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Synthesis, Characterization, and Controlling Morphology of an Aryl Ether Dendrimer Containing a Dichalcogenide Bond as the Core

Yutaka Takaguchi,* Shinji Suzuki, Takahiro Mori, Jiro Motoyoshiya, and Hiromu Aoyama

Faculty of Textile Science & Technology, Shinshu University, Ueda, Nagano 386-8567

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A poly(benzyl ether) dendron with a thiol group or a selenocyanate group at the focal point was synthesized and well characterized, and then used for the controlling morphology. The molecules show a reversible redox behavior between dendrons and dendrimer dichalcogenides, being achieved under chemical reactions, although a dendrimer having selenium atoms has never been reported. Furthermore, dendrimer dichalcogenides underwent an dechalcogenation reaction upon a treatment with hexaethylphosphorous triamide or photoirradiation to give dendrimer chalcogenides.

Recently, a new kind of well-defined regularly branched macromolecules of nanoscopic size, called dendrimers, have widely attracted scientific attentions.[1] Unlike most synthetic macromolecules of linear chains, dendrimers are believed to be essentially free of chain entanglement, and they possibly adopt defined (conical and spherical) morphologies which are known to influence the basic physical and chemical properties in solution such as self-assembly,[2] liquid crystallinity,[2c,3] intramolecular singlet energy transduction,[4] biological recognition,[5] and encapsulation.[6,7] In practical applications (e.g., drug delivery), reversible configurational and constitutional changes of a dendritic box[6] should be play an important role. For this reason, there is an increasing focus on developing applications for dendrimers that respond to environmental stimuli.[8—12] In particular, Vögtle et al. reported on the synthesis and characterization of dendrimers containing azobenzene units in the periphery toward photoswitchable dendritic hosts.[10] Meanwhile, it is well-known that dichalcogenide bonds undergo an efficient and fully reversible redox reaction. Dendritic systems containing a dichalcogenide bond at the core are especially attractive targets, because they should possess redox properties, and could be controlled their morphology (Fig. 1).

During our studies on the structural control of organochalcogen compounds,[13] we found that dichalcogenide bonds efficiently acted as a stimuli-responsible switch of the dendritic architecture. This paper describes the synthesis, characterization, and controlling morphology of prototype systems, (**4**) and (**5**), having a dichalcogenide bond at the core, although a dendrimer having interior switchable moieties is quite rare. In particular, the first example of a dendrimer having selenium atoms is reported. The dechalcogenation reactions of dendrimer disulfide **4** and diselenide **5** are also discussed.

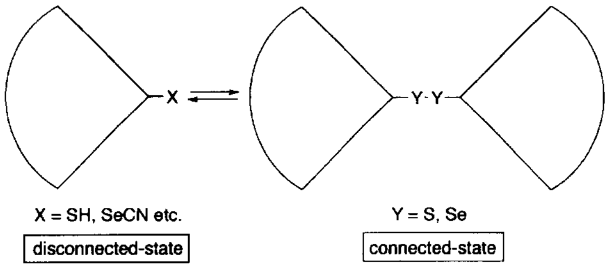
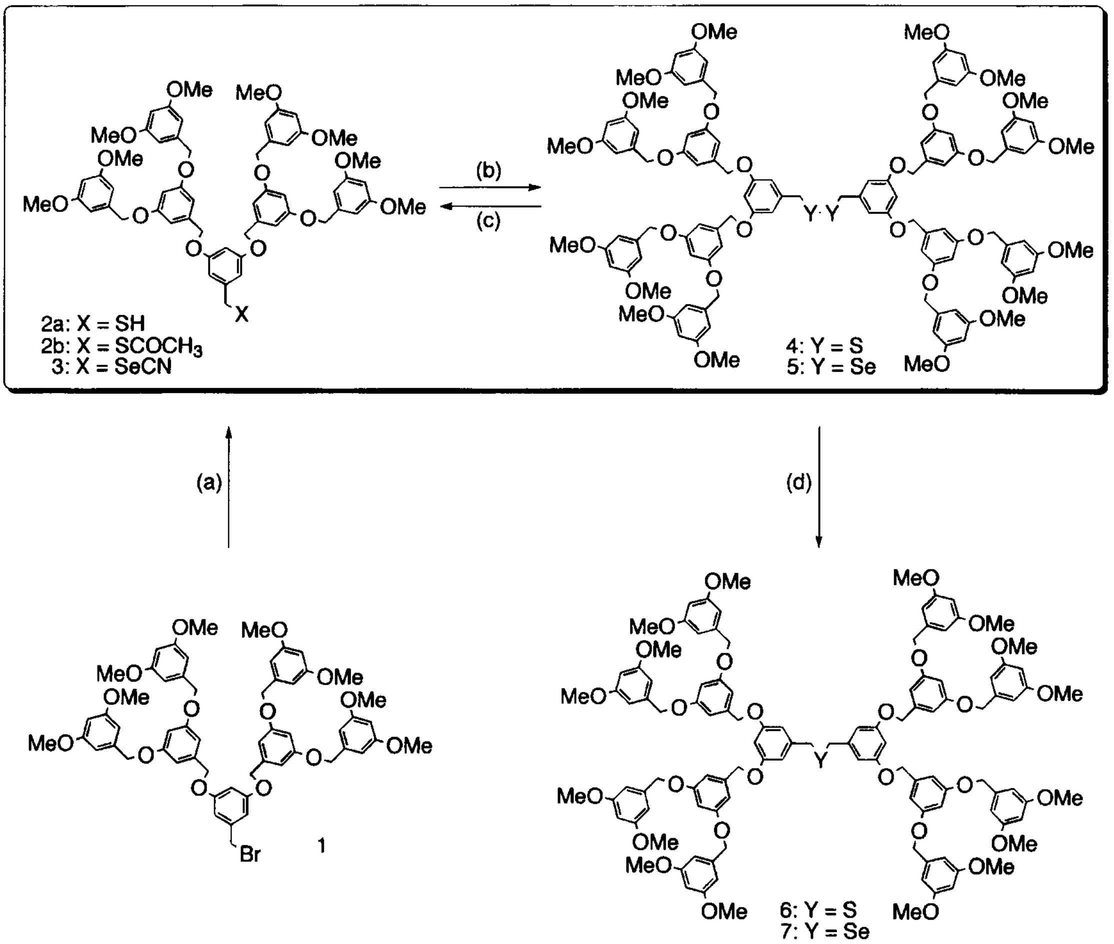


Fig. 1. Morphology control of dendrimer dichalcogenide between connected- and disconnected-states.

Results and Discussion

Disconnected-state dendrimers (**2a**), (**2b**), and (**3**) were synthesized as shown in Scheme 1. A dendritic bromide (**1**) was selected as the starting material, which was prepared according to the literature.[14] After dendron **1** was treated with thiourea in ethanol under reflux in a nitrogen atmosphere for 10 h, aqueous potassium hydroxide was added to the mixture and refluxed for 8 h, and then acidified with HCl to produce the aryl ether dendron thiol (**2a**) in 90% yield. Because the dendron **2a** is unstable and is easily oxidized to give the corresponding aryl ether dendrimer disulfide (**4**),[15] we examined protection of the thiol group. The treatment of **2a** with acetyl chloride in the presence of triethylamine in THF under a nitrogen atmosphere at room temperature for 4 h afforded the aryl ether dendron thioacetate (**2b**) in 93% yield. On the other hand, the dendron **1** led to the aryl ether dendron selenocyanate (**3**) upon treatment with potassium selenocyanate at room temperature in 100% yield. The structures of **2a**, **2b**, and **3** were confirmed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopies, elemental analysis, and MALDI-TOF MS.

Furthermore, the controlling morphology of the dendrons **2a**, **2b**, and **3** were examined as follows (Scheme 1). The dendron **2b** was treated with potassium hydroxide to give **2a** quantitatively. Then, the treatment of **2a** with I_2 in the presence of triethylamine at room temperature for 1 h afforded a dendrimer disulfide **4**, a connected-state dendrimer, in 80% yield. The doublet signal at 3.65 ppm, which was



Scheme 1. Synthesis and controlling morphology of dendrimer dichalcogenides **4** and **5**. Reaction conditions: (a) thiourea, EtOH, reflux then aq KOH, reflux, and aq HCl (for **2a**); KSeCN, CH_3CN (for **3**); (b) I_2, NEt_3 (for **4**); KOH, MeOH (for **5**); (c) $LiAlH_4$, THF (for **2a**); Br_2, NaCN, CH_3CN (for **3**); (d) $h\nu$ or $P(NEt_2)_3$.

assigned to the methylene protons at the core of **2a**, disappeared and a new singlet peak appeared at $\delta = 3.53$, which is consistent with disulfide structure. Furthermore, dendron **3** was converted to dendrimer diselenide (**5**) by treatment with potassium hydroxide in 100% yield. The ^{77}Se NMR spectrum of **5** showed a marked downfield shift at 403 ppm (relative to Me_2Se) as a singlet peak, which is consistent with diselenide structure, while the dendron **3** shows a single peak at 285 ppm. It is noteworthy that the reaction of dendrimer **4** with lithium aluminium hydride (lithium tetrahydridoaluminate) gives dendron **2a** in 86% yield. Furthermore, the dendrimer **5** was initially reacted with bromine to cleave a diselenide bond. Subsequently, the treatment with sodium cyanide to afford dendron **3**, quantitatively. These results indicated that the disconnected-state dendrimers, dendrons **2a**, **2b**, and **3**, are reversibly switched to the connected-state.

Since ^{1}H NMR pulse relaxation times (T_1) are informative of conformational change dynamics, we measured T_1 of the **2a**, **3**, **4**, and **5** at 27 °C in $CDCl_3$. The T_1 value for the methoxy protons on the exterior surface decreased sharply to 1.20 s of **4** from 1.34 s of **2a**. Furthermore, the T_1 of the exterior methoxy signal displayed a significant drop to 1.10 s of **5** from 1.39 s of **3**.

It is well-known that dichalcogenide bonds undergo an dechalcogenation reaction upon a treatment with hexaethylphosphorous triamide or irradiation. Thus, the dendrimer disulfide **4** and diselenide **5** were irradiated with a high-pressure mercury lamp ($\lambda \geq 300$ nm) at room temperature under a nitrogen atmosphere to give the aryl ether dendrimer sulfide (**6**) (63%) and the aryl ether dendrimer selenide (**7**) (69%), respectively (Scheme 1). Similarly, dendrimers **4** and **5** when treated with $P(NEt_2)_3$ gave the dendrimer chalcogenides **6** and **7** in 59 and 52% yields, respectively. The structures of **6** and **7** were confirmed by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopies, elemental analysis, and MALDI-TOF MS. Furthermore, the T_1 value of dendrimers **6** and **7** were 1.09 and 0.98 s, respectively. This result suggests that dendrimers **4** and **5** could be fixed in the connected-state, since diorgano chalcogenides were stable in marked contrast to diorgano dichalcogenides.

The results described herein show the first example of a controlling morphology of a dendrimer having dichalcogenide bond at the core. A dendrimer having selenium atoms has never been reported. Although dendrimer dichalcogenides **4** and **5**, of which structures were disk-like rather than spherical, were prototype systems, controlling morphologies by means of reversible redox reaction of dichalcogenide bond could be applied to higher generations. Further work is in progress to explore the applications and advantages of the dendrimer dichalcogenides.

Experimental

NMR spectra were measured on a Bruker AVANCE400 spectrometer. ^{1}H NMR pulse relaxation times (T_1) were measured in a saturation recovery data processing mode. The concentrations of **2a**, **3**, **4**, **5**, **6**, and **7** for T_1 measurement were 40, 19, 20, 19, 20, and 20 mmol^{-1} in $\mathrm{CDCl_3}$. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a Voyager Elite mass spectrometer using dithranol as a matrix. Elemental analysis was carried out on a Perkin–Elmer 2400 CHN elemental analyzer. GPC experiments were performed on a Japan Analytical Industry Co. model LC-918V with JAIGEL 1H, 2.5H columns, and chloroform was used as the eluting solvent. Photoirradiation was carried out in a Pyrex reactor. Prior to irradiation, the samples were degassed with nitrogen for 15 min. A 500 W high-pressure mercury lamp was used as the light source.

Aryl ether dendron bromide **1** was synthesized according to the literature.[14] The other reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Preparation of the Aryl Ether Dendron Thiol 2a. A mixture of dendron bromide **1** (2.03 g, 1.94 mmol), thiourea (0.74 g, 9.69 mmol), and 95% ethanol (100 ml) was refluxed with stirring for 10 h under a nitrogen atmosphere. Removal of the solvent afforded a white solid, which was dissolved in 6% sodium hydroxide solution (80 ml). After refluxing under a nitrogen atmosphere for 8 h, the solution was allowed to cool and the acidified with 6 M hydrochloric acid (1 M = 1 mol dm^{-3}). After the usual work-up, the residue was purified by GPC to afford the aryl ether dendron thiol **2a** (1.75 g, 1.75 mmol) as a thick oil in 90% yield: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.76 (t, J = 3.8 Hz, 1H), 3.65 (d, J = 3.8 Hz, 2H), 3.77 (s, 24H), 4.94 (s, 4H), 4.96 (s, 8H), 6.39—6.66 (m, 21H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 29.2, 55.3, 70.0, 70.1, 100.0, 100.8, 101.7, 105.3, 106.5, 107.3, 139.2, 139.3, 143.5, 160.0, 160.1, 161.0. MALDI-TOF-MASS, Calcd for $\mathrm{C_{57}H_{60}O_{14}S}$: [M$^+$], 1000.2. Found: *m/z* 999.7.

Preparation of the Aryl Ether Dendron Thioacetate 2b. A solution of acetyl chloride (55 mg, 0.70 mmol) in dry THF (4 ml) was added dropwise to a solution of dendron thiol **2a** (150 mg, 0.15 mmol) and triethylamine (73 mg, 0.72 mmol) in dry THF (6 ml) under a nitrogen atmosphere. The whole mixture was stirred at room temperature for 4 h. After the usual work-up, the residue was purified by silica-gel column chromatography (eluent, chloroform) and GPC to afford the aryl ether dendron thioacetate **2b** (146 mg, 0.14 mmol) as a thick oil in 93% yield: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 2.32 (s, 3H), 3.77 (s, 24H), 4.04 (s, 2H), 4.92 (s, 4H), 4.96 (s, 8H), 6.39—6.67 (m, 21H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 30.3, 33.6, 55.3, 69.9, 70.1, 100.0, 101.1, 101.7, 105.3, 106.5, 108.0, 139.2, 139.2, 139.9, 160.0, 160.1, 161.0, 194.9. MALDI-TOF-MASS, Calcd for $\mathrm{C_{59}H_{62}O_{15}S}$: MLi$^+$, 1050.1. Found: *m/z* 1049.6.

Preparation of the Aryl Ether Dendron Selenocyanate 3. To a solution of dendron bromide **1** (5.75 g, 5.49 mmol) in acetonitrile (130 ml) was added potassium selenocyanate (940 mg, 6.58 mmol) under a nitrogen atmosphere. The mixture was stirred for 5 h. After the usual work-up, the residue was purified by GPC to afford the aryl ether dendron selenocyanate **3** (5.89 g, 5.49 mmol) as a light yellow thick oil in 100% yield: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 3.74 (s, 24H), 4.09 (s, 2H), 4.91 (s, 4H), 4.92 (s, 8H), 6.38—6.64 (m, 21H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 32.7, 55.1, 69.8, 99.7, 101.4, 102.0, 102.1, 105.0, 106.2, 107.8, 135.9, 137.5, 138.8, 139.0, 159.8, 159.9, 160.8; ^{77}Se NMR ($\mathrm{CDCl_3}$) δ = 285 (relative to $\mathrm{Me_2Se}$). MALDI-TOF-MASS, Calcd for $\mathrm{C_{58}H_{59}NO_{14}Se}$: MNa$^+$, 1096.06. Found: *m/z* 1095.74.

Hydrolysis of the Dendron Thioacetate 2b. A solution of the dendron thioacetate **2b** (130 mg, 0.12 mmol) in chloroform (5 ml) was added dropwise to a solution of KOH (25 mg, 0.37 mmol) in methanol (3 ml) under a nitrogen atmosphere. The mixture was stirred at room temperature for 1 h. After the usual work-up, the residue was purified by GPC to afford the dendron thiol **2a** (120 mg, 0.12 mmol) in 100% yield.

Formation of the Aryl Ether Dendrimer Disulfide 4. Solutions of dendron thiol **2a** (1.75 g, 1.75 mmol) in chloroform (70 ml) and iodine (1.11 g, 4.37 mmol) in chloroform (70 ml) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (0.44 g, 4.37 mmol) in chloroform (70 ml). After the usual work-up, the residue was purified by silica-gel column chromatography (eluent, chloroform) and GPC to give dendrimer disulfide **4** (1.40 g, 0.70 mmol) as a light yellow thick oil in 80% yield: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 3.53 (s, 4H), 3.73 (s, 48H), 4.86 (s, 16H), 4.89 (s, 8H), 6.17—6.47 (m, 42H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 43.5, 55.3, 69.9, 70.0, 99.9, 101.5, 101.6, 105.3, 106.4, 108.5, 139.2, 139.2, 139.7, 159.8, 160.1, 161.0; UV/vis ($\mathrm{CHCl_3}$) $\lambda_{\max}(\varepsilon)$ = 282 (33000). MALDI-TOF-MASS, Calcd for $\mathrm{C_{114}H_{118}O_{28}S_2}$: MNa$^+$, 2023.3 Found: *m/z* 2023.1. Found: C, 68.53; H, 5.94%. Anal. Calcd for $\mathrm{C_{114}H_{118}O_{28}S_2}$: C, 68.45; H, 5.95%.

Formation of the Aryl Ether Dendrimer Diselenide 5. To a solution of dendron selenocyanate **3** (3.05 g, 2.84 mmol) in chloroform (100 ml) was added a solution of KOH (560 mg, 8.53 mmol) in methanol (60 ml). The mixture was stirred for 4 h. After the usual work-up, the residue was purified by silica-gel column chromatography (eluent, chloroform) and GPC to afford the aryl ether dendrimer diselenide **5** (2.97 g, 1.42 mmol) as a light-yellow thick oil in 100% yield: ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 3.69—3.79 (m, 52H), 4.86 (s, 16H), 4.89 (s, 8H), 6.38—6.61 (m, 42H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ = 32.6, 55.2, 69.7, 69.8, 99.8, 101.1, 101.4, 105.1, 106.2, 108.0, 139.0, 139.1, 141.1, 159.6, 159.9, 168.8; ^{77}Se NMR ($\mathrm{CDCl_3}$) δ = 403; UV/vis ($\mathrm{CHCl_3}$) $\lambda_{\max}(\varepsilon)$ = 282 (33000). MALDI-TOF-MASS, Calcd for $\mathrm{C_{114}H_{118}O_{28}Se_2}$: MNa$^+$, 2117.1. Found: *m/z* 2117.3. Found: C, 65.12; H, 5.60%. Anal. Calcd for $\mathrm{C_{114}H_{118}O_{28}Se_2}$: C, 65.38; H, 5.68%.

Conversion of Dendrimer 4 into Dendron 2a. A solution of dendrimer **4** (1.00 g, 0.50 mmol) in dry THF (20 ml) was added dropwise to a suspension of lithium aluminium hydride (100 mg, 2.64 mmol) in dry THF (10 ml) at 0 °C. The whole mixture was stirred at room temperature for 4 h. After the usual work-up the residue was purified by GPC to give the dendron **2a** (860 mg, 0.86 mmol) in 86% yield.

Conversion of Dendrimer 5 into Dendron 3. To a solution of dendrimer **5** (289 mg, 0.14 mmol) in chloroform (20 ml) was added bromine (30 mg, 0.19 mmol) under a $\mathrm{N_2}$ atmosphere. The mixture was stirred for 5 h. After removal of the solvent, the residue was dissolved in 20 ml acetonitrile and added NaCN (20 mg, 0.41 mmol). The mixture was stirred at room temperature for 12 h. After the usual work-up, the residue was purified by GPC to afford the dendron **3** (148 mg, 0.14 mmol) in 100% yield.

Photoirradiation of Dendrimer 4. A solution of dendrimer **4** (130 mg, 0.065 mmol) in chloroform (6 ml) was irradiated with a high-pressure mercury lamp at room temperature under a nitrogen atmosphere for 4 h. After removal of the solvent, the residue was purified by GPC to afford the aryl ether dendrimer sulfide **6** (80 mg, 0.041 mmol) as a thick oil in 63% yield: ^{1}H NMR ($CDCl_3$) δ = 3.70 (s, 4H), 3.72 (s, 48H), 4.86 (s, 16H), 4.89 (s, 8H), 6.31—6.68 (m, 42H); ^{13}C NMR ($CDCl_3$) δ = 43.5, 55.3, 69.98, 70.02, 99.9, 101.5, 101.6, 105.2, 106.39, 106.41, 139.2, 139.4, 139.7, 159.9, 160.0, 161.0. Found: C, 69.23; H, 6.04%. Anal. Calcd for $C_{114}H_{118}O_{28}S$: C, 69.57; H, 6.04%.

Photoirradiation of Dendrimer 5. A solution of dendrimer **5** (100 mg, 0.048 mmol) in chloroform (6 ml) was irradiated with a high-pressure mercury lamp at room temperature under a nitrogen atmosphere for 4 h. After removal of the solvent, the residue was purified by GPC to afford the aryl ether dendrimer selenide **7** (66 mg, 0.033 mmol) as a thick oil in 69% yield: ^{1}H NMR ($CDCl_3$) δ = 3.71 (s, 4H), 3.73 (s, 48H), 4.80 (s, 8H), 4.87 (s, 16H), 6.38—6.63 (m, 42H); ^{13}C NMR ($CDCl_3$) δ = 27.9, 55.2, 69.7, 69.8, 99.7, 100.7, 101.4, 105.1, 106.2, 107.9, 139.0, 139.0, 141.5, 159.6, 159.9, 168.8; ^{77}Se NMR ($CDCl_3$) δ = 330.7. MALDI-TOF-MASS, Calcd for $C_{114}H_{118}O_{28}Se$: MH^+, 2016.13. Found: *m/z* 2016.46. Found: C, 68.22; H, 6.12%. Anal. Calcd for $C_{114}H_{118}O_{28}Se$: C, 67.95; H, 5.90%.

Reaction of Dendrimer 4 with Hexaethylphosphorous Triamide. To a solution of dendrimer **4** (102 mg, 0.051 mmol) in 6 ml of dry benzene was added 15 mg (0.06 mmol) of hexaethylphosphorous triamide. The mixture was stirred for 8 h at 80 °C under a nitrogen atmosphere. After the usual work-up, the products were purified by GPC to afford **6** (60 mg, 0.030 mmol) in 59% yield.

Reaction of Dendrimer 5 with Hexaethylphosphorous Triamide. To a solution of dendrimer **5** (100 mg, 0.048 mmol) in 6 ml of dry benzene was added 15 mg (0.06 mmol) of hexaethylphosphorous triamide. The mixture was stirred for 8 h at 80 °C under a nitrogen atmosphere. After the usual work-up, the products were purified by GPC to afford **6** (50 mg, 0.025 mmol) in 52% yield.

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