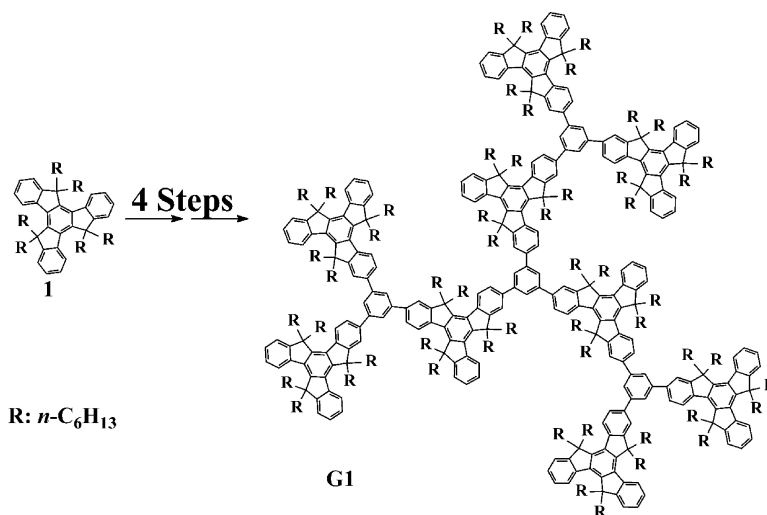


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Extended π -Conjugated Dendrimers Based on Truxene

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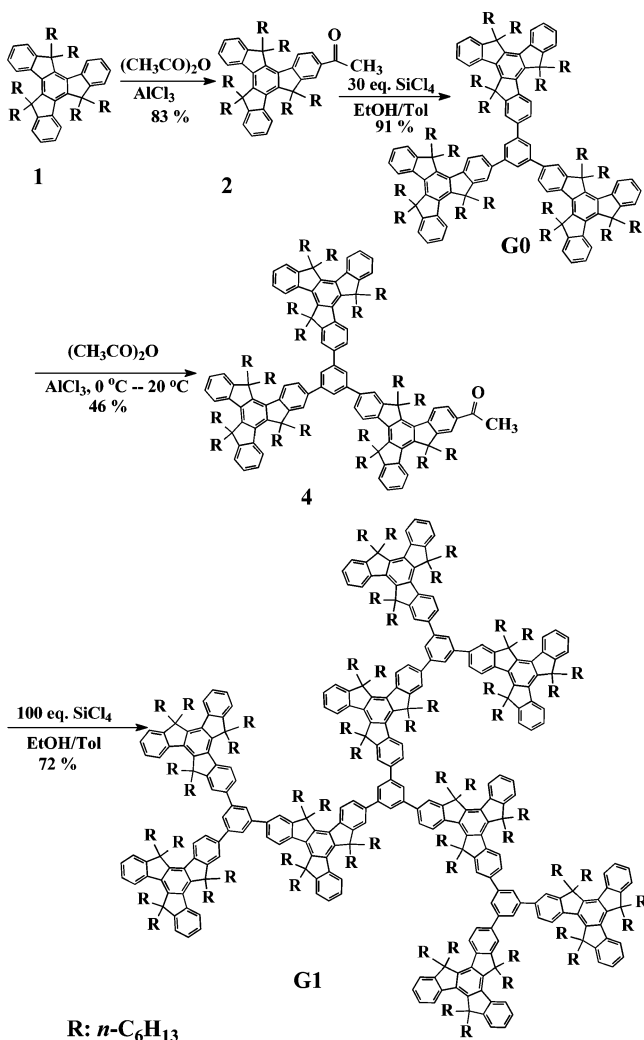
In the last two decades, there has been a dramatic expansion in the field of dendrimers as a consequence of their fascinating structures and unique properties.¹ Control of three distinct architectural regions of these treelike dendrimers (the central core, the interior building blocks, and the chain ends) associated with variations in the synthetic approach (the convergent and the divergent) gives tailor-made dendrimers with predetermined properties.² A substantial amount of the earlier work has focused on dendrimers with flexible cores and interiors which significantly affect the overall shapes. By contrast, a few types of π -conjugated dendrimers with rigid structures have been reported.³ These shape-persistent molecules with well-defined nanometer sizes and intrinsic rigidity have proved to exhibit interesting physical and chemical properties.⁴ However, the building blocks of such dendrimers are generally five- or six-member ring aromatics. To the best of our knowledge, there have never been any reports on π -conjugated dendrimers based on polyarene units, although the creation of such a regulated nanoscale assembly around functional polycyclic aromatics might provide unique properties. Unraveling the poor solubility and the large steric hindrance has already become a major challenge for the synthesis of such types of dendrimers.

Truxene, a heptacyclic polyarene, has been explored as a starting material for the construction of larger polyarenes and bowl-shaped fragments of fullerenes, liquid crystals, and C₃ tripods materials in asymmetric catalysis and chiral recognition.⁵ The truxene moiety by virtue of its unique three-dimensional topology is an attractive building motif for use as a potential dendrimer building block via readily available functionalization at C-2, -7, -12 positions and at C-5, -10, -15 positions, respectively.

In this Communication, we report the preparation of a novel dendrimer **G1** containing up to nine truxene moieties with good yields. Along with good solubility and intermediate molecular size (5 nm), we also investigate truxene and dendrimers (**G0** and **G1**) to indicate that the torsion angle between the benzene ring and truxene skeleton might play a key role in determining optical and physical properties.

The approach to **G1** is illustrated in Scheme 1. The synthetic strategy for the preparation of **G1** involved the initial preparation of compound **1**.^{5c} The introduction of hexahexyl groups greatly enhanced the solubility of truxene moiety. The Friedel–Crafts acetylation reactions carried out smoothly under classical procedures afforded **2** with a good yield (83%). However, the subsequent cyclotrimerizations met severe difficulties due to the steric hindrance of the giant truxene moiety. The initial attempts to obtain **G0** by SiCl₄–ethanol⁶ led to unfavorable results, giving either no desired products or poor yields as shown in Table S1. It is noteworthy that the reactions catalyzed by TiCl₄ were the most powerful strategy to convert **2** into **G1** molecule (almost quantitative!). Unfortunately, we failed to exclude dark black impurities from our products by all methods used. We observed that increasing the amount of SiCl₄ from 20 to 30 equiv dramatically improved the yield (from 23% to

Scheme 1



91%). The relatively low yield (46%) in the subsequent Friedel–Crafts acetylation reactions to **4** could be attributed to the relatively poor π -electron conjugation among the truxene moiety and the benzene core, which produced large amounts of side products (di-, tri-, and tetraacetylation of **G0**). Because the more steric hindrance existed in **4**, we successfully increased the amount of SiCl₄ to ensure complete conversion to **G1**. Considering the rigid nature and the severe steric hindrance of **4**, the yield (72%) was quite remarkable. The cyclotrimerization reactions were relatively clean, and only a few side products were formed in addition to our desired products. Up to now, this represents the first time that such a large and precisely defined macromolecule ($M_w = 7908$ for **G1**) has been successfully prepared by four steps from **1**. Molecular modeling indicated that the **G1** molecule spans 5.0 nm in its planar

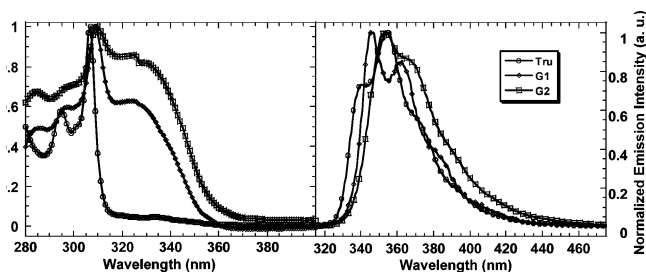


Figure 1. Absorption (left) and emission (right) spectra for dendrimers in THF solutions.

conformation. Although the rigidity and aromaticity was similar to that of the iptycene-based dendrimer,⁷ the strategy for constructing our dendrimers was much more efficient, while our dendrimers exhibited larger molecular weights, higher conjugation, and thus potential new properties.

All new compounds have been fully characterized by a variety of spectroscopic techniques. Not only did we obtain appropriated ¹H and ¹³C NMR and analytical data, we but also employed MALDI-TOF/MS measurements to characterize the precise structure, the molecular weight, and the purity of all new compounds (**2** and **4**) and the dendrimers (**G0** and **G1**). The results are summarized in Table S2 and in Figure S1.

The absorption and emission spectra for **1**, **G0**, and **G1** in THF solutions are shown in Figure 1. Normally, π -conjugated dendrimers show a very strong π - π^* electron absorption band in the UV-visible region, which progressively red-shifts with an increase of the effective conjugation length. From absorption spectra in Figure 1, we observed that absorption λ_{max} (309 nm for **G0** and 310 nm for **G1**, respectively) exhibited a small red-shift with the increase of the truxene moiety and of the generation of the dendrimer in comparison with that of **1** (307 nm). However, absorption spectra showed very strong shoulder peaks at 320 nm for **G0** and 330 nm for **G1**, respectively, while the intensity of such peak of **G1** was higher than that of **G0**. We also observed that onsets of absorption spectra were obviously red-shifted from **1** to **G1**. The absorption λ_{max} for these compounds might belong to the π - π^* electron absorption band of the truxene skeleton, and we did not observe the very obvious π - π^* delocalization with the increase of the truxene moiety, which was because of the large torsion angle between the benzene ring and the truxene system caused by three giant truxene skeletons at one smaller benzene ring. However, the intensity of shoulder peaks augmented from **G0** to **G1**, which suggested that the relative delocalization might be promoted by an increase of the generation of dendrimers.

In conclusion, we have presented a facile approach, which allows facile purification of trimerized products to prepare large-size and precisely well-defined dendrimers via “in-situ” generation of the benzene core. The largest two-generation π -conjugated dendrimers containing up to nine truxene moieties are afforded through the repetitive Friedel-Crafts acetylation and acid-promoted cyclotrimerization reactions with good yields from truxene using a four-step procedure. Investigation of the cyclotrimerization reactions promoted by acids provides us with a convenient approach to the various dendrimers utilizing the benzene ring as the core. The photo properties of such dendrimers indicate that the large torsion angle between the giant truxene moiety and the benzene ring might affect full π -delocalization of the whole molecule. To the best of our knowledge, our dendrimers based on the giant truxene skeleton

might be out of the largest π -conjugated systems known. We have developed a platform to synthesize a new family of dendrimers utilizing giant polycyclic aromatics and to understand the photo-physical properties of polycyclic dendrimers through the investigation of such dendrimers.

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Supporting Information Available: Experimental procedures and all characterization data of new compounds **2–8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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