

Snowflake-Like Dendrimers via Site-Selective Synthesis of Dendrons

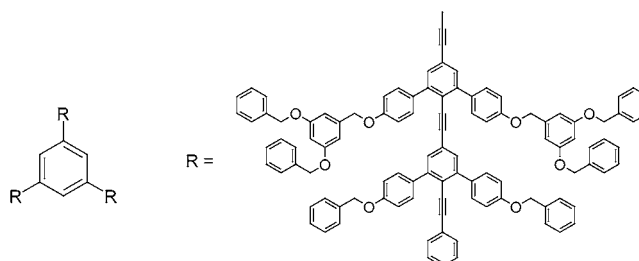
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Received October 15, 2003

ABSTRACT



Snowflake-shaped dendrimers were prepared via site-selective synthesis of dendrons, where an attachment of encapsulating dendritic branches and an extension of phenylacetylenic units were alternatively manipulated on the structure of AB_2 (diethyltriazeno for A and bromo for B) substituted diphenylacetylene using a combination of Suzuki and Sonogashira cross-coupling reactions.

Highly branched and regularly repeating building blocks of dendrimers effectively isolate a core and an interior space in creating a specific microenvironment.¹ An electron transfer from/to an encapsulated redox-active core through the building blocks has attracted much attention for a model for both some biological systems and a charge injection into isolated nanoscale devices.² We have imagined a snowflake-shaped dendrimer (Figure 1) that has an electron-carrying path as an encapsulated π -conjugated system. The snowflake-like dendrimer is different from any dendrimer reported so far. It is difficult to synthesize this dendrimer by means of the simple application of divergent and/or convergent procedures. A site-selective synthesis of the branch (dendron)

structure is essential; the size of the encapsulating part in the dendron is altered depending on the π -conjugation sites, i.e., the larger ones in the inner and the smaller in the outer region. Here, we report on such a procedure using a dialkyltriazeno group as a key protecting group³ and demonstrate the synthesis of snowflake-like dendrimers **1** and **2** possessing a linear oligo(phenylene ethynylene) as a molecular wire⁴ inside branched poly(benzyl ether)s (Figure 1).⁵

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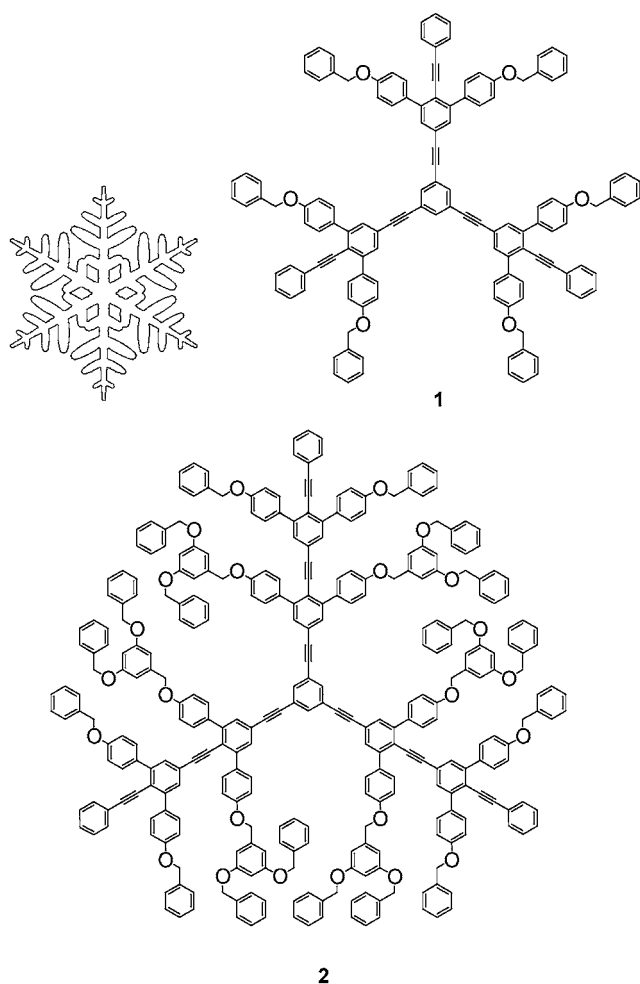


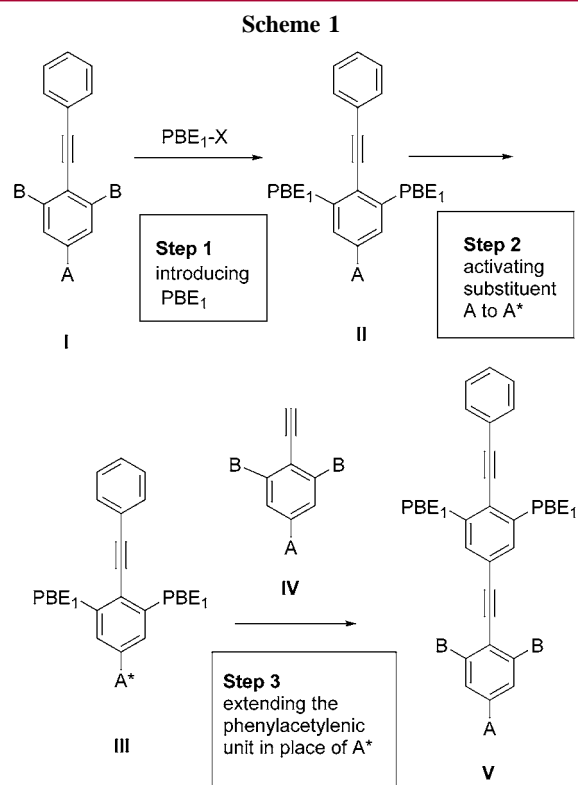
Figure 1. Snowflake-shaped dendrimers.

A snowflake has six branch structures. Scheme 1 illustrates the strategy of the site-selective synthesis of the branched dendrons. The synthesis is accomplished by repeating three steps: introducing branched poly(benzyl ether) branches (PBE_n, where *n* is the number of generation) in place of B on the AB₂-diphenylacetylene **I** (step 1), activating A to the A* leading to **III** (step 2), and extending the phenylacetylenic unit in place of A* giving **V** (step 3). The generation number (*n*) of the incorporating PBE_n increases as the repetition cycles.

Key intermediates were prepared according to Scheme 2. A reduction of the nitro group in **3**⁶ using iron powder afforded **4** in a moderate yield. We used diethyltriazene as a key in the protection-activation of group A. The amino

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group of **4** was converted to a diethyltriazeno group by treating it with *tert*-butyl nitrate, trifluoroborane etherate, and then diethylamine to give key compound **5**.⁷ The Sonogashira coupling of **5** with phenylacetylene or trimethylsilylacetylene using Pd(0)/Cu(I) gave the compounds **6-1**⁸ (**I**, A = N₃Et₂, B = Br) or **7**, respectively. A deprotection of **7** gave **8** (**IV**, A = N₃Et₂, B = Br). In addition, an encapsulating **10-n** (PBE_n-X (X = B(OH)₂) was synthesized from bromophenol through condensation with benzyl bromides P_n-Br (*n* = 1, 2)⁹ followed by treatment with *n*-butyllithium-(trimethyl borate)-H⁺.¹⁰

With these key compounds in hand, snowflake-like dendrimers **1** and **2** were synthesized in a convergent way (Scheme 3). A Suzuki coupling of diphenylacetylene **6-1** with **10-1** (2 equiv) produced fir tree-like dendritic branch **11-1** (**II** in Scheme 1) in 88% yield. Dendritic branch **11-1** was heated to 120 °C with iodomethane in a sealed tube to give first generation dendritic branch **12-1** (**III**, A* = I) in 87% yield³ with no detectable cleavage of benzyl ethers. A second cycle of a series of reactions gave second generation dendritic branch **12-2** in 57% yield (3 steps). A Sonogashira coupling

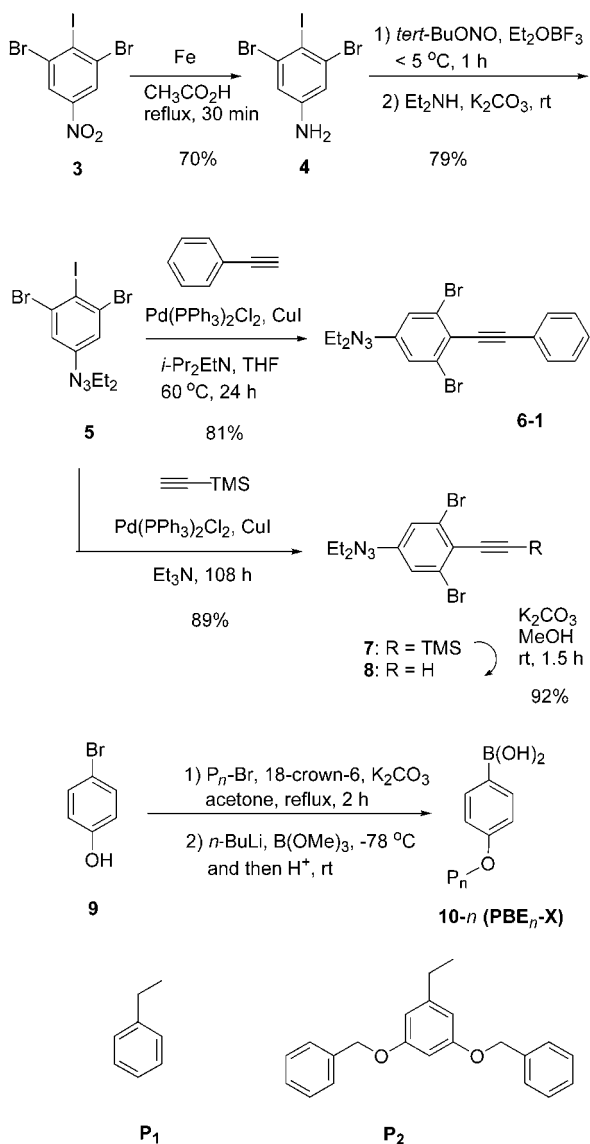
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Scheme 2

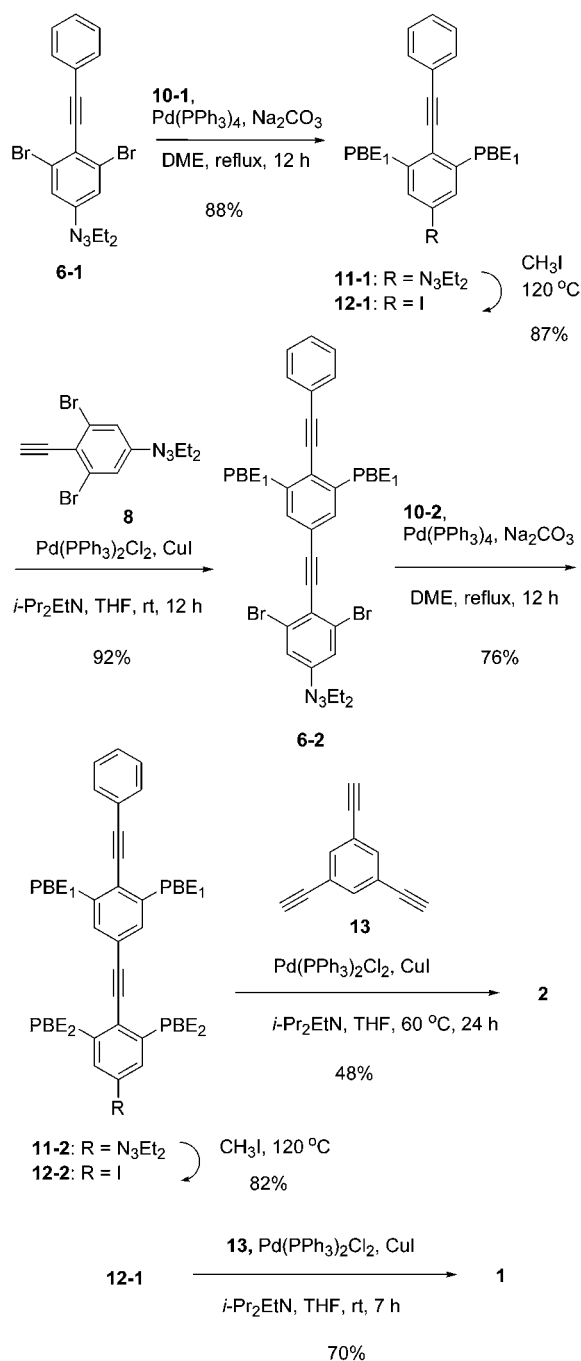


of dendritic branches **12-*n*** (*n* = 1 or 2) with 1,3,5-triethynylbenzene (**13**) provided target dendrimers **1** (70%) and **2** (48% yield) as white and yellow powders, respectively.

The dendrimers **1** and **2** were soluble in various organic solvents such as chloroform, dichloromethane, THF, and toluene and were characterized by standard spectroscopic measurements. The ¹H NMR spectrum (CDCl₃) of **1** showed sharp and well-resolved signals at room temperature. On the other hand, the signals of **2** were broad at room temperature because of the slow conformational change of the dendritic chain and became sharp at 55 °C (Figure 2). A sharp singlet signal due to three equivalent protons on the core benzene ring appeared at 7.67 ppm for **1** and 7.65 ppm (*) for **2** at 55 °C. The benzylic protons appeared around 5.0 ppm as a singlet for **1** and three overlapping singlets with 2:1:1 ratio (**) for **2**. These results indicate the expected symmetric conformations for **1** and **2**. The molecular weights were

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Scheme 3



determined by FAB-MS for **1** and MALDI-TOF-MS for **2**.

These dendrimers had absorptions at 292, 342, and 362 nm for **1** and at 287, 370, and 392 nm for **2** in THF (Figure 3). The shortest absorption is mainly ascribed to the dendritic cone structure, and the longer two absorptions are due to the conjugated main chain structure, oligo(phenylene ethynylene)s.^{5,9} Direct excitation of the conjugated chain (342 nm for **1** and 370 nm for **2**) gave strong fluorescence spectra (Figure 3). Sensitized excitation of the dendritic cone structure (292 nm for **1** and 287 nm for **2**) resulted in the same fluorescence pattern. No emission from the cone

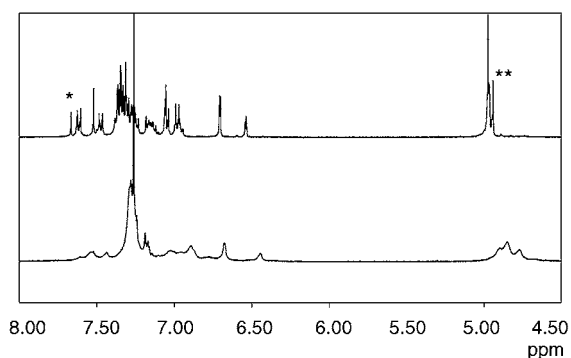


Figure 2. ^1H NMR spectra of **2** in CDCl_3 at room temperature (bottom) and $55\text{ }^\circ\text{C}$ (top).

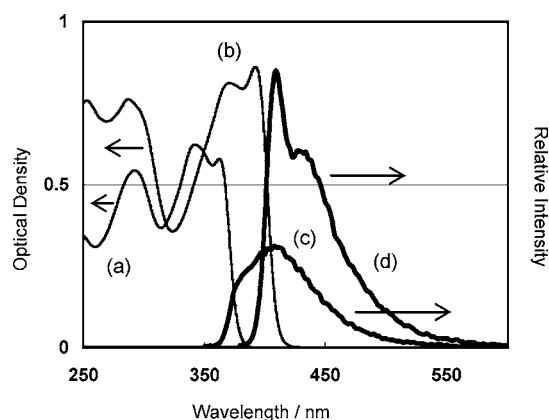


Figure 3. Absorption spectra (plain lines) [(a) for **1** and (b) for **2**, $[\mathbf{1}] = [\mathbf{2}] = 4.0 \times 10^{-6}\text{ M}$] and emission spectra (bold lines) [(c) for **1** (342 nm excitation) and (d) for **2** (370 nm excitation), $[\mathbf{1}] \approx [\mathbf{2}] = 8.0 \times 10^{-8}\text{ M}$] in THF.

structure was observed. Fluorescence quantum yields of the direct and sensitized excitations showed efficient intra-

molecular energy transfer from the cone to the conjugated chain structures in both dendrimers (Table 1).^{5e}

Table 1. Fluorescence Quantum Yields of Dendrimers **1** and **2**

compd	λ_{exc} (nm)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	ϕ_f^a
1	292	411	0.50
	342	408	0.53
2	287	409	0.67
	370	409	0.76

^a 9,10-Diphenylanthracene was used as actinometer ($\phi_f = 0.90$ in cyclohexane).¹¹

In summary, we have established a synthetic route to the snowflake-shaped dendrimers **1** and **2**. A developed site-selective synthesis of dendrons is quite general and could be applied to higher analogues. In these dendrimers, oligo-(phenylene ethynylene)s should provide unique electron circuit paths covered by bulky dendritic cones. Research is currently progressing toward (1) electron-transfer processes of this type of dendrimers involving redox-active molecules at the core and at terminals, and (2) introduction of metal-molecule anchored interfaces at the ends of conjugated chains.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Young Scientists (B) (no.14740354) from the Ministry of Education, Culture, Science, Sports, and Technology Japan. Financial support from Asahi glass foundation is also gratefully acknowledged by M.K.

Supporting Information Available: Synthetic procedures and characterization of compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL036011P