

Large Rigid Blue-Emitting π -Conjugated Stilbenoid-Based Dendrimers: Synthesis and Properties

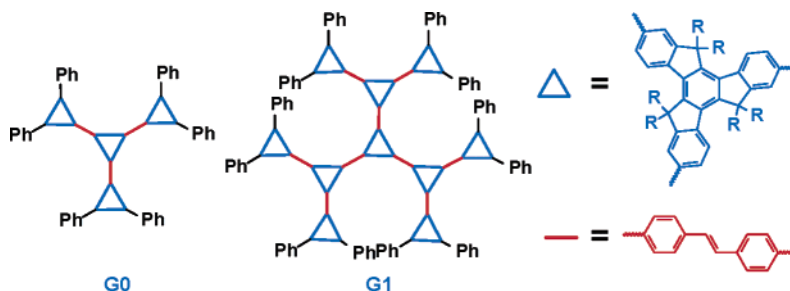
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ABSTRACT



Two large π -conjugated dendrimers (G0 and G1) employing the stilbenoid moiety as the bridge unit have been developed through the Suzuki and the Horner–Wadsworth–Emmons reactions. The molecular weight of G1 is 10 973 Da. Both G0 and G1 have good fluorescence quantum yields and exhibit similar absorption and emission behaviors in solutions and in thin films. They emit strong blue fluorescence in films under the irradiation of UV light.

In the past few decades, π -conjugated dendrimers with an intrinsic stiff nature have attracted considerable interest due to their potential applications in optoelectronic devices.^{1,2} In comparison with well-known linear semiconducting oligomers and polymers, π -conjugated dendritic systems with large branching building blocks can exhibit intrinsic two- or three-dimensional architectures, which bring new electri-

cal, optical, and morphological properties to the system. Such large dendritic structures also efficiently improve the film formation ability of the desired materials. They have become one of the most promising prospects among π -conjugated materials, and have been applied as the active materials in electronic and photoelectronic devices.¹ Therefore, to develop new conjugated dendrimers can further allow us to gain a deep insight into the photophysical properties and possibly the supramolecular structure of conjugated systems.^{1a–c}

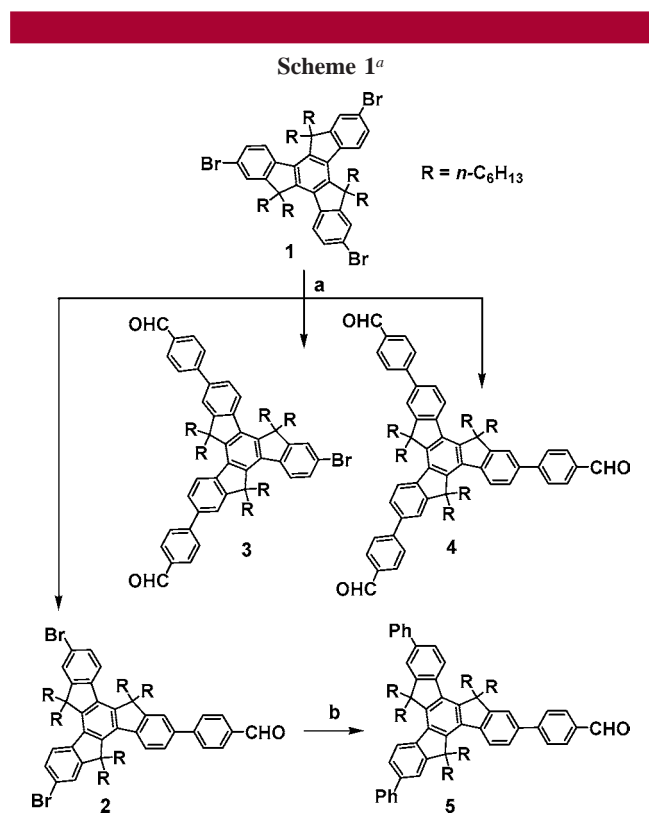
Stilbenoid-based compounds have been synthesized by various methods, and the interesting photochemical and

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photophysical properties have been studied comprehensively.^{2,3} Herein, we present the synthesis of π -conjugated dendrimers **G0** and **G1**, each constructed with stilbenoid spacers via a convergent synthetic route. In our previous contribution, we reported the synthesis and photophysical properties of a family of π -conjugated dendrimers based on truxene and thienylethynylene units, which exhibited potential as light harvesting materials for optoelectronic devices.⁴ Our focus is now on the stilbenoid framework owing to its structural similarity to the *p*-phenylene vinylene moiety as well as the interesting photochemical and photophysical properties of stilbenoid compounds and their applications in material science.^{2,3,5} As a result, we make use of the stilbenoid unit as the bridge to connect the trifunctional truxene and finally obtain the blue-emitting π -conjugated dendrimers. It is envisioned that this new family of dendritic architectures will be helpful in understanding the structure–property relationship within such rigid structures by investigating their physical and chemical properties.

Scheme 1 outlines the synthetic approach to the basic



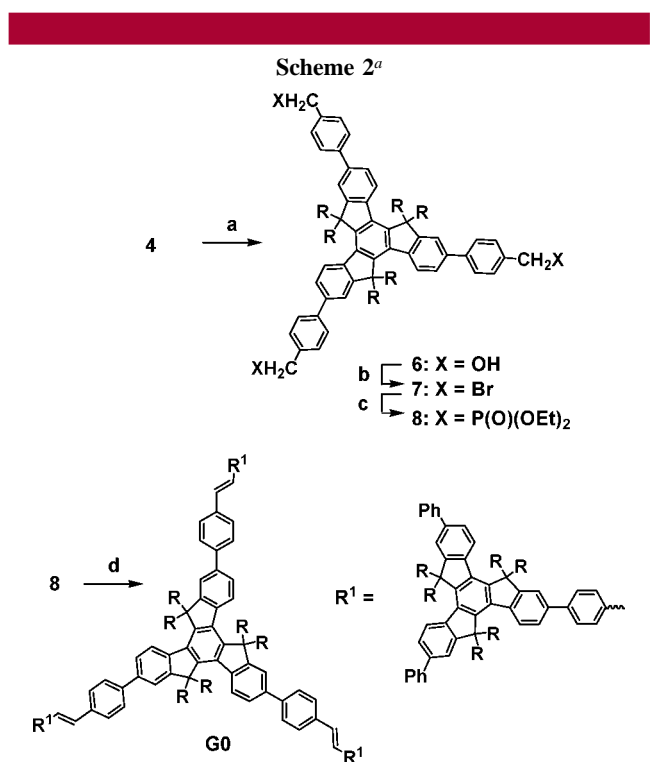
^a Reagents and conditions: (a) 4-formylphenylboronic acid, Pd(PPh₃)₄, 2 M Na₂CO₃, THF, reflux, **2** (34%), **3** (23%), **4** (9%); (b) phenylboronic acid, Pd(PPh₃)₄, 2 M Na₂CO₃, THF, reflux, 92%.

building blocks of the desired dendrimers. A Suzuki cross-coupling of readily prepared **16** with 4-formylphenylboronic acid in the presence of Pd(PPh₃)₄ afforded aldehydes **2**, **3**,

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and **4** in one pot.⁷ We easily separated these three compounds by column chromatography due to their different polarity. The subsequent Suzuki cross-coupling reaction between **2** and phenylboronic acid gave phenyl-terminating monoaldehyde **5** in 92% yield.

As shown in Scheme 2, a reduction of trialdehyde **4** with



^a Reagents and conditions: (a) LiAlH₄, Et₂O, reflux, 90%; (b) PBr₃, Et₂O, rt, 95%; (c) P(OEt)₃, 150 °C, 92%; (d) KO^tBu, **5**, THF, –78 °C to rt, 62%.

LiAlH₄ in refluxing ethyl ether produced triol **6** in high yield. The bromination of **6** with phosphorus tribromide afforded **7** as a white solid in 95% yield. However, it was observed that **7** partially hydrolyzed while we removed excess PBr₃ with ice–water.⁸ We thus employed methanol to remove the excess PBr₃ to prevent such hydrolysis. Bromide **7** was then reacted with triethyl phosphite in a solvent-free system to produce the Horner reagent **8**. Meanwhile, a reduction of dialdehyde **3** formed diol **9** and further bromination gave dibromide **10**, which also reacted with triethyl phosphite to afford another Horner reagent **11** (in Scheme 3).

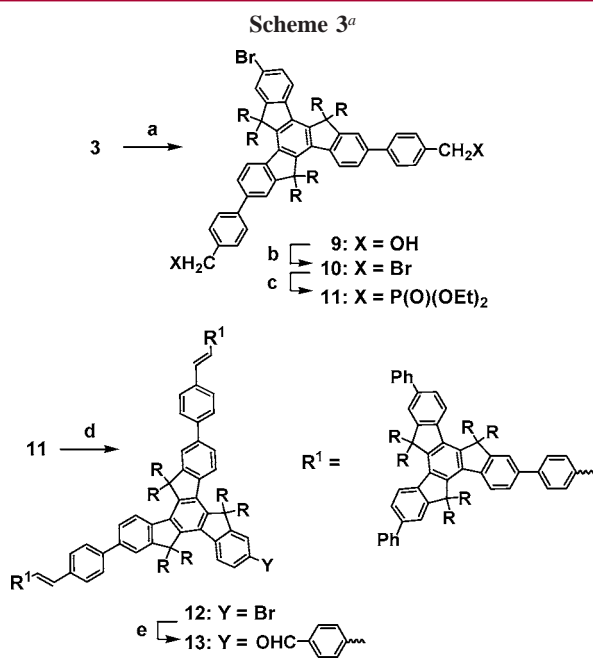
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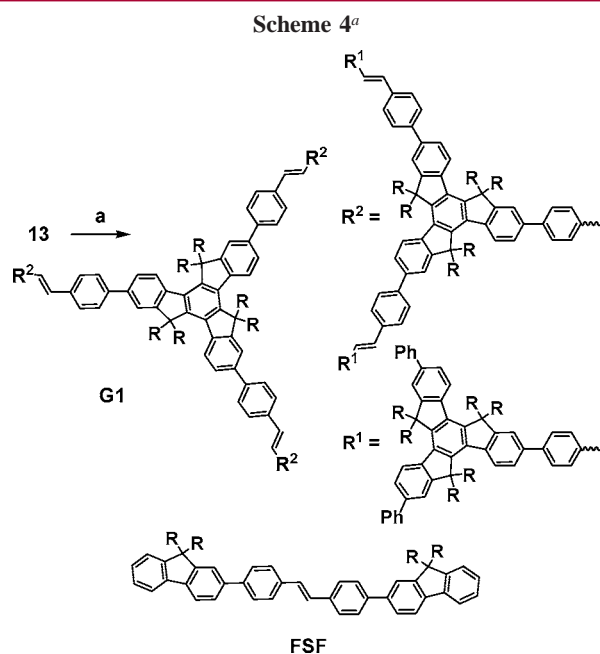
^a Reagents and conditions: (a) LiAlH₄, Et₂O, reflux, 91%; (b) PBr₃, Et₂O, rt, 94%; (c) P(OEt)₃, 150 °C, 89%; (d) KO^tBu, **5**, THF, -78 °C to rt, 65%; (e) 4-formylphenylboronic acid, Pd(PPh₃)₄, THF, reflux, 90%.

As shown in Scheme 2, the Horner–Wadsworth–Emmons (HWE)^{2e,9} reaction between **8** and trialdehyde **5** in the presence of KO^tBu afforded the stilbenoid linkages to produce **G0**. Meanwhile, we also employed the HWE reaction between **11** and **5** to produce dendron **12**. The Suzuki coupling of dendron **12** with 4-formylphenylboronic acid with catalyst Pd(PPh₃)₄ gave a new precursor of the HWE reaction, aldehyde **13**, which reacted with **8** to afford **G1** as illustrated in Scheme 4. Considering the rigidity and steric hindrance within these large molecules, the yields of **G0** and **G1** were satisfying. Therefore, we developed a convergent strategy to construct the desired dendrimers **G0** and **G1** via the Suzuki coupling and HWE reactions. For comparison, we also prepared the model compound **FSF** as illustrated in Scheme 4 (see the Supporting Information for its synthesis).

Dendrimers **G0** and **G1** were readily soluble in common organic solvents, such as CH₂Cl₂, CHCl₃, and THF, which allowed us to conveniently obtain their ¹H and ¹³C NMR spectra, MALDI-TOF MS, and GPC characterization data to verify the structure and the purity of dendrimers (see the Supporting Information). From their NMR spectra, we also observed that the double bonds predominately exist as the *E*-isomer at room temperature. **G1** contains up to 10 truxene moieties, and its molecular weight is 10 973 Da, which was confirmed by the MALDI-TOF MS.

For their photophysical properties, the absorption and the photoluminescent (PL) spectra of **G0**, **G1**, and **FSF** both in

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^a Reagents and conditions: (a) KO^tBu, **8**, THF, -78 °C to rt, 53%.

dilute toluene solutions and in thin films were recorded. The concentration of all compounds in toluene solutions was ca. 1.0×10^{-6} M. The photophysical properties of **G0**, **G1**, and

Table 1. Photophysical Properties of **FSF**, **G0**, and **G1**

compds	$\lambda_{\text{abs}}/\text{nm}$		$\lambda_{\text{em}}/\text{nm}$	
	sol	Φ_F	films	sol
FSF	363	0.99	364	414, 440
G0	330, 372	0.99	332, 378	423, 448
G1	331, 376	0.98	332, 374	424, 448

FSF are summarized in Table 1. Figure 1 illustrates the absorption and PL spectra of **G0**, **G1**, and **FSF** in dilute

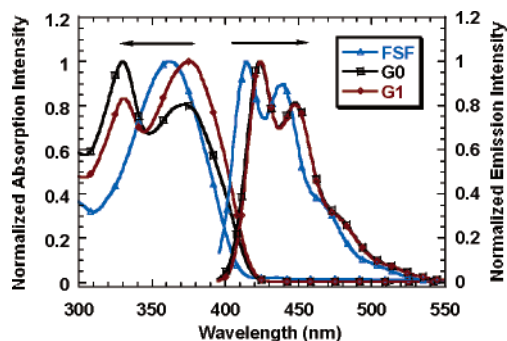


Figure 1. Normalized absorption and emission spectra of **G0** and **G1** in dilute toluene solutions. Emission spectra were obtained upon excitation at the absorption maximum.

toluene solutions. For the UV–vis absorption spectrum in toluene solution, **G0** displayed two absorption peaks at 330 and 378 nm, which were ascribed to the absorption of the peripheral phenyl-functionalized truxene skeleton and the stilbene-modified truxene unit, respectively.¹⁰ A red shift in the absorption maximum of **G0** was observed in comparison with the parent stilbenoid dendrimers ($\lambda_{\text{max}} = 329 \text{ nm}$)^{2e} and **FSF** ($\lambda_{\text{max}} = 363 \text{ nm}$), which was indicative of enhanced effective conjugation length. For our stilbenoid dendrimers, the absorption λ_{max} values were similar to those of some oligo- and poly(*p*-phenylenevinylene) derivatives (about 370–380 nm).¹¹ It was also observed that **G1** exhibited similar behaviors to **G0**. Nonetheless, the intensity of the peak at about 331 nm decreased in comparison with that of **G0**; correspondingly, the relative number of phenyl-functionalized truxene moieties in **G1** was also reduced. These UV–vis spectroscopy results showed that there was no obvious π – π^* delocalization with the increase of the generation of dendrimers. These results also demonstrated that the effective conjugation length did not significantly improve with the increasing generation of the dendrimers. For the emission spectra in dilute solutions, **G0** and **G1** also displayed similar behaviors. Two strong emission bands in the visible region were observed for both **G0** and **G1**, both of which red-shifted about 10 nm compared to those of **FSF**. The fluorescence quantum yields (Φ_{F}) of **G0** and **G1** in dilute toluene solution were 0.99 and 0.98, respectively, using 9,10-diphenylanthracene as the standard.¹²

Figure 2 outlines the absorption and emission spectra of **G0**, **G1**, and **FSF** in the solid films. The absorption behaviors of **G0**, **G1**, and **FSF** in solid films were quite similar to those in solution. This reflected that no obvious interchain and/or intermolecular aggregation of both dendrimers was formed in ground states due to large branches and lots of alkyl groups. These results also demonstrated that good amorphous states of both dendrimers were formed, which was very important for applicants in optical and electronic devices such as OLEDs. The emission spectra of **G0**, **G1**, and **FSF** in the solid films also showed slight red-shift (about 10–20 nm) in comparison with those in solution, which could be due to the geometrical change of the molecules in solid films. These three compounds showed the same emission behaviors in

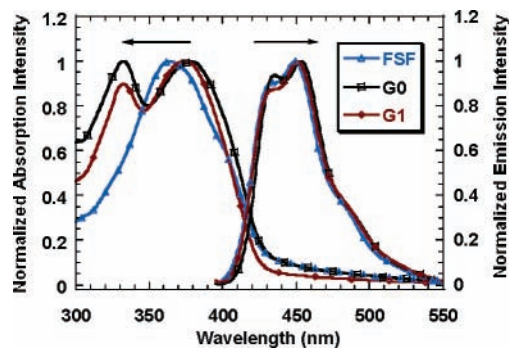


Figure 2. Normalized absorption and emission spectra of **G0** and **G1** in thin films. Emission spectra were obtained upon excitation at the absorption maximum.

the thin films. These films emitted bright blue light under the irradiation of UV light.

In conclusion, we design and synthesize **stilbenoid-containing** π -conjugated dendrimers **G0** and **G1** by employing powerful reactions including the Suzuki coupling and the Horner–Wadsworth–Emmons reactions. The convergent methodology, which has been widely used to prepare functional dendrimers, is used here to construct these structures. The synthetic route described herein is practical for synthesizing such blue-emitting dendrimers with large size, and provides a suitable platform for accessing a wide range of chemical structures of dendrimers with properties appropriate for incorporation in electronic and optoelectronic devices. The similar absorption behaviors of **G0** and **G1** in thin films demonstrate that both dendrimers form amorphous states. Both dendrimers could be good candidates as blue-light emitting materials for OLEDs. Further experiments of the devices fabrication are in progress.

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Supporting Information Available: Experimental procedures and ¹H and ¹³C NMR data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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