1**, **G2**, and **G3** were studied by thermogravimetric analysis (TGA, see Supporting Information, Figure S4). In a nitrogen atmosphere, they exhibit degradation above 450 °C, which is similar to other reported polyphenylene dendrimers.[20] The photoluminescence spectra of dendrimers **G2** and **G2′** before and after annealing at 200 °C show no significant changes, even after annealing in air (Figure S5 in the Supporting Information). The above measurements demonstrate the high thermal stability of these dendrimers, making them promising materials for DLEDs.

To test the electroluminescent properties of dendrimers **G2** and **G2′**, DLEDs were fabricated in a standard sandwich geometry using the following configuration: indium tin oxide (ITO)/ poly(styrene sulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS)/**G2** (or **G2′**)/1,3,5-tris(1-phenyl-1H-2-benzimidazolyl)benzene (tpbi)/CsF/Al. To avoid recombination at the chemically unstable cathode interface,[21] tpbi was applied as an additional electron transport and hole-blocking layer.

Figure 3 shows the current–voltage (*I*–*V*) and luminance–voltage (*L*–*V*) characteristics of a DLED with dendrimer **G2** as the emitting layer. The device emitted a sky-blue electroluminescence (EL) with a maximum brightness of 300 cd m^{-2} at a bias voltage of 8 V and corresponding Commission Internationale de L'Eclairage (CIE) coordinates of (0.19, 0.18). The maximum of the electroluminescence spectrum peaked at 430 nm. Both the maximum and the shape of the electroluminescence spectrum are similar to the corresponding photoluminescence spectrum of a **G2** film. Excimer emission from chromophore aggregation and keto-defect emission from oxidative degradation, which were always found for blue LEDs, however, could not be observed in our dendritic system, which indicates that the dendritic branches efficiently suppress the intermolecular interaction. The device displayed an onset of electroluminescence at approximately 6 V and maximum efficiency of 0.4 cd A^{-1}. According to the energy level diagram (see Supporting Information, Figure S6), the rather poor efficiency is most probably attributed to the large electron-injection barrier from CsF (−4.1 eV) to tpbi (−2.8 eV). This large barrier also explains the relatively high turn-on voltage of this device. Therefore, the device efficiency could be improved by choosing appropriate cathodes and electron transporting materials. Investigations into device optimization are underway.

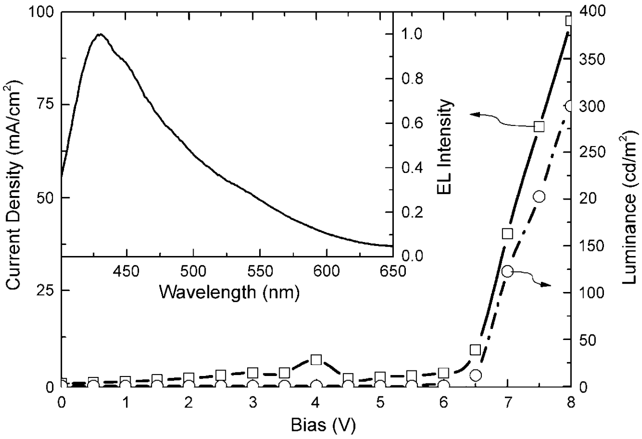


Figure 3. *I*–*V*–*L* characteristics of an ITO/PEDOT:PSS/**G2**/tpbi(10 nm)/CsF/Al device. Inset: normalized electroluminescence (EL) spectrum at 8 V bias.

For comparison, the performance of the DLED based on dendrimer **G2′** was measured under identical conditions (see Supporting Information, Figure S7). The normalized electroluminescence spectrum resembles the thin film photoluminescence spectrum very well and is located in a deeper blue region than **G2** with a maximum at 415 nm and corresponding CIE coordinates of (0.17, 0.10). At 10 V driving voltage, a maximum luminance of 400 cd m^{-2} was found with an efficiency of 0.1 cd A^{-1}. Compared to **G2**, this lower efficiency is mainly due to the relatively lower quantum yield found for photoluminescence (Table 1). Another possibility may be that a significant part of the electroluminescence spectrum of **G2′**, that from the pentaphenyl shell, is in the UV region and therefore does not contribute to the luminance value.

Overall it becomes clear that the performance of the presented devices can compete with the best reported fluorescence-based blue-emitting DLEDs with respect to device efficiency and brightness,[1,22] which also holds true for a comparison with fluorescent blue-light-emitting polymeric devices based on poly(*para*-phenylene)-type polymers.[23] Utilizing transport moieties in the outer shell of the dendrimer and tuning of the emission color more from the UV to the blue region, both strategies that are successfully implemented in PLED materials,[23] will further allow for improvement of device performance in fluorescence-based blue-emitting DLEDs.

In conclusion, we have synthesized a series of blue light-emitting dendrimers by a unique procedure. The synthesis of polytriphenylene dendrimers starting from AB_2-type building blocks is not catalyst driven and gives essentially quantitative yield. Most importantly, the twisted triphenylene units not only function as chromophores, but also effectively prevent inter- or intramolecular fluorescence quenching, as demonstrated by the increase in photoluminescence quantum yield with increasing generation. These dendrimers exhibit stable and pure-blue emission in both photoluminescence and electroluminescence spectra and could provide an avenue for dendritic emitters with the optimized electroluminescence efficiency/color purity compromise needed for pure blue light, which is still a great challenge in the field of blue emitters.

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