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# Nanosized Gradient $\pi$-Conjugated Thienylethynylene Dendrimers for Light Harvesting: Synthesis and Properties

**Jin-Liang Wang, Jia Luo, Liang-Hui Liu, Qi-Feng Zhou, Yuguo Ma,* and Jian Pei***

*The Key Laboratory of Bioorganic Chemistry and Molecular Engineering and the Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China*

*jianpei@pku.edu.cn; ygma@pku.edu.cn*

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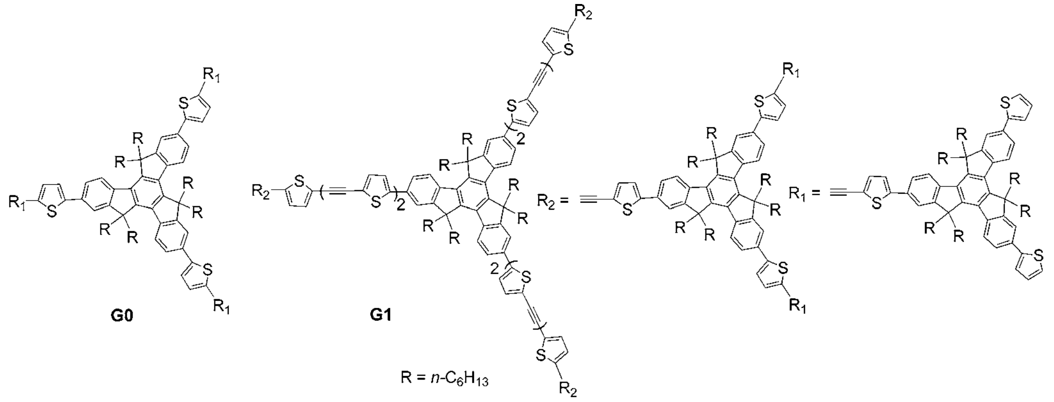
## ABSTRACT



**A family of $\pi$-conjugated dendrimers based on truxene and thienylethynylene units are synthesized via a mixed divergent/convergent growth approach. These dendrimers possess an intrinsic energy gradient from the periphery to the core through branches and thus show a broad absorption in the UV–vis range and an efficient energy transfer to the lower-energy center. The molecules hence have the potential to be used as light harvesting materials.**

In recent years, $\pi$-conjugated dendrimers have been extensively studied because of their unusual molecular structures and the potential of acting as the active chemical components in a wide range of electronic and optoelectronic devices.[1,2] In particular, the unique features of conjugated dendrimers have made them attractive candidates as new synthetic light harvesting materials. The convergent surface-to-core structure and the stepwise synthetic protocol of dendrimers offer the

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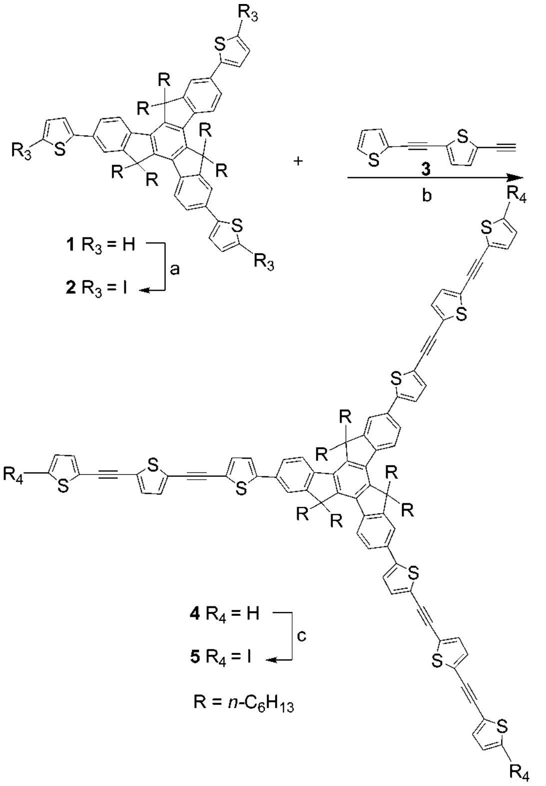
opportunity for fine tuning of the electronic properties of each generation so that an energy gradient may be built into the dendrimer structure. Thereby, a directional energy flow from the peripheral branches to the core may be realized. Indeed, several examples of conjugated dendrimers and/or dendrons acting as an energy funnel for light harvesting have been reported by Moore et al.[3−5] Tour and co-workers demonstrated the incorporation of triple bonds in linear oligo(thienylethynylene)s and studied their applications in electronic devices as "molecular wires".[6] Yet, so far few dendrimers containing thienylethynylene units have been reported, possibly because of the difficulty in synthesizing such molecules with well-controlled structures.

In this communication, we present an efficient preparation of novel dendrimers **G0** and **G1**, which contain building block **1** as the branching moiety joining oligo(thienylethynylene) units of different lengths. The photophysical properties of these dendrimers are also investigated. Our design is to establish a gradient in the length of the thienylethynylene units from the dendrimer periphery to the core. The longer oligo(thienylethynylene)s near the core of the dendrimer not only allow the energy to be funneled inward but also entail a greater void at the molecule interior and reduce congestion around building block **1** at higher generation. Considering the large number of steps required in the synthesis, we achieved these dendrimers via a mixed divergent/convergent growth approach based on the large building blocks obtained through either divergent or convergent synthetic methods. In our syntheses, two protocols, the Sonogashira and Wittig, followed by a dehydrohalogenation reaction, were alternatively utilized to construct the carbon−carbon triple bond. These dendritic compounds exhibit good solubility in common organic solvents. The relationships of their structures and properties have been investigated. Unusually broad absorptions were observed, rendering these dendrimers good candidates as antenna molecules for light harvesting.

Schemes 1 and 2 illustrate the synthetic approaches to the branches and the core. Thiophene-functionalized truxene **1**[7] was easily converted to compound **2** by treatment with NIS.[8] A Sonogashira coupling of **2** with **3**[9] catalyzed by Pd(0) afforded compound **4**. A deprotonation of **4** by LDA at a low temperature followed by its reaction with iodine produced the corresponding triiodo compound **5** in 76% yield.[10] A Wittig reaction between **6**[11] and bromomethylenetriphenylphosphorane followed by further treatment with potassium *tert*-butoxide afforded **7** having a monoterminal acetylene in 72% yield.[12] Compound **8** was obtained by reacting aldehyde **6** with NIS. The Sonogashira reaction between **7** and **8** produced **9** in 87% yield. The desired product **9**, which was significantly more polar due to the presence of the aldehyde group, can easily be separated by column chromatography from the homocoupling byproduct. Compound **9** was then converted to alkyne **10** through the Wittig reaction.

The final steps to **G0** and **G1** are outlined in Scheme 3. To suppress the undesired homodimerization, the more reactive catalyst, $Pd_2(dba)_3$, was employed in the final Sonogashira reaction.[3a,b] It is noteworthy that the final

**Scheme 1.** Synthesis of the Core of Dendrimers



Reagents and conditions: (a) NIS, $CH_2Cl_2$, AcOH, 0 °C, 2 h, 92%. (b) $Pd_2(dba)_3$, CuI, $PPh_3$, $Et_3N$, 40 °C, 10 h, 87%. (c) i) LDA, -78 °C,1 h. ii) $I_2$, -78 °C to rt, 76%.

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[11] The structure of compound **6** was verified by $^1H$, $^{13}C$ NMR, MS, and elemental analysis. The procedure to make **6** is described in another publication. Wang, J.-L.; Duan, X.-F.; Jiang, B.; Gan, L.-B.; Pei, J.; He, C.; Li, Y.-F. *J. Org. Chem.* **2006**, in press.

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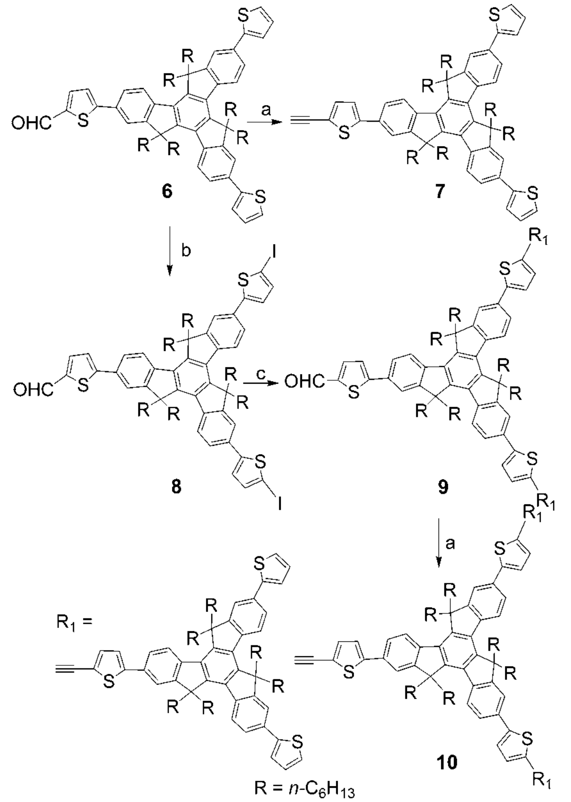
**Scheme 2.** Synthesis of Branches of the Dendrimers



Reagents and conditions: (a) i) $Br_2CH_2PPh_3$, $KO^tBu$, -78 °C, 1 h. ii) $KO^tBu$,-78 °C,1 h, 72% for **7**, 71% for **10.** (b) NIS, $CH_2Cl_2$/AcOH, 0 °C, 2 h, 98% (c) $Pd_2(dba)_3$, **7**, CuI, $PPh_3$, $Et_3N$, 40 °C, 10 h, 87%.

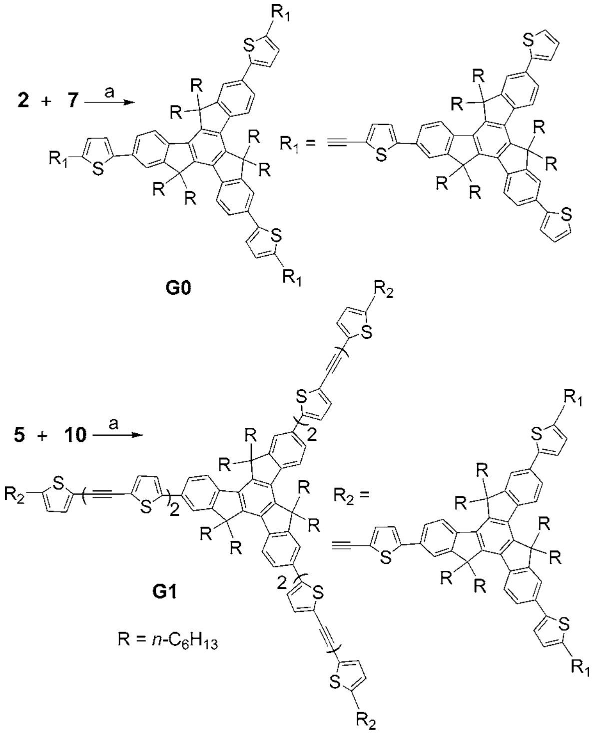
Sonogashira couplings afforded **G0** and **G1** in excellent yields (90% and 82%, respectively), which were quite satisfying for the preparation of such large dendrimers. Thus, owing to the stiff nature of the truxene unit, a rapid growth in the size of these dendrimers was efficiently achieved by such a double-stage divergent/convergent growth approach.

As we anticipated, all compounds were readily soluble in common organic solvents. All new compounds were fully characterized, and their structures were verified by $^1$H and $^{13}$C NMR, elemental analysis, as well as MALDI-TOF MS. $^1$H NMR spectra of the dendrimers became complicated with the increasing generation, but **G1** does possess the correct ratio of aliphatic and aromatic protons in agreement with the expected dendritic structure (see the Supporting Information).

The photophysical properties of all dendrons and dendrimers were first examined in dilute THF solution (ca. $10^{-6}$ M) as shown in Figure 1. Then, thin films used for UV−vis and fluorescence measurements were obtained by spin coating toluene solution (ca. 10 mg/mL) onto quartz plates at 1000 rpm. All compounds exhibited excellent film-forming properties. Photophysical data from both the solutions and thin films are summarized in Table S1 (see the Supporting Information).

The absorption spectra of the core unit **1**, dendrons **7** and **10**, and dendrimers **G0** and **G1** exhibited a peak at about 343 nm owing to the same moiety, the thiophene-functionalized truxene chromophore.[7] The absorption of **4** exhibited a maximum peak at 398 nm with a minor shoulder peak at 343 nm. Another absorption peak was observed for **G0**, **10**,

**Scheme 3.** Synthesis of **G0** and **G1**



Reagents and conditions: (a) $Pd_2(dba)_3$, CuI, $PPh_3$, $Et_3N$, 40 °C,10 h, 90% for **G0**, 82% for **G1**.

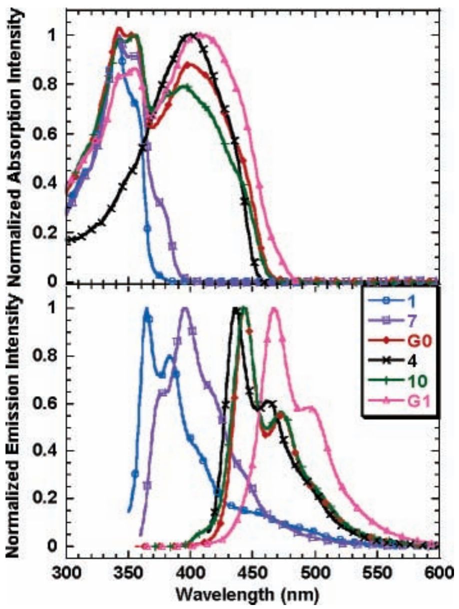


**Figure 1.** Absorbance (top) and emission (bottom) spectra of the dendrimers in THF solution at room temperature.

and **G1** at 398, 395, and 410 nm, respectively. We observed that the effective conjugation length was enhanced with the increasing dendrimer size because longer chromophores were incorporated. In addition, this family of dendrimers covered a much broader absorption range than meta-linked dendrimers.[3] Especially in the case of **G1**, the absorbance ranged from 250 to 490 nm. The molar extinction coefficient of **G1** was $2.7 \times 10^8$ $M^{-1}$ $cm^{-1}$, which was higher than those of other dendrimers.[3,4] It suggests a potentially significant improvement in the energy utilization efficiency if our dendrimers are used in the light harvesting application. The excitation spectra of both dendrimers were also similar to their absorption ones (see the Supporting Information).

The emission behaviors of all compounds showed well-defined vibronic structures. As shown in Figure 1, the maximum emission wavelengths for **G0** and **G1** are 444 and 468 nm, respectively. A red shift of the fluorescence emission maximum was observed for **G1**. As shown in Figure 2, regardless of the various excitation wavelengths (343, 355, and 398 nm), nearly identical emission maxima and behaviors were found for **G0**. A complete overlap was observed between the absorption of **G0** and the emission of its corresponding donor unit **1**, which may suggest an efficient intramolecular energy transfer within molecule **G0**. As also shown in Figure 2, the same phenomena were also observed for **G1**. All emission behaviors of the dendrimers were independent of the excitation wavelengths. These results further demonstrated that our dendrimers may be promising candidates as light harvesting materials for optoelectronics devices.

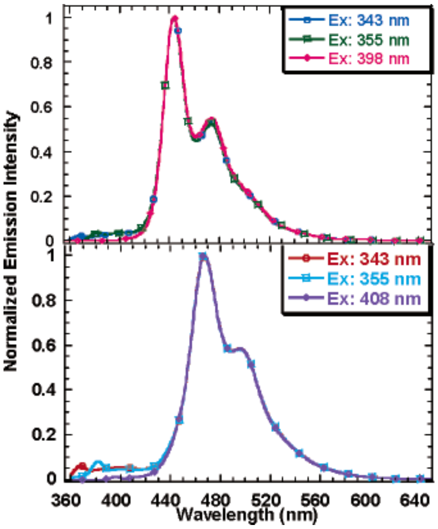


**Figure 2.** Emission spectra of **G0** (top) and **G1** (bottom) recorded at varied excitation wavelengths in THF solution at room temperature.

We also investigated the behaviors of absorption and emission of our dendrimer in thin films (see the Supporting Information). We observed that their absorption spectra in films were nearly identical with those in solution, without showing a significant red shift, which implied that intermolecular interaction in the ground states might be suppressed in films, possibly because of such large sizes of the molecules with multiple hexyl substituents and truxene moieties. However, their emission spectra in film states became very broad and featureless, and the maximum peaks were red shifted by 33 nm for **G0** and by 23 nm for **G1**, respectively, in comparison with those in dilute solutions, which indicated that the excimer for **G0** and **G1** was formed in the excited states. Moreover, we also found that more efficient energy transfer in films was exhibited due to both the intermolecular and the intramolecular energy transfer.

In conclusion, the synthetic strategy outlined herein represents a double-stage divergent/convergent growth approach without any protection−deprotection chemistry, and it was used to construct novel gradient dendrimers **G0** and **G1**. These two dendritic structures contain up to four and ten thiophene-functionalized truxenes, respectively, with an increase in the length of thienylethynylene spacers with generation. They were achieved with full control over the molecular architecture by a sequence of coupling reactions, leading to expanded, rigid structures. The photophysical properties of these dendrimers, characterized by very broad absorptions and efficient intermolecular and/or intramolecular energy transfer, make them promising light harvesting materials.

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**Supporting Information Available:** Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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