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Snowflake-Like Dendrimers via Site-Selective Synthesis of Dendrons

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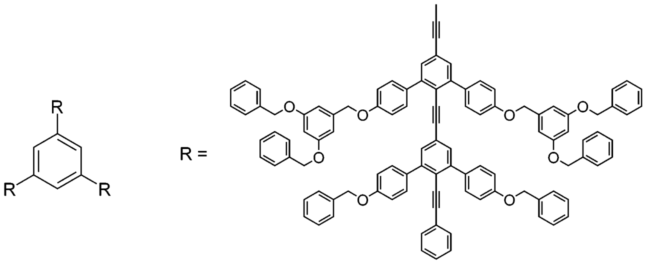
ABSTRACT



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 group[3] and demonstrate the synthesis of snowflake-like dendrimers **1** and **2** possessing a linear oligo(phenylene ethynylene) as a molecular wire[4] inside branched poly(benzyl ether)s (Figure 1).[5]

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[1] Recent reviews for dendrimers, see: (a) Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C.-W. *Tetrahedron* **1998**, *54*, 8543−8660. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665−1688. (c) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74−91. (d) Newcome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; VCH: Weinheim, Germany, 2001.

[2] For some recent papers concerning electron transfer in dendrimers, see: (a) Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; S.-Gracz, H.; Haney, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 9958−9966. (b) Toba, R.; Quintela, J. M.; Peinador, C.; Román, E.; Kaifer, A. E. *Chem. Commun.* **2001**, 857−858. (c) Stone, D. L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856−864 and references therein.

[3] (a) Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465−2466. (b) Patrick, T. B.; Juehne, T.; Reeb, E.; Hennessy, D. *Tetrahedron Lett.* **2001**, *42*, 3553−3554 and references therein.

[4] For some selected papers for olgo(phenylene ethynylene)s as a molecular wire, see: (a) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunber, T. D.; Burgin, T. P.; Jones, L., II; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705−1708. (b) Tour, J. M.; Kozaki, M.; Seminario, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 8486−8493. (c) Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118−5134.

[5] For dendrimer with both phenylene ethynylene and ester linkage, see: (a) Zeng, F.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1996**, *118*, 5326−5327. (b) Kiang, Y.-H.; Gardner, G. B.; Lee, S.; Xu, Z. *J. Am. Chem. Soc.* **2000**, *122*, 6871−6883. For linear π-conjugated polymers and oligomers with poly(benzyl ether) dendritic wedges, see: (c) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296−3301. (d) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691−7695. (e) Sato,

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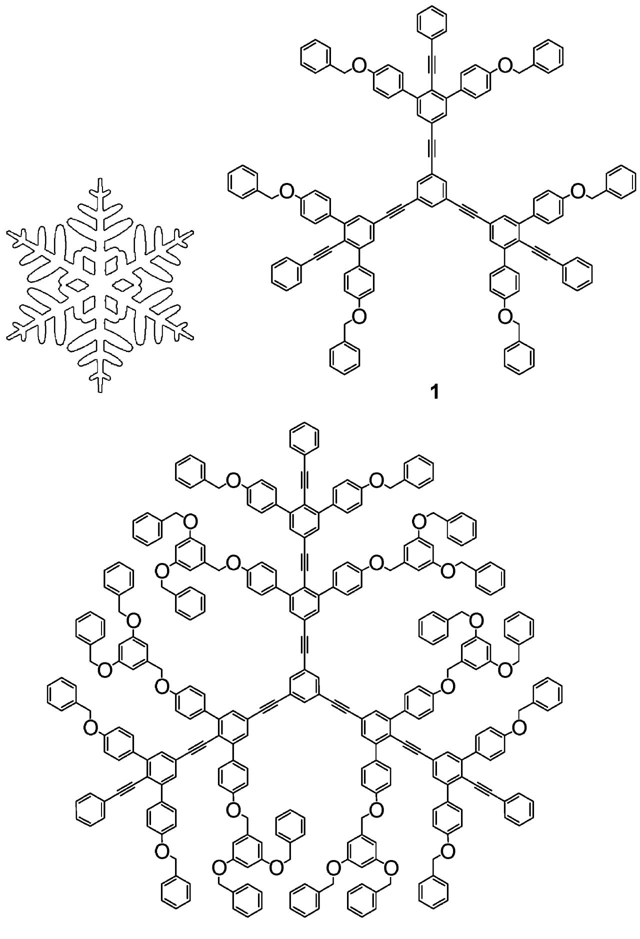
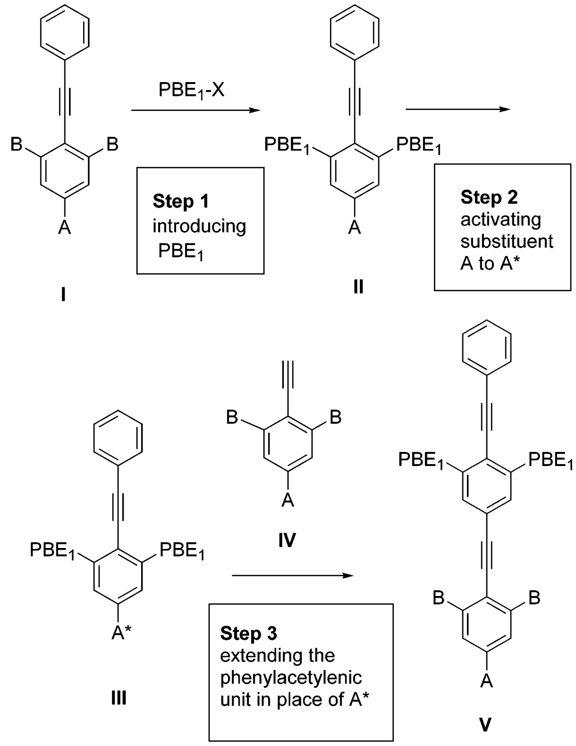

1

2

Figure 1. Snowflake-shaped dendrimers.

Scheme 1



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 AB$_2$-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 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 = N$_3$Et$_2$, B = Br) or **7**, respectively. A deprotection of **7** gave **8** (**IV**, A = N$_3$Et$_2$, 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% yield[3] 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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T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658−10659. (f) Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 7042−7051. (g) Schenning, A. P. H. J.; Arndt, J.-D.; Ito, M.; Stoddart, A.; Schreiber, M.; Siemsen, P.; Martin, R. E.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Gramlich, V.; Diederich, F. *Helv. Chim. Acta* **2001**, *84*, 296−334. (h) Miller, L. L.; Schlechte, J. S.; Zinger, B.; Burrell, C. J. *Chem. Mater.* **2002**, *14*, 5081−5089. (i) Furuta, P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13173−13181.

(6) Schoutissen, H. A. J. *J. Am. Chem. Soc.* **1933**, *55*, 4531−4534.

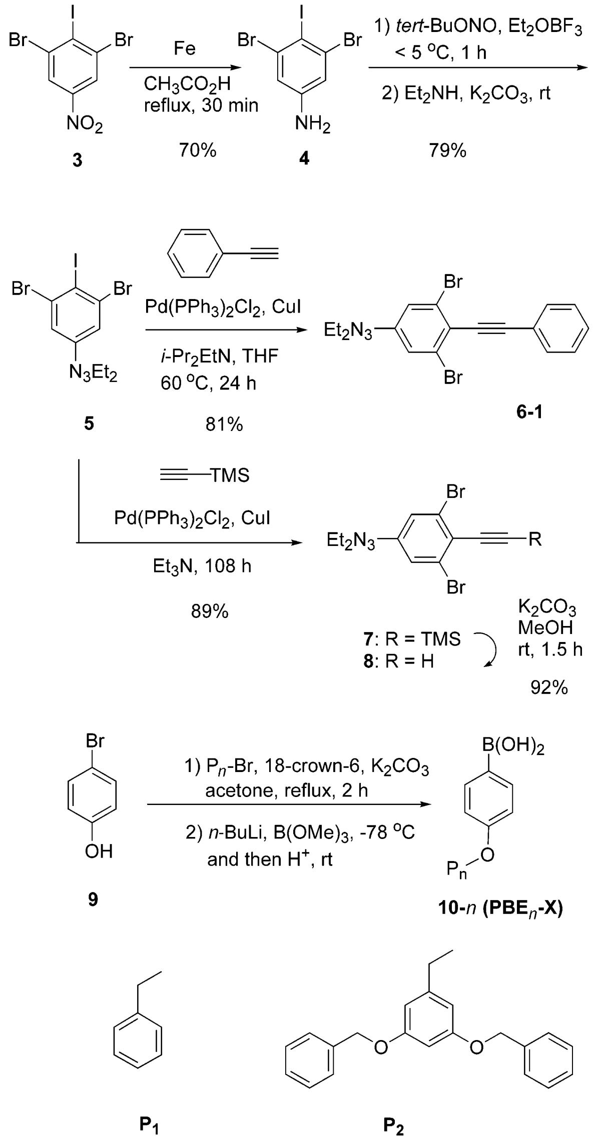
(7) Friedman, L.; Chlebowski, J. F. *J. Org. Chem.* **1968**, *33*, 1636−1638.

(8) In the following discussion about newly developed iterative convergent method, the notation **X**-*n* will be used for some compounds where *n* refers to the generation number.

(9) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647.

(10) (a) Percec, V.; Johansson, G. *J. Mater. Chem.* **1993**, *3*, 83−96. (b) Trollsås, M.; Hult, A.; Percec, V. *Macromol. Chem. Phys.* **1995**, *196*, 1821−1837. (c) Imrie, C.; Loubser, C.; Engelbrecht, P.; McCleland, C. W. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2513−2523. (d) Donnelly, D. M. X.; Finet, J.-P.; Guiry, P. J.; Rea, M. D. *Synth. Commun.* **1999**, *29*, 2719−2730.

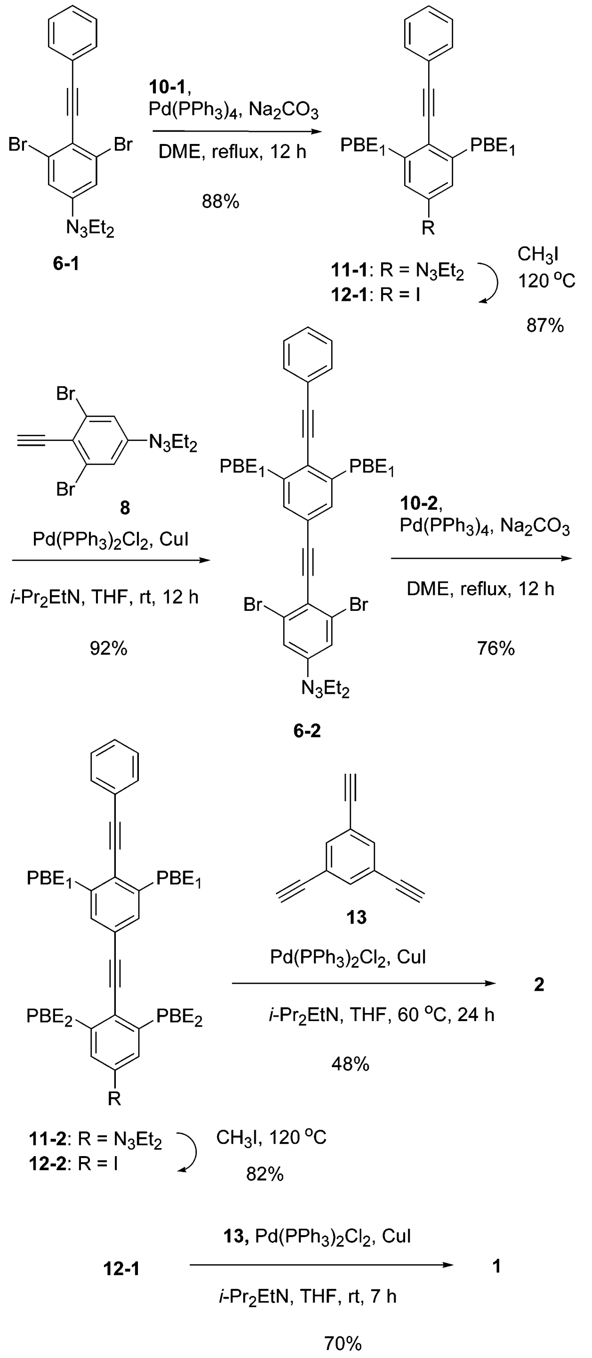
Scheme 2



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 ^{1}H NMR spectrum ($CDCl_3$) 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 determined by FAB-MS for **1** and MALDI-TOF-MS for **2**.

Scheme 3



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

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(11) Hamai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83−89.

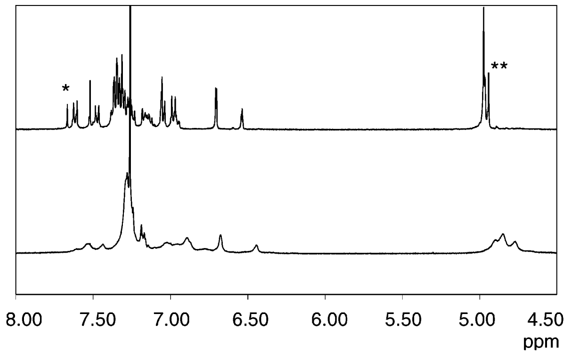

Figure 2. ^{1}H NMR spectra of **2** in $CDCl_3$ at room temperature (bottom) and 55 °C (top).

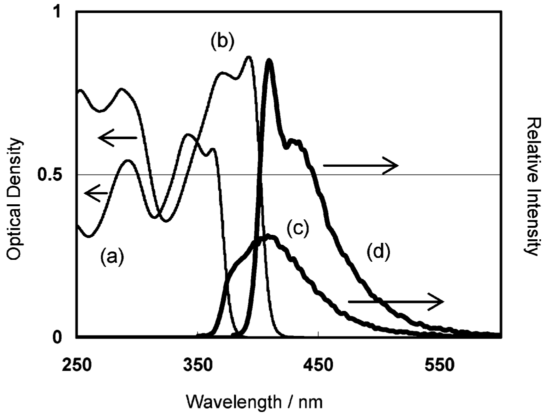

Figure 3. Absorption spectra (plain lines) [(a) for **1** and (b) for **2**, [**1**] = [**2**] = 4.0×10^{-6} M] and emission spectra (bold lines) [(c) for **1** (342 nm excitation) and (d) for **2** (370 nm excitation), [**1**] ≈ [**2**] = 8.0×10^{-8} M] in THF.

structure was observed. Fluorescence quantum yields of the direct and sensitized excitations showed efficient intramolecular 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)	$\lambda^{max}{}_{em}$ (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 (ϕ_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.

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

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