Dendrimers

DOI: 10.1002/anie.200600063

Palladium-Catalyzed Convergent Synthesis and Properties of Conjugated Dendrimers Based on Triarylethene Branching**

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Dendrimers are molecular architectures that offer an enormous opportunity for creating new functional materials.[1] Their highly branched, globular architectures give rise to a number of interesting properties that contrast with those of linear polymers. Although a number of dendrimers exist that are based on various core and branching units, the development of new core and branching units should pave the way for a generation of new functional materials.[1] In particular, the evolution of novel and effective π-branching units is necessary in the emerging field of π-conjugated dendrimers,[2–6] because most of the branches of known π-conjugated dendrimers are based on benzene structures with 1,3,5-linkages, which considerably interrupt any interbranch π conjugation.

Triggered by the tremendous progress in the field of stilbenoid compounds, and in particular the oligophenylenevinylenes,[7] the development of electroactive and light-emitting stilbenoid dendrimers is of great interest to many researchers. However, all the stilbenoid dendrimers reported to date are based on 1,3,5-benzene branching and thereby suffer from disrupted interbranch conjugation (Figure 1).[8]

Over the last few years, we have explored the chemistry of extended π systems based on highly substituted C=C cores (i.e., triarylethene- and tetraarylethene-based extended π systems) which has involved methodological challenges associated with selective synthesis and the potential application of these compounds as functional materials.[9] We

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[**] This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. K.T. is a recipient of the JSPS Predoctoral Fellowships for Young Scientists. We thank Dr. Atsushi Wakamiya and Professor Shigehiro Yamaguchi (Nagoya University) for valuable discussions.

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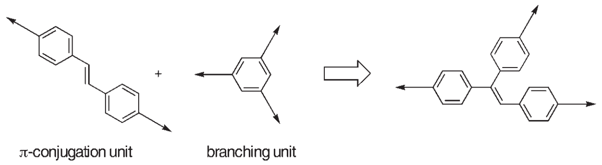


Figure 1. Triarylethene (right) as a π-conjugated branching unit for conjugated dendrimers.

envisaged that a strategic modification of our triarylethene synthesis would lead to the generation of novel conjugated dendrimers that incorporate the triarylethene structure as a new π-conjugated branching unit (Figure 1). We expected such dendrimers to be different from previous stilbenoid dendrimers with respect to their properties, which reflect the effective delocalization of the π electrons as well as their unique structure. Herein, we describe the convergent synthesis of novel triarylethene-based conjugated dendrimers using palladium-catalyzed iterative triarylation of vinylboronate esters. The results of preliminary examinations of the photophysical properties of the dendrimers are also described.

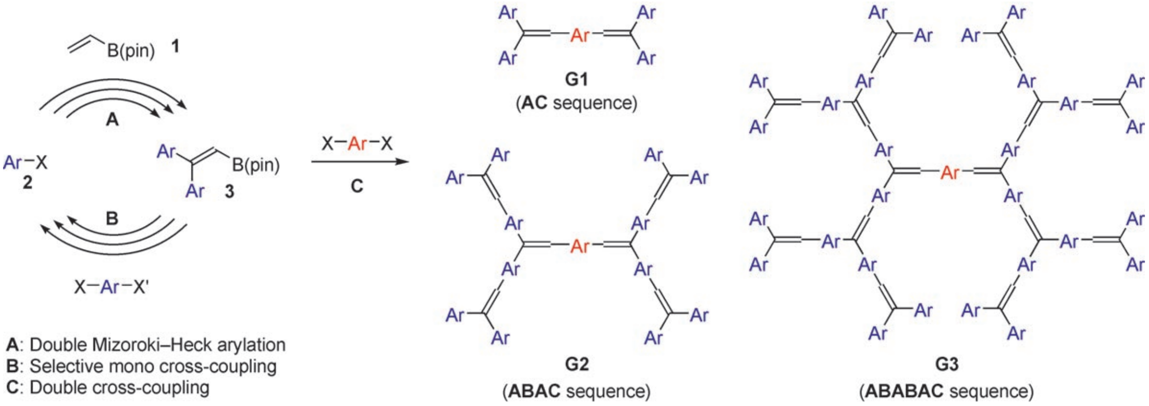
We previously reported the rapid synthesis of triarylethenes using a catalytic one-pot triarylation on the C=C core of vinylboronate pinacol ester CH_2=CHB(pin) (**1**).[10] Under the influence of a Pd catalyst and an amine, **1** undergoes a double Mizoroki–Heck-type arylation[11,12] with two equivalents of aryl halides to generate β,β-diarylated vinylboronates Ar_2C=CHB(pin). The subsequent Suzuki–Miyaura coupling[13] of the resultant boronates with aryl halides rapidly affords triarylethenes Ar_2C=CHAr.[10] We envisaged that a convergent synthesis of triarylethene-based dendrimers would be possible by using these aryl-assembling reactions (i.e., double C–H arylation and C–B arylation) with the strategic use of di- and trifunctional aryl units (aryl dihalides and trihalides). Our strategy that employs aryl dihalides is shown in Scheme 1.

The treatment of vinylboronate **1** with two equivalents of aryl halides **2** in the presence of a Pd catalyst and amine afforded β,β-diarylated vinylboronates **3** (step A, a double Mizoroki–Heck arylation).[10] Although the subsequent double cross-coupling of **3** with aryl dihalides produced the 2:1 coupling adduct **G1**, the selective mono-cross-coupling at either of the Ar–X bonds of the aryl dihalides produced the 1:1 coupling adduct with unreacted Ar–X (step B, selective mono-cross-coupling). This simple sequence allowed us to quickly prepare π-extended aryl halides **2**. Thus, the repetition of the sequence of steps A and B resulted in the production of highly π-extended alkenylboronates **3**. In each cycle, the boronates **3** were doubly cross-coupled with aryl dihalides (step C, double cross-coupling) to produce triarylethene-based dendrimers **G*n*** (where *n* is the generation number) in a convergent manner. The power of this synthetic strategy is apparent, as all of these dendrimers are prepared from common reagents using standard reactions.

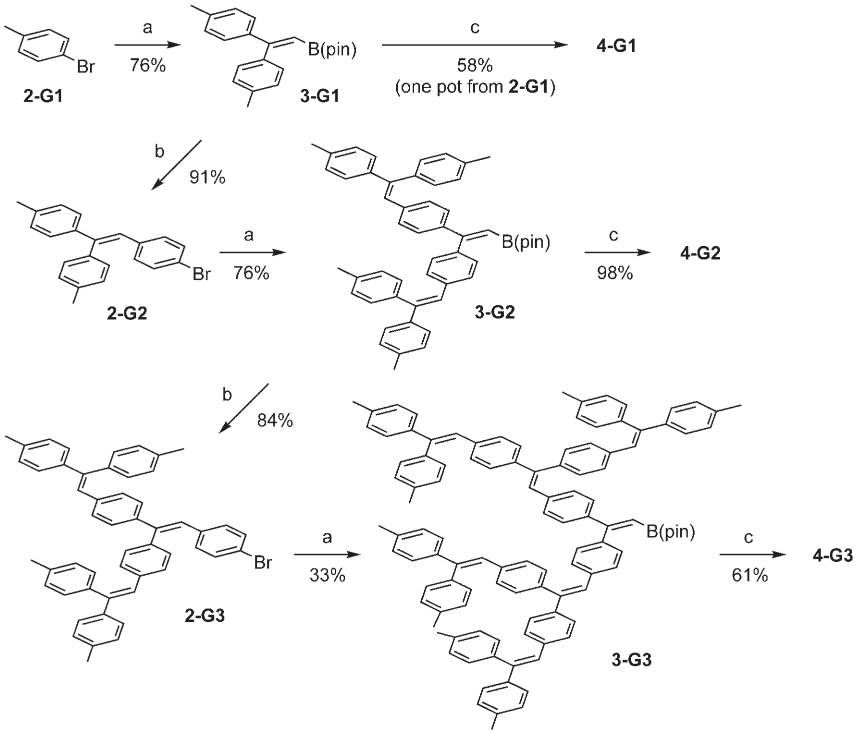
A representative synthesis of **4-G*n*** ($n = 1$–3) dendrimers, which include triphenylethene branching units, is shown in Scheme 2. The use of the highly active [Pd($PtBu_3$)$_2$] catalyst[14] in combination with $i$$Pr_2$NH was useful in the double Mizoroki–Heck arylation (step A in Scheme 1). These conditions were particularly effective for the selective arylation of C–H over C–B, which is otherwise favorable (Suzuki–Miyaura coupling). For selective mono-cross-coupling reactions (step B in Scheme 1), the use of 1-bromo-4-iodobenzene as the aryl dihalide under the catalytic influence of moderately active [Pd(PPh_3)$_4$] was effective. When a highly active catalyst such as [Pd($PtBu_3$)$_2$] was used, then double cross-coupling often took place to afford **4-G1** (see Figure 2) in high yields. Therefore, we used [Pd(PPh_3)$_4$] for mono-cross-coupling reactions (step B) and [Pd($PtBu_3$)$_2$] for the final double cross-coupling reactions (step C).[15] Gratifyingly, the third generation dendrimer **4-G3** was obtained in reasonable overall yield upon repeating these reactions.

When the double cross-coupling reactions (step C, Scheme 1) were performed at earlier stages, such as, with **3-G1** and **3-G2**, then lower generation dendrimers **4-G1** and **4-G2**, respectively, were obtained in good yields (Scheme 2). The application of various core units in the final double cross-coupling rapidly afforded various conjugated dendrimers in a convergent manner (Figure 2). When Mizoroki–Heck arylations (step A) were conducted in a mono fashion, then dendrimers with fewer branches, such as **12**, were easily prepared. Such dendrimers are useful for elucidating the effect of branching of the dendrimers on their properties.

Our strategy could be extended to the synthesis of conjugated dendrimers with mixed branching units by



Scheme 1. Convergent synthesis of triarylethene-based conjugated dendrimers. pin = pinacolyl.



Scheme 2. Synthesis of triarylethene-based dendrimers **4-G*n*** ($n = 1$–3). a) **1**, [Pd(P*t*Bu$_3$)$_2$], *i*Pr$_2$NH, toluene, 80°C; b) 1-bromo-4-iodobenzene, [Pd(PPh$_3$)$_4$], aq. Cs$_2$CO$_3$, toluene, 90°C; c) 1,4-diiodobenzene, [Pd(P*t*Bu$_3$)$_2$], NaOH, H$_2$O, toluene, 90°C.

simply applying aryl trihalides in place of the aryl dihalides in the reaction scheme described in Scheme 1. For example, when 1,3,5-tribromobenzene was used as a trifunctional unit, then the highly branched dendrimer **13**, which contains triphenylethene and benzene branching units (Figure 2), was obtained in high yield (Scheme 3).

Most of the dendrimers prepared were soluble in common organic solvents and, thus, allowed us to characterize them using standard methods such as ^{1}H NMR and ^{13}C NMR spectroscopy and high-resolution FAB mass spectrometry (HRMS). In many cases, the methyl groups at the surface of the dendrimers were well distinguished (although not fully) in the ^{1}H and ^{13}C NMR spectra. In addition, analysis of the samples by gel permeation chromatography showed that all the dendrimers were monodispersed, as would be expected from their well-ordered construction.

Interestingly, many of the conjugated dendrimers prepared emitted fluorescence in both solution and the solid state. The photophysical properties (UV/Vis and fluorescence) of these conjugated dendrimers in chloroform are listed in Table 1. As expected, the wavelength of the emission maximum (λ_{em}) increases with increasing dendrimer generation (i.e., λ_{em}(**4-G3**) > λ_{em}(**4-G2**) > λ_{em}(**4-G1**)) and is ascribed to the extension of the π conjugation. We also found that the quantum yield of fluorescence (Φ_F) also increased with increasing dendrimer generation (Φ_F(**4-G1**) = 0.024, Φ_F(**4-G2**) = 0.58, Φ_F(**4-G3**) = 0.62). Note the 24-fold increase from **4-G1** to **4-G2**. Such a dramatic effect of the dendrimer generation in the color and efficiency of the fluorescence emission has not been reported for 1,3,5-benzene-branched stilbenoid dendrimers. We believe that the enhanced emission of the higher generation dendrimers is attributable to their unique structure. Owing to the sterically congested environment, the higher dendrimers such as **4-G2** probably adopt a nonplanar structure, which reduces the probability of effective intermolecular fluorescence-quenching interactions and molecular motions that may trigger radiationless transitions, thereby enhancing the overall fluorescence efficiency.[16]

To examine the effect of branching on the properties of these dendrimers, the less-branched dendrimer **12** was prepared as a reference for **4-G2**. As the absorption and emission maxima and emission color of **12** are similar to those of **4-G2**, it is reasonable to assume that the extent of the π conjugation seen in **4-G2** is already established in the substructure **12** and that the remaining four *p*-tolyl branches in **4-G2** contribute to its enhanced fluorescence efficiency (Φ_F(**12**) = 0.32 vs Φ_F(**4-G2**) = 0.58).

Moreover, the solubility of these π systems was found to generally increase as the degree of branching increases. For example, the solubility of **4-G2** in chloroform (61.4 mM) and benzene (63.8 mM), as saturated solutions, is 6–10 times higher than that of **12** in the same solvents (11.3 and 6.7 mM, respectively). The increased solubility of **4-G2** is also thought to be attributable to its unique nonplanar structure, which reduces intermolecular interactions and thereby facilitates solvation. The current focus of research into oligophenylenevinylenes and stilbenoid dendrimers lies in enhancing their solubility and processability while preserving the planarity and rigidity of the phenylenevinylene unit, which is responsible for their unique functional properties. Therefore, the exploitation of π branching as observed in our work may be a useful approach toward this goal.

The photophysical properties of the dendrimers were found to depend significantly on the nature of the core structure. For example, the second generation dendrimers based on 1,2- and 1,3-benzene cores (**5** and **6**) emitted blue light with a low efficiency, which was significantly different to the yellow light emitted by **4-G2** with $\Phi_F = 0.58$. The low emissions of the "half-dendrimer" **7** and dendrimer **8** with a nonconjugated core also support the importance of the core structure with regard to the fluorescence properties. Such "core-tuning" is also useful in the generation of materials with interesting properties. For example, the second generation dendrimer **9** with a fluorene core emitted yellow light with an extremely high quantum yield ($\Phi_F = 0.82$). The finding of a hydrocarbon that strongly emits yellow light is of great interest. Moreover, the replacement of the above core structure with bithiophene to give **10** and fluorenone to give **11** gives rise to orange and red light emissions, respectively.

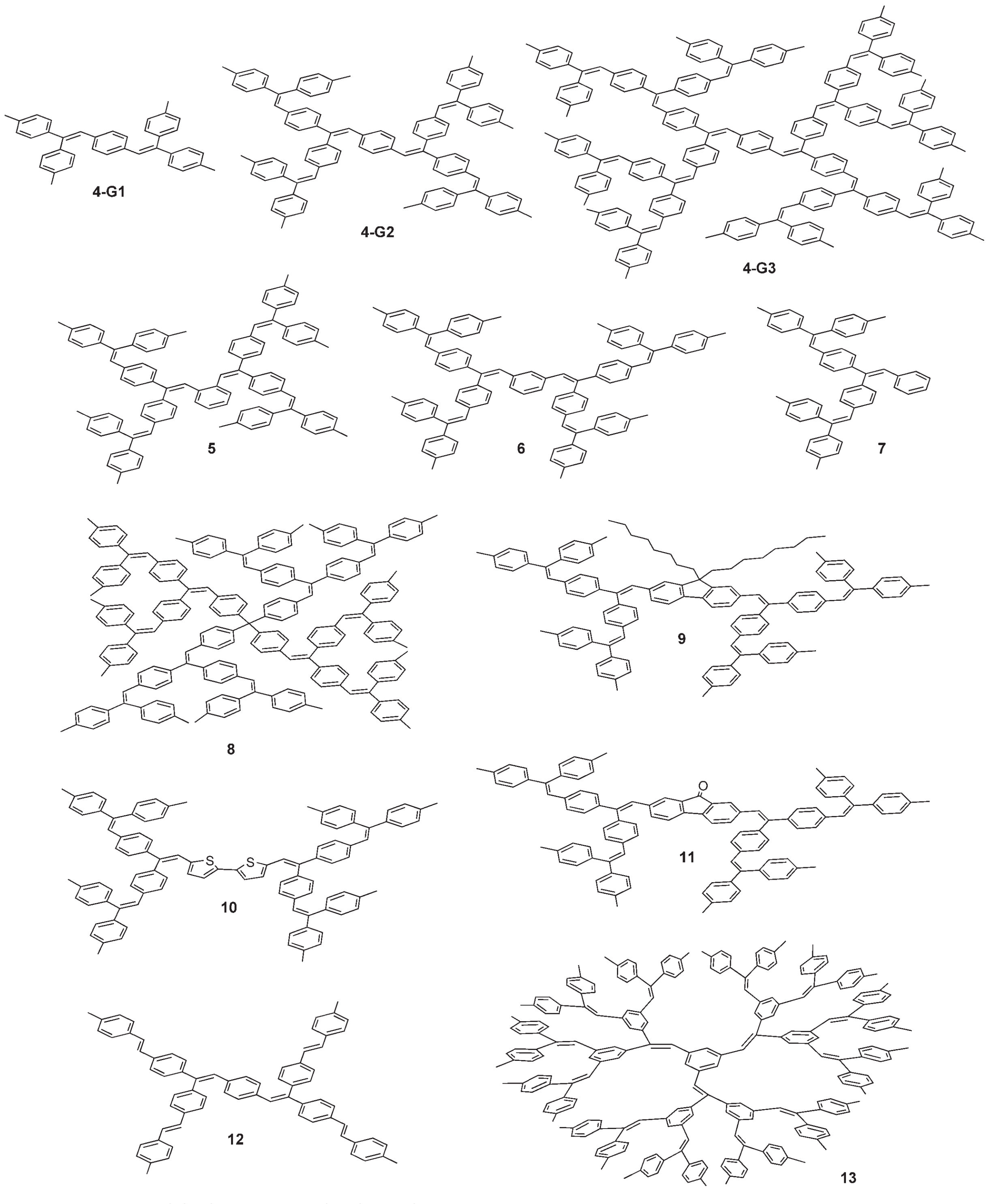
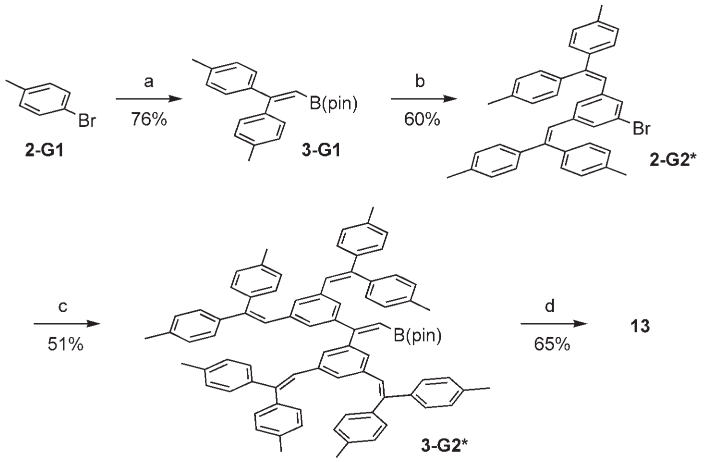


Figure 2. Various conjugated dendrimers prepared in this study.

These results clearly show that the photophysical properties can be conveniently tuned at the final double cross-coupling stage (step C in Scheme 1) rather than at the earlier stages.

In summary, we have developed an extremely useful and flexible method for the convergent synthesis of novel conjugated dendrimers based on triarylethene branching. A simple yet powerful strategy using common reagents (aryl halides) and reactions (Pd-catalyzed arylations) allowed us to quickly and systematically prepare various fluorescent dendrimers. Moreover, our highly branched dendrimers revealed both a high efficiency of fluorescence emission and high solubility in common organic solvents, which are useful attributes for future applications. This branching effect may find many uses in the emerging field of stilbenoid materials[7,8]



Scheme 3. Synthesis of conjugated dendrimer **13** with mixed branching units. a) **1**, [Pd(P*t*Bu$_3$)$_2$], *i*Pr$_2$NH, toluene, 80°C; b) 1,3,5-tribromobenzene, [Pd(PPh$_3$)$_4$], NaOH, H$_2$O, toluene, 90°C; c) **1**, [Pd(P*t*Bu$_3$)$_2$], *i*Pr$_2$NH, toluene, reflux; d) 1,3,5-tribromobenzene, [Pd(P*t*Bu$_3$)$_2$], NaOH, H$_2$O, toluene, 90°C. Compounds **2-G2*** and **3-G2*** are related to **2-G2** and **3-G2**, respectively (see Scheme 2).

Table 1: Photophysical properties of conjugated dendrimers.

Compounds	UV/Vis data[a]	Fluorescence data[a]		
	λ_{max} [nm], (log ε)	λ_{em} [nm]	Color	Φ_F[b]
4-G1	359 (4.56)	473	blue	0.024
4-G2	402 (4.72), 343 (4.86)	518	yellow	0.58
4-G3	343 (5.20), 248 (5.13)	520	yellow	0.62
5	340 (5.00)	492	blue	0.15
6	340 (5.00)	489	blue	0.050
7	340 (4.71)	471	blue	0.015
8	345 (5.31)	484	blue	0.099
9	406 (4.89), 340 (4.92)	497	yellow	0.82
10	451 (4.72), 335 (4.79)	559	orange	0.17
11	473 (3.97), 388 (4.88), 332 (4.97)	616	red	0.010[c]
12	344 (5.03)	511	yellow	0.32

[a] Measured in chloroform, unless otherwise stated. [b] Determined with reference to 9,10-diphenylanthracene (λ_{exc} = 350 nm), unless otherwise stated. [c] Determined with reference to fluorescein in ethanol (λ_{exc} = 400 nm).

as well as in the development of novel functional materials, where there remain problems with respect to solubility and undesirable intermolecular interactions (aggregation) of the currently used materials.

Received: January 7, 2006

Keywords: C–C coupling · dendrimers · fluorescence · homogeneous catalysis · palladium

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[16] It may also be possible that irradiation of the sample during spectroscopy induces electrocyclization to give partially cyclized products that are highly emissive. However, we could not detect such products in the samples by UV or NMR spectral analysis after irradiation.