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Synthesis of Giant Rigid π-Conjugated Dendrimers

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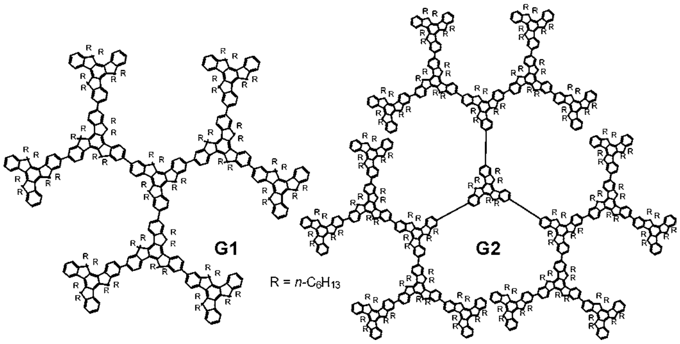
ABSTRACT



A novel family of giant π-conjugated dendrimers (G0, G1, and G2) solely constructed by 5,5,10,10,15,15-hexahexyltruxene units has been developed in a convergent manner through a Suzuki cross-coupling reaction. The overall yields to such large rigid conjugated dendrimers are quite satisfying. The structures and purity of these nanosize rigid dendrimers are verified by ^{1}H and ^{13}C NMR, MALDI-TOF MS, and elemental analysis.

In the past decades, the design and synthesis of π-conjugated dendrimers have been explored extensively because of their unusual molecular structures and their potential applications as active chemical components in a wide range of electronic and optoelectronic devices.[1] In comparison with linear π-conjugated oligomers and polymers,[2] such rigid dendritic systems with large branching building blocks exhibit intrinsic two- or three-dimensional architectures, which bring them new electrical, photophysical, and morphological properties.[1i]

Therefore, development of new, large π-conjugated dendrimers can allow us to further expand their potential applications in the plastic electronic field.

In our previous contributions, we reported the synthesis and photophysical properties of several π-conjugated dendrimers based on truxene units, which exhibited good properties as active materials for optoelectronic devices including organic light-emitting diodes (OLEDs).[3] Herein, we design and develop a novel family of π-conjugated dendrimers (**G0**, **G1**, and **G2**) constructed solely with 5,5,10,10,15,15-hexahexyltruxene units. A Suzuki cross-coupling reaction is employed to construct such giant dendrimers with large steric hindrance. The numbers of the 5,5,10,10,15,15-

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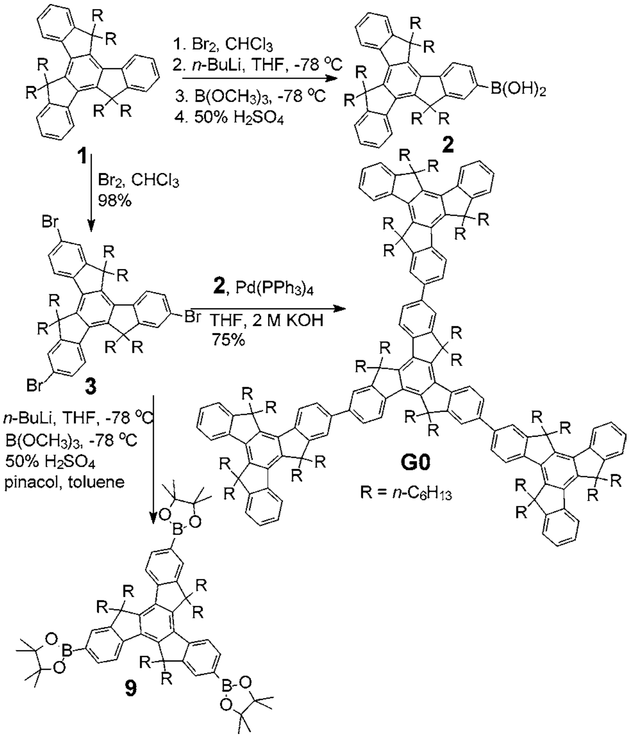
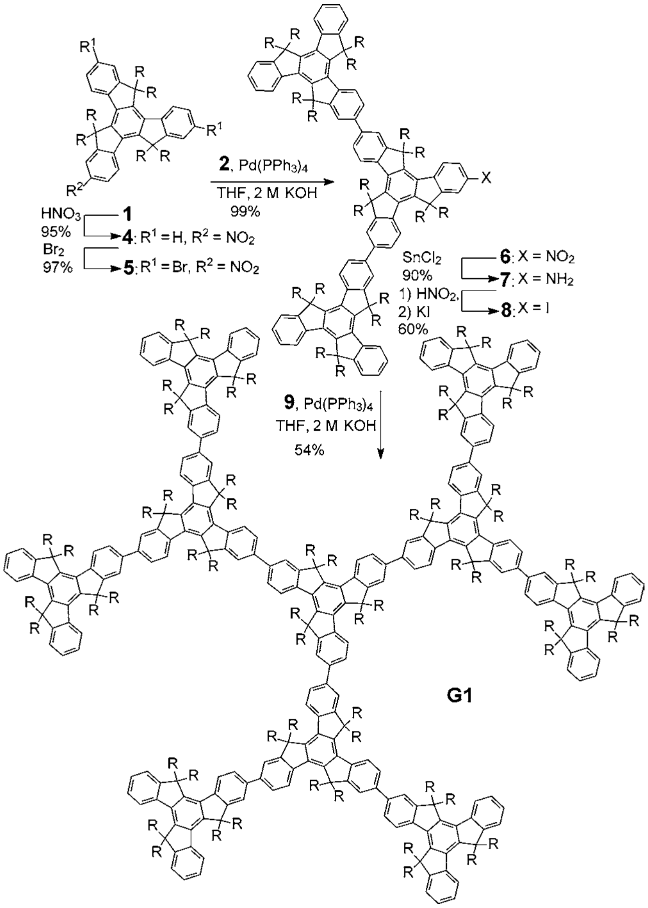
hexahexyltruxene units in the structures of **G0**, **G1**, and **G2** are 4, 10, and 22, respectively. According to molecular modeling, the diameter of **G2** is about 7.9 nm with molecular weights up to 18600 Da.

Scheme 1



Scheme 2



Scheme 1 illustrates the synthetic route to the zeroth generation dendrimer **G0**. Following our previous reaction sequences,[4] a brominated derivative of 5,5,10,10,15,15-hexahexyltruxene **1** was lithiated using *n*-BuLi followed by quenching with trimethyl borate and then acidic hydrolysis to afford boronic acid **2**. Full bromination of **1** afforded tribromide **3** in 98% yield.[4] Originally, Na_2CO_3 or K_3PO_4 was used as base to promote a Suzuki cross-coupling of **2** and **3** with large steric hindrance. However, since bulky coupling dendrons became less reactive,[5] the Suzuki reaction gave very low yield (<20%). Then, a strong base, KOH, was used instead to promote the Suzuki coupling reaction to afford **G0** in 75% yield. From this observation, KOH was employed to conduct the subsequent Suzuki cross-coupling reactions in this contribution.

A convergent strategy to synthesize **G1** is outlined in Scheme 2. One of the important steps is to synthesize AB_2-type intermediates, such as **8** and **13** (Scheme 4) in this contribution. Trimethylsilyl (TMS-) was usually used as a protection group during the preparation of conjugated dendrimers based on phenyl units.[6] However, in our case, the nitro group was chosen as a substitution group, which could be easily converted to halogen groups via a reaction sequence of its reduction and a Sandmeyer reaction. Compound **1** was nitrated in 1,2-dichloroethane (DCE) under mild and efficient conditions to afford **4** after about 5 min. Further bromination of **4** formed key intermediate **5** in 97% yield. A Suzuki cross-coupling reaction of **5** with boronic acid **2** afforded **6** in an excellent yield (99%). Such a high yield was attributed to the electron-withdrawing effect of the nitro group. Reduction of **6** with $SnCl_2$ produced amine **7** in 90% yield. Since amine **7** was insoluble in aqueous media, which was commonly used in a Sandmeyer procedure,[7] very low conversion was afforded. Finally, we overcame this problem by dispersing amine **7** in silica, and then it reacted with HNO_2 in aqueous media followed by treatment with KI to form iodide **8** in 60% yield. Triboronate **9** (Scheme 1) was obtained starting with **3** through procedures similar to those for the preparation of **2**.[4] It is well-known that triboronic acids are readily subjected to dimerization and cyclic trimerization by loss of water to form anhydrides and boroxines.[8] These side reac-

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tions brought difficulties for purification and characterization of desired products. To overcome this obstacle, pure triboronic ester **9** was obtained through the esterification of the crude boronic acid with pinacol in toluene, and the total yield over four steps was 41% (as shown in Scheme 1). Subsequently, another Suzuki coupling reaction between dendron **8** and triboronate ester **9** ended the synthesis of dendrimer **G1** in 54% yield.

Toward the synthesis of **G2**, another important intermediate boronate **10** was prepared from **5** as shown in Scheme 3. The synthesis of arylboronates developed by Miyaura[9] provides a facile access to boronic acid derivatives in the presence of sensitive functionalities such as nitro groups in **5**. Unfortunately, no desired arylboronate **10** was obtained according to the typical Miyaura procedure (entry 1). After failure to promote this reaction by using other Pd catalysts,[10] we tried to employ ligand PPh_3 with Pd catalysts (entries 2−5, Table 1); no conversion was observed. Prolonged heating resulted in an insignificant change in the reaction mixture. The replacement of PPh_3 by PCy_3 (Cy = cyclohexyl) afforded such arylboronate formation.[11] Consequently, under catalyst system $Pd_2(dba)_3/PCy_3$, the conversion was about 20% (entry 8). Finally, catalyst system $Pd(OAc)_2/PCy_3$ was employed to afford arylboronate **10** in 70% yield (entry 9). Moreover, no symmetric biaryl was observed accompanied by the formation of arylboronate **10** in the reaction mixture.

Scheme 3

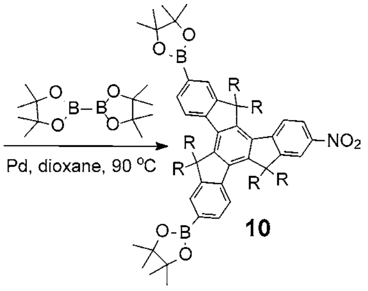
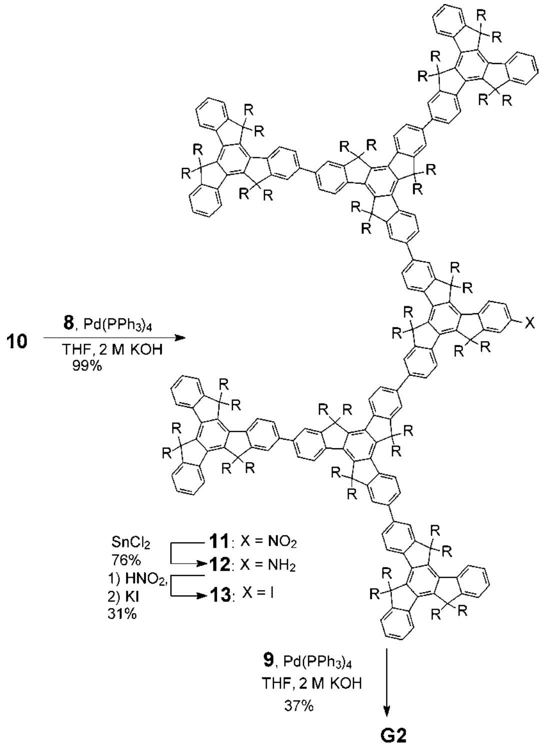


Table 1. Arylboronate Formation under Various Conditions

entry	catalyst	ligand	isolated yield (%)
1	$PdCl_2(dppf)$		0
2	$PdCl_2(dppf)$	PPh_3	0
3	$Pd(PPh_3)_4$	PPh_3	0
4	$Pd_2(dba)_3$	PPh_3	0
5	$Pd(OAc)_2$	PPh_3	0
6	$PdCl_2(dppf)$	PCy_3	5
7	$Pd(PPh_3)_4$	PCy_3	5
8	$Pd_2(dba)_3$	PCy_3	20
9	$Pd(OAc)_2$	PCy_3	70

Scheme 4



Scheme 4 illustrates the synthetic approach to **G2**. A Suzuki coupling reaction between iodide **8** and diboronate **10** gave **11** in 77% yield. The reaction sequence converting the nitro group to iodide substituents was employed again to produce **13** in 24% overall yield. The final Suzuki cross-coupling reaction between iodide **13** and triboronate **9** using KOH afforded giant dendrimer **G2** in 37% yield. Considering the rigidity and steric hindrance within the large molecule **G2**, the yield was satisfying. Therefore, we developed a convergent strategy to construct the desired dendrimers **G0**, **G1**, and **G2** via the Suzuki coupling reactions.

Three dendrimers **G0**, **G1**, and **G2** are readily soluble in hexane, chloroform, THF, which facilitates the final characterization and confirmation of their structures and purity. Almost identical characteristics of their ^1H and ^{13}C NMR spectra proved that the protons and carbons of three generation dendrimers have similar chemical environments, which is consistent with their structural similarity (see the Supporting Information). Gel permeation chromatography (GPC) data exhibited a stepwise decrease of elution time as the generation grew (Figure 1). A narrow polydispersity index (PDI = 1.02−1.05) was observed, indicating their purity. Figure 2 illustrates MALDI-TOF MS spectra of **G0**, **G1**, and **G2**. The signal assigned to molecular ions in MALDI-TOF MS directly verified the presence of the desired

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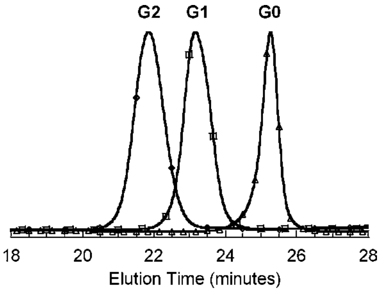

Figure 1. GPC traces of **G0**, **G1**, and **G2** in THF.

dendrimers. Furthermore, their MALDI-TOF MS behaviors also demonstrated that no structural defects were found in the desired dendrimers **G0**, **G1**, and **G2**. For **G0**, the clear molecular ion signal peaked at 3383.4 Da (calcd m/z 3383.5); moreover, other two signals corresponding to fragments $[M - C_6H_{13}]^+$ (calcd m/z 3298.3, found m/z 3298.3) and $[M - C_6H_{12} + Li]^+$ (calcd m/z 3306.3, found m/z 3306.0) were observed. For **G1**, the predominant MALDI-TOF MS signal exhibited at 8453.7 Da (calcd m/z 8455.8) for the molecular ion. MALDI-TOF analysis of **G2** exhibited five peaks, which corresponded to the molecular ion (calcd m/z 18600, found m/z 18594) and other fragments assigned to the removal of one to four 5,5,10,10,15,15-hexahexyltruxene units, respectively. Such agreement of ^{1}H and ^{13}C NMR, GPC, and MALDI-TOF results, associated with elemental analysis, unambiguously proved the structures and purity of three generation dendrimers, **G0**, **G1**, and **G2** (see the Supporting Information).

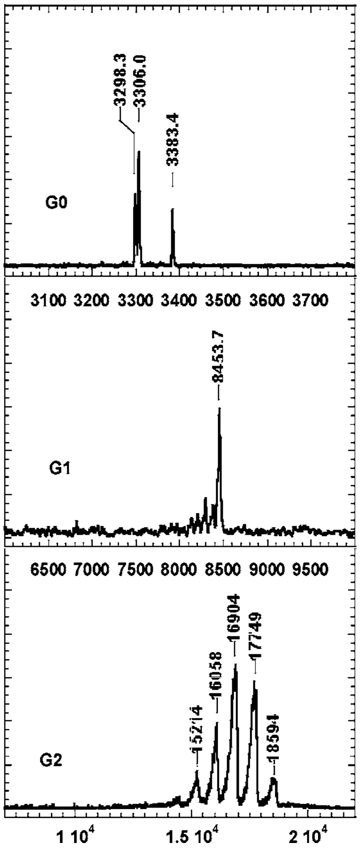

Figure 2. MALDI-TOF MS of **G0**, **G1**, and **G2**.

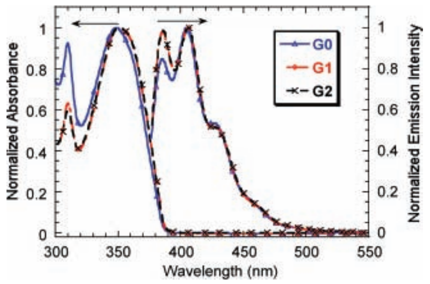

Figure 3. Absorption and emission spectra of **G0**, **G1**, and **G2** in toluene solutions (10^{-6} M). Emission spectra were recorded upon excitation at absorption maximum.

Figure 3 illustrates the photophysical behaviors of dendrimers **G0**, **G1**, and **G2** in dilute toluene solutions (10^{-6} M). From the absorption spectra, besides characteristic absorbance of the $\pi-\pi^*$ electron absorption band of the truxene unit at 310 nm, three dendrimers showed the same absorption λ_{max} at around 350 nm. They also exhibited similar emission spectra with two main peaks at about 386, 405 nm and a shoulder at 430 nm. Similar photophysical behaviors of three generation dendrimers implied that the effective conjugation length did not improve as the generation increased.

In summary, three giant π-conjugated dendrimers (**G0**, **G1**, and **G2**) built from 5,5,10,10,15,15-hexahexyltruxene units have been designed and successfully synthesized in a convergent strategy. The Suzuki cross-coupling provides a facile approach in constructing such giant dendrimers with large steric hindrance. The reaction conditions of the Miyaura arylboronates are also investigated to obtain large arylboronates with sensitive functionalities in a good yield. According to molecular modeling, the diameters are 3.6 nm for **G0**, 5.6 nm for **G1**, and 7.9 nm for **G2**, respectively. The three dendrimers show similar UV−vis and photoluminescent properties in dilute solution, indicating their similar effective conjugation length.

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

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