

## Photoresponsive Azobenzene-cored Dendrons with Terminal Vinyl Groups

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Azobenzene-cored dendrons having the photoisomerizable azobenzene core and terminal vinyl groups have been prepared. Absorption bands of azobenzene-cored dendrons are similar except more intense 280 nm band in higher generation azobenzene dendron. All three azobenzene-cored dendrons show reversible photoisomerization similar to simple azobenzene, irrespective of the generation of dendron. On 350 nm irradiation, absorption band around 344 nm decreases and 436 nm band increases. Photoisomerization reactions are very fast for all three azobenzene-cored dendron and the reaction efficiency is dependent of its generation and solvent. In the dark, slow thermal reversion to original absorption spectrum is observed.

**Key Words :** Azobenzene, Dendrimer, Isomerization, Absorption spectrum

### Introduction

Dendritic compounds with multifunctionality are a subject of current interest.<sup>1-12</sup> Dendrimer is a macromolecular system having well-defined structure, in which the position and number of functional component can be precisely controlled. Switchable molecular systems, in which their properties are controlled by external stimuli such as light, electricity, and pH, are of particular interest. Especially, dendrimers containing photo-active moiety in their interior core or exterior branches has attracted much attention due to their potential availability for photocontrol of molecular recognition and sensing, information processing and transport, photoswitch, and molecular electronic device.<sup>1</sup> Nano-sized photoresponsive molecules could be prepared by introducing the photoresponsive molecules into the core<sup>13,14</sup> or the periphery<sup>15,16</sup> of dendrimer.

Azobenzene<sup>17,18</sup> is a typical photoresponsive unit showing the well-established reversible photoisomerization behavior among the variety of photoactive chromophore. Azobenzene-functionalized dendrimer is one of the actively studied subjects and various dendrimers with azobenzene moiety in the core<sup>19-21</sup> or exterior<sup>16,22,23</sup> have been reported. Momotake and Arai reported water-soluble azobenzene-cored aryl ether dendrimers as potential photoresponsive micelles to which the aggregation is triggered by irradiation.<sup>19</sup> Jiang and Aida reported the synthesis of a series of azobenzene-cored aryl ether dendrimers and showed that low energy IR excitation induced photoisomerization by multi-photon intramolecular energy transfer.<sup>20</sup> Poly (propyleneimine) dendrimers bearing azobenzene groups in the periphery prepared by Balzani *et al.* played the role of their photoswitchable host as potential drug delivery system.<sup>16,22</sup>

For dendrimer with a photoisomerizable azobenzene unit in the core and terminal vinyl groups in the periphery, it would be expected that simple *trans-cis* geometrical change of core molecule may result in the large conformational change throughout the dendritic entity and the introduction of various functional group by the reaction of terminal vinyl

group could allow the easy modification of periphery.

We report here the preparation of azobenzene-cored dendrons of first, second, and third generations with terminal vinyl groups and their clean reversible isomerization behavior.

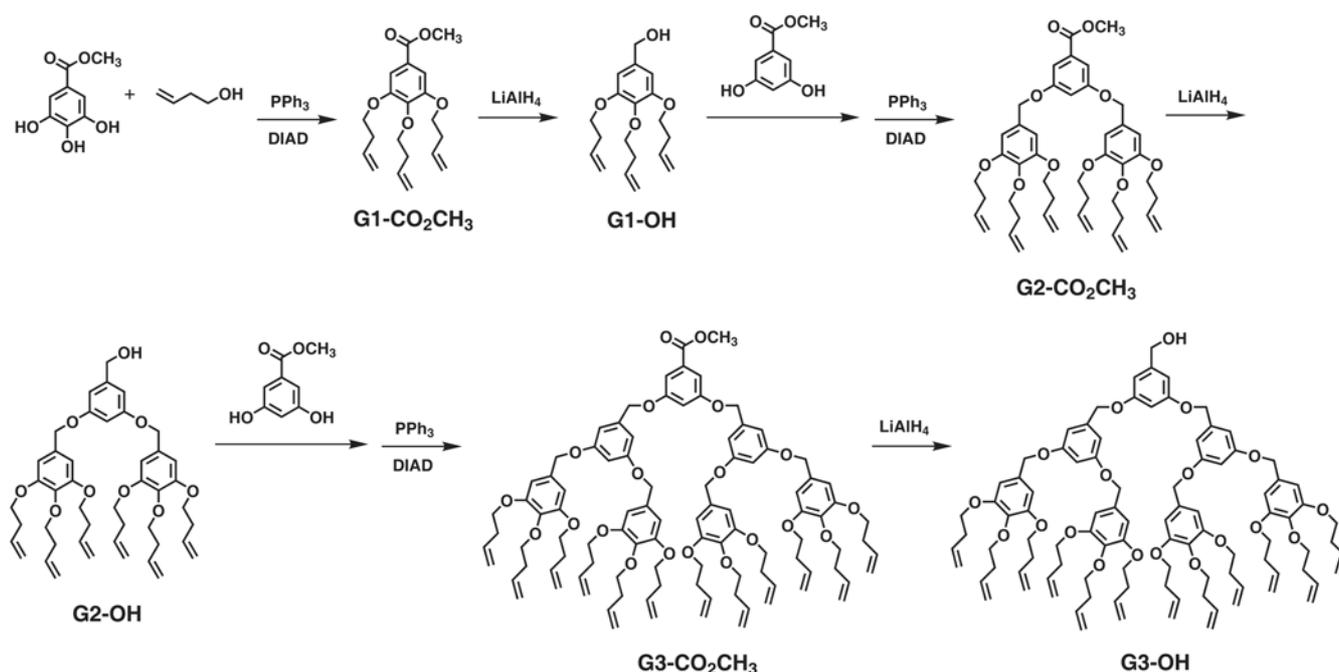
### Experimental Section

#### Synthesis.

*General procedure for synthesis of Gn-OH (n = 1-3):* Synthetic procedure of **Gn-OH** (n = 1-3) is shown in Scheme 1. **Gn-OH** (n = 1-3) was prepared by Mitsunobu etherification reaction.

To a mixture of methyl 3,4,5-trihydroxy benzoate (or methyl 3,5-dihydroxybenzoate), homoallyl alcohol (but-3-en-1-ol) (or **G1-OH** or **G2-OH**), and triphenylphosphine (PPh<sub>3</sub>) in THF, a solution of diisopropyl azodicarboxylate (DIAD) in THF was added dropwise at 0 °C with an ice bath. The reaction was allowed to warm to room temperature and stirred until the reaction was complete as indicated by TLC. The reaction was stopped by adding water and the THF was removed under reduced pressure. The resulting aqueous layer was extracted with ethyl acetate. The organic layers were combined, washed with water, dried over sodium sulfate and filtered. The ethyl acetate was removed under reduced pressure and the resulting white precipitate (triphenylphosphineoxide) was triturated with hexanes and filtered off and then washed with ethyl acetate and hexanes (1:9) mixture. The resulting filtrate was condensed under reduced pressure. The product aromatic ester **Gn-CO<sub>2</sub>Me** was isolated by silica gel column chromatography using ethyl acetate and hexanes mixture as an eluent.

To a suspension of lithium aluminum hydride in THF cooled to 0 °C with an ice bath was added a solution of the aromatic ester **Gn-CO<sub>2</sub>Me** in THF. The suspension was allowed to warm to room temperature and stirred until the reaction was complete as indicated by TLC. The reaction was quenched by adding water and the THF was removed under reduced pressure. The resulting aqueous layer was brought to a neutral pH with the addition of 3 N aqueous

Scheme 1. Synthesis of **Gn-OH** ( $n=1-3$ ).

HCl solution and extracted with diethyl ether. The organic layers were combined, washed with water, dried over sodium sulfate, filtered and concentrated under reduced pressure. The product **Gn-OH** was isolated by silica gel column chromatography using ethyl acetate and hexanes mixture as an eluent.

**Synthesis of G1-OH:** Following the general procedure described above for the Mitsunobu etherification reaction, 7.0 g (38 mmol) of methyl 3,4,5-trihydroxy benzoate, 9.1 g (125 mmol) of homoallyl alcohol (but-3-en-1-ol) and 35.9 g (137 mmol) of triphenylphosphine in 120 mL THF was treated with a solution of 27.7 g (137 mmol) of diisopropyl azodicarboxylate (DIAD) in 100 mL THF to afford crude **G1-CO<sub>2</sub>Me**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexanes mixture (1:9) as an eluent to give 11.0 g (84%) of **G1-CO<sub>2</sub>Me** as a clear, colorless oil.

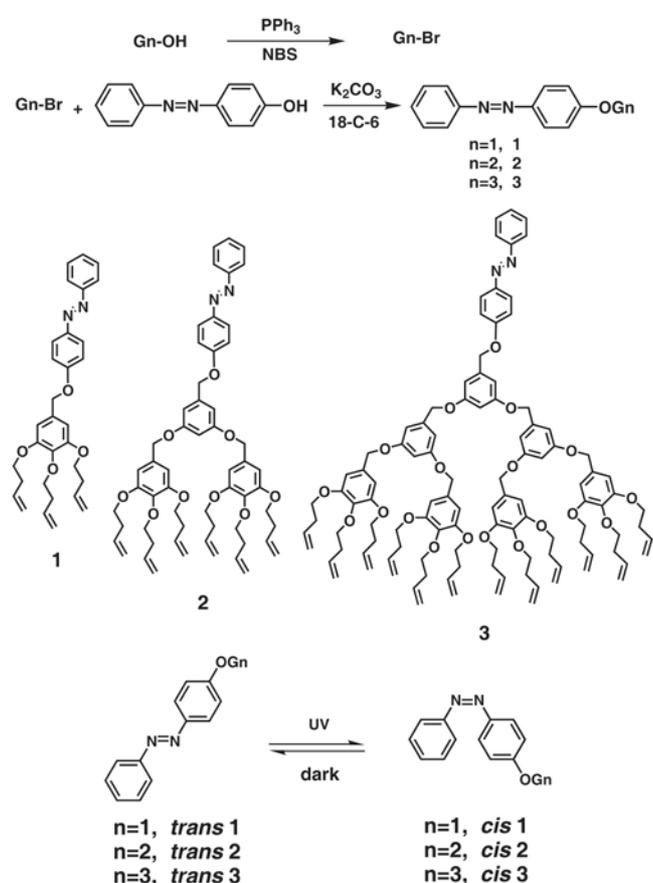
Following the general LAH reduction procedure described above, the reaction of 1.81 g (48 mmol) of lithium aluminum hydride in 50 mL THF with a solution of 11.0 g (32 mmol) of **G1-CO<sub>2</sub>Me** in 100 mL THF afforded crude **G1-OH**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexanes mixture (1:4) as an eluent to give 8.34 g (82%) of **G1-OH** as a clear, colorless oil; IR (Nujol) 3403 (bs), 3075, 2723, 2671, 1641, 1591, 1459, 1459, 1377, 1236, 1116, 915  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.57 (s, 2H, aromatic H), 5.75-6.00 (m, 3H,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 5.00-5.20 (m, 6H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.59 (brs, 2H,  $\text{HOCH}_2\text{Ar}$ ), 3.95-4.10 (m, 6H,  $-\text{ArOCH}_2-\text{CH}_2\text{CH}=\text{CH}_2$ ), 2.45-2.65 (m, 6H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 137.1, 136.8, 135.3, 134.7, 117.1, 116.3, 105.4, 72.5, 68.4, 65.2, 34.7, 33.9 ppm. MALDI-TOP-MS  $m/z$  317.96 ( $\text{M}^+$ ), 340.98 ( $\text{M}+\text{Na}^+$ ),

356.97 ( $\text{M}+\text{K}^+$ ) ( $\text{C}_{19}\text{H}_{26}\text{O}_4$  requires 318.18).

**Synthesis of G2-OH:** Following the general procedure described above for the Mitsunobu etherification reaction, 0.42 g (2.5 mmol) of methyl 3,5-dihydroxy benzoate, 1.76 g (5.5 mmol) of 3,4,5-tris(homoallyloxy)benzyl alcohol (**G1-OH**) and 1.70 g (6.5 mmol) of triphenylphosphine in 20 mL THF was treated with a solution of 1.57 g (7.8 mmol) of diisopropyl azodicarboxylate (DIAD) in 15 mL THF to afford crude **G2-CO<sub>2</sub>Me**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexane mixture (1:9) as an eluent to give 1.5 g (78%) of **G2-CO<sub>2</sub>Me** as a clear, colorless oil.

Following the general LAH reduction procedure described above, the reaction of 125 mg (3.3 mmol) of lithium aluminum hydride in 15 mL THF with a solution of 1.5 g (1.95 mmol) of **G2-CO<sub>2</sub>Me** in 10 mL THF afforded crude **G2-OH**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexanes mixture (1:4) as an eluent to give 0.94 g (65%) of **G2-OH** as a clear, colorless oil; IR (Nujol) 3407 (bs), 3076, 2721, 2363, 2342, 1744, 1594, 1458, 1375, 1237, 1116, 1047, 915  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.45-6.65 (m, 7H, aromatic H), 5.80-6.00 (m, 6H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.00-5.20 (m, 12H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.92 (brs, 4H,  $-\text{ArCH}_2\text{OAr}$ ), 4.64 (brs, 2H,  $-\text{ArCH}_2\text{OH}$ ), 3.90-4.10 (m, 12H,  $-\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ ), 2.40-2.60 (m, 12H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ ) ppm;  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 153.1, 143.8, 137.8, 135.3, 134.7, 132.2, 117.2, 116.4, 106.5, 105.7, 101.3, 72.6, 70.4, 68.5, 65.1, 34.7, 33.9 ppm. MALDI-TOP-MS  $m/z$  740.38 ( $\text{M}^+$ ), 763.35 ( $\text{M}+\text{Na}^+$ ), 779.26 ( $\text{M}+\text{K}^+$ ) ( $\text{C}_{45}\text{H}_{56}\text{O}_9$  requires 740.39).

**Synthesis of G3-OH:** Following the general procedure described above for the Mitsunobu etherification reaction, 68 mg (0.4 mmol) of methyl 3,5-dihydroxy benzoate, 0.66 g



**Scheme 2.** Synthesis and isomerization reaction of dendrons 1-3.

(0.89 mmol) of **G2-OH** and 0.27 g (1.04 mmol) of triphenylphosphine in 10 mL THF was treated with a solution of 0.25 g (7.8 mmol) of diisopropyl azodicarboxylate (DIAD) in 5 mL THF to afford crude **G3-CO<sub>2</sub>Me**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexanes mixture (1:4) as an eluent to give 0.56 g (86%) of **G3-CO<sub>2</sub>Me** as clear, colorless oil.

Following the general LAH reduction procedure described above, the reaction of 20 mg (0.53 mmol) of lithium aluminum hydride in 10 mL THF with a solution of 0.56 g (0.35 mmol) of **G3-CO<sub>2</sub>Me** in 5 mL THF afforded crude **G3-OH**. The resulting residue was purified by silica gel column chromatography using ethyl acetate and hexanes mixture (1:4) as an eluent to give 0.4 g (75%) of **G3-OH** as a clear, colorless oil; IR (Nujol) 3148, 2724, 2699, 2370, 1459, 1376, 1305, 1155, 938 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.45-6.65 (m, 17H, aromatic H), 5.85-6.00 (m, 12H, -CH<sub>2</sub>CH=CH<sub>2</sub>), 5.00-5.20 (m, 24H, -CH<sub>2</sub>CH=CH<sub>2</sub>), 4.97 (s, 4H, -ArCH<sub>2</sub>OArCH<sub>2</sub>OH), 4.92 (s, 8H, -ArCH<sub>2</sub>OArCH<sub>2</sub>OArCH<sub>2</sub>OH), 4.55-4.65 (m, 2H, -ArCH<sub>2</sub>OH), 3.95-4.15 (m, 24H, -OCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>), 2.45-2.60 (m, 24H, -CH<sub>2</sub>CH=CH<sub>2</sub>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.2, 160.0, 153.1, 144.0, 139.5, 137.8, 135.35, 134.7, 132.1, 117.2, 116.4, 106.5, 106.4, 105.6, 101.7, 101.1, 72.6, 70.5, 70.0, 68.5, 65.0, 34.8, 33.9 ppm. MALDI-TOP-MS m/z 1587.25 (M<sup>+</sup>), 1607.17 (M+Na<sup>+</sup>), 1623.10 (M+K<sup>+</sup>) (C<sub>97</sub>H<sub>116</sub>O<sub>19</sub> requires 1584.81).

*General Procedure for Synthesis of Azobenzene-cored*

*Dendrons 1-3:* Structures and synthetic procedure of azobenzene-cored dendrons **1-3** (n = 1-3) are shown in Scheme 2.

To a stirred solution of **Gn-OH** in dichloromethane, NBS and PPh<sub>3</sub> were added successively at -5 °C and stirred for 15 min at room temperature. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with diethyl ether. The combined organic extract was washed with water, saturated aqueous solution of NaHCO<sub>3</sub> and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude **Gn-Br** (n = 1-3) was used directly for the synthesis of azobenzene-cored dendrons **1-3** (n = 1-3) without further purification.

Dendrons **1-3** were synthesized by Williamson ether synthesis using 4-hydroxyazobenzene and corresponding crude **Gn-Br** (n = 1-3). To a stirred solution of crude **Gn-Br** (n = 1-3) in acetone, 4-hydroxyazobenzene and K<sub>2</sub>CO<sub>3</sub> and 18-crown-6 were added successively and the mixture was heated at reflux and stirred until the reaction was complete as indicated by TLC. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with diethyl ether. The combined organic extract was washed with water, dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product was purified by silica gel column chromatography using ethyl acetate and hexane mixture as an eluent to afford azobenzene-cored dendrons **1-3**.

*First Generation Azobenzene-cored Dendron 1:* To a stirred solution of **G1-OH** (50 mg, 0.16 mmol) in dichloromethane (2 mL), NBS (50 mg, 0.28 mmol) and PPh<sub>3</sub> (74 mg, 0.28 mmol) were added successively at -5 °C and stirred for 15 min at room temperature. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with diethyl ether. The combined organic extract was washed with water, saturated aqueous solution of NaHCO<sub>3</sub> and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product **G1-Br** was dissolved in 3 mL of acetone.

To a stirred solution of crude **G1-Br** (61 mg, 0.16 mmol) in 3 mL of acetone, 4-hydroxyazobenzene (32 mg, 0.16 mmol) and K<sub>2</sub>CO<sub>3</sub> (44 mg, 0.32 mmol) and 18-crown-6 (4 mg, 0.02 mmol) were added successively and the mixture was heated at reflux for 1.5 hr. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with diethyl ether and washed with water, dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product was purified by silica gel column chromatography using ethyl acetate and hexanes (1:4) mixture as an eluent to afford 54 mg (0.11 mmol, yield 69%, yellow solid) of azobenzene-cored dendron **1**; IR (KBr) 3079, 2929, 2871, 1592, 1464, 1239, 1120, 832 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.91 (d, 2H, *J* = 8.9 Hz, azo-side aromatic

H -N=N-Ar-O-), 7.86 (d, 2H,  $J = 8.3$  Hz, *ortho*-aromatic H Ar-N=N-), 7.54-7.61 (m, 3H, *meta*- & *para*-aromatic H Ar-N=N-), 7.23 (d, 2H,  $J = 8.9$  Hz, oxy-side aromatic H -N=N-Ar-O-), 6.82 (s, 2H, aromatic H -O-CH<sub>2</sub>-Ar-), 5.88-5.94 (m, 3H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.07-5.20 (m, 8H, -O-CH<sub>2</sub>-Ar- & -CH<sub>2</sub>-CH=CH<sub>2</sub>), 4.04 (t, 4H,  $J = 6.5$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.91 (t, 2H,  $J = 6.7$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.47-2.51 (m, 4H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.39-2.41 (m, 2H, -CH<sub>2</sub>-CH=CH<sub>2</sub>) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  162.9, 154.1, 153.7, 148.0, 138.5, 137.1, 136.7, 133.6, 132.6, 131.1, 126.3, 124.0, 118.7, 118.0, 117.2, 108.4, 73.4, 71.6, 69.4, 35.8, 35.0 ppm; MALDI-TOP-MS  $m/z$  520.95 (M+Na<sup>+</sup>), 538.93 (M+K<sup>+</sup>) (C<sub>31</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub> requires 498.61).

**Second Generation Azobenzene-cored Dendron 2:** To a stirred solution of **G2-OH** (0.2 g, 0.27 mmol) in dichloromethane (5 mL), NBS (0.087 g, 0.49 mmol) and PPh<sub>3</sub> (0.13 g, 0.49 mmol) were added successively at -5 °C and stirred for 15 min at room temperature. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with diethyl ether. The combined organic extract was washed with water, saturated aqueous solution of NaHCO<sub>3</sub> and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product **G2-Br** was dissolved in 10 mL of acetone.

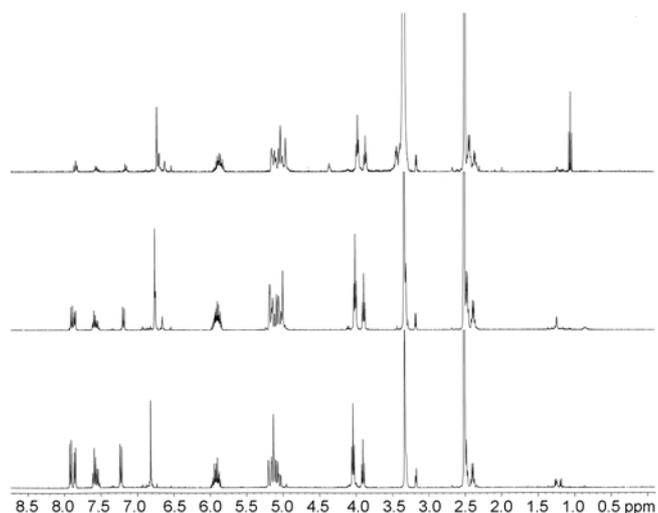
To a stirred solution of crude **G2-Br** (0.21 g, 0.27 mmol) in 10 mL of acetone, 4-hydroxyazobenzene (54 mg, 0.27 mmol) and K<sub>2</sub>CO<sub>3</sub> (75 mg, 0.54 mmol) and 18-crown-6 (5 mg, 0.03 mmol) were added successively and the mixture was heated at reflux for 5 hr. The crude product was purified by silica gel column chromatography using ethyl acetate and hexanes (1:9) mixture as an eluent to afford 138 mg (0.15 mmol, yield 56%, yellow oily solid) of azobenzene-cored dendron **2**; IR (KBr) 3073, 2926, 2872, 1592, 1441, 1247, 1123, 1028, 912, 830 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.89 (d, 2H,  $J = 9.0$  Hz, azo-side aromatic H -N=N-Ar-O-), 7.85 (d, 2H,  $J = 8.3$  Hz, *ortho*-aromatic H Ar-N=N-), 7.54-7.61 (m, 3H, *meta*- & *para*-aromatic H Ar-N=N-), 7.18 (d, 2H,  $J = 8.9$  Hz, oxy-side aromatic H -N=N-Ar-O-), 6.75 (m, 6H, aromatic H -O-CH<sub>2</sub>-Ar-), 5.86-5.91 (m, 6H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.00-5.18 (m, 18H, -O-CH<sub>2</sub>-Ar- & -CH<sub>2</sub>-CH=CH<sub>2</sub>), 4.01 (t, 8H,  $J = 6.4$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.89 (t, 4H,  $J = 6.7$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.45-2.48 (m, 8H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.38-2.39 (m, 4H, -CH<sub>2</sub>-CH=CH<sub>2</sub>) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  162.7, 161.3, 154.0, 153.7, 148.0, 138.4, 137.1, 136.7, 134.0, 132.6, 131.1, 126.2, 124.0, 118.6, 118.0, 117.2, 108.4, 108.2, 73.4, 71.3, 69.4, 35.8, 35.0 ppm; MALDI-TOP-MS  $m/z$  921.31 (M<sup>+</sup>), 943.23 (M+Na<sup>+</sup>), 961.21 (M+K<sup>+</sup>) (C<sub>57</sub>H<sub>64</sub>N<sub>2</sub>O<sub>9</sub> requires 921.13).

**Third Generation Azobenzene-cored Dendron 3:** To a stirred solution of **G3-OH** (0.1 g, 0.065 mmol) in dichloromethane (3 mL), NBS (0.021 g, 0.12 mmol) and PPh<sub>3</sub> (0.031 g, 0.12 mmol) were added successively at -5 °C and stirred for 15 min at room temperature. The reaction was stopped by adding water and the solvent was removed under reduced pressure. The resulting aqueous layer was extracted with

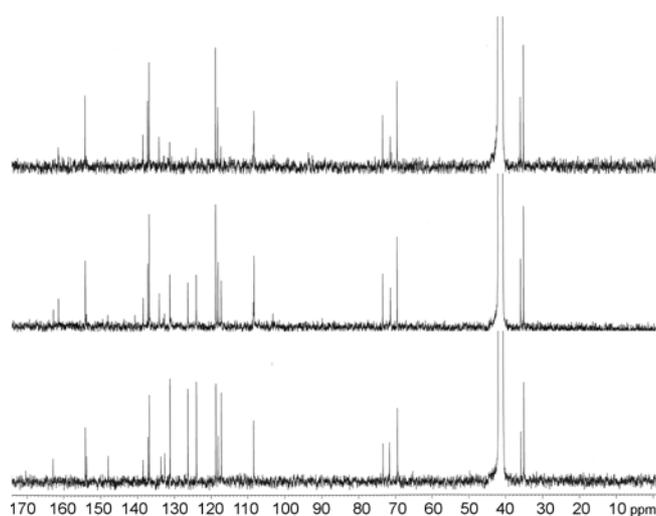
diethyl ether. The combined organic extract was washed with water, saturated aqueous solution of NaHCO<sub>3</sub> and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product **G3-Br** was dissolved in 3 mL of acetone.

To a stirred solution of crude **G3-Br** (107 mg, 0.065 mmol) in 3 mL of acetone, 4-hydroxyazobenzene (13 mg, 0.065 mmol) and K<sub>2</sub>CO<sub>3</sub> (18 mg, 0.13 mmol) and 18-crown-6 (1 mg, 0.004 mmol) were added successively and the mixture was heated at reflux for 1 hr. The crude product was purified by silica gel column chromatography using ethyl acetate and hexanes (1:4) mixture as an eluent to afford 55 mg (0.031 mmol, yield 48%, yellow oily solid) of azobenzene-cored dendron **3**; IR (KBr) 3079, 2929, 2873, 1595, 1440, 1155, 1116, 1016, 915, 835 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.88-7.93 (m, 4H, azo-side aromatic H -N=N-Ar-O- & *ortho*-aromatic H Ar-N=N-), 7.46-7.54 (m, 3H, *meta*- & *para*-aromatic H Ar-N=N-), 7.16 (d, 2H,  $J = 9.0$  Hz, oxy-side aromatic H -N=N-Ar-O-), 6.53-6.73 (m, 12H, aromatic H -O-CH<sub>2</sub>-Ar-), 5.82-5.89 (m, 12H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 4.96-5.15 (m, 38H, -O-CH<sub>2</sub>-Ar- & -CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.97 (t, 16H,  $J = 6.4$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.85 (t, 8H,  $J = 6.6$  Hz, -O-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.43-2.45 (m, 12H, -CH<sub>2</sub>-CH=CH<sub>2</sub>), 2.36-2.37 (m, 8H, -CH<sub>2</sub>-CH=CH<sub>2</sub>) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.3, 154.0, 138.4, 137.1, 136.7, 134.0, 131.1, 123.9, 118.6, 118.0, 117.1, 108.2, 73.3, 71.3, 69.4, 35.8, 35.0 ppm; MALDI-TOP-MS  $m/z$  1787.19 (M+Na<sup>+</sup>), 1803.12 (M+K<sup>+</sup>) (C<sub>109</sub>H<sub>124</sub>N<sub>2</sub>O<sub>19</sub> requires 1766.15).

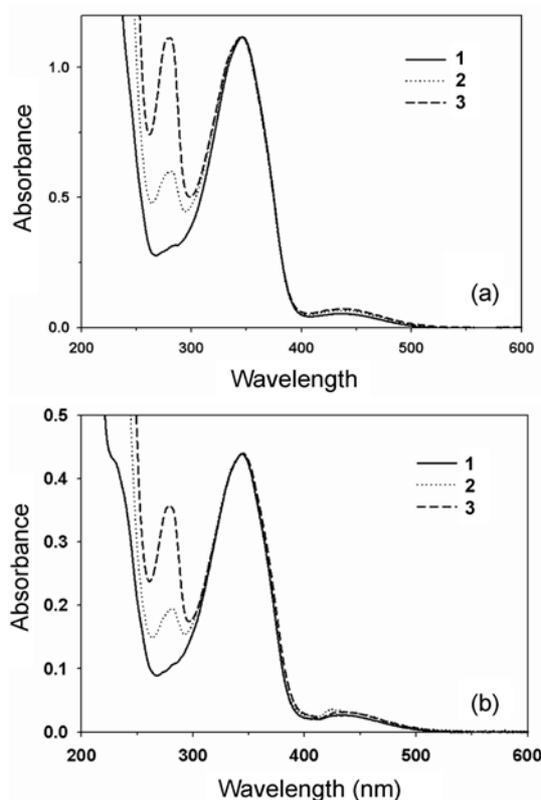
**Spectroscopic Measurements and Photolysis.** IR spectra were obtained in Nujol or KBr pellets on Midac Prospect-IR spectrometer. <sup>1</sup>H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-*d*<sub>1</sub> or DMSO-*d*<sub>6</sub> and a 500 MHz JEOL ECA FT-NMR spectrometer in chloroform-*d*<sub>1</sub>. MALDI-TOP Mass spectra were measured on Applied Biosystem Voyager-DE'STR System 4407 Mass Spectrometer using 2,5-dihydroxybenzoic acid in THF as a matrix. Absorption spectra were recorded on a Shimadzu UV-



**Figure 1.** <sup>1</sup>H NMR spectra of azobenzene-cored dendrons **1** (bottom), **2** (middle), and **3** (top) in DMSO-*d*<sub>6</sub>.



**Figure 2.**  $^{13}\text{C}$  NMR spectra of azobenzene-cored dendron **1** (bottom), **2** (middle), and **3** (top) in  $\text{DMSO-}d_6$ .

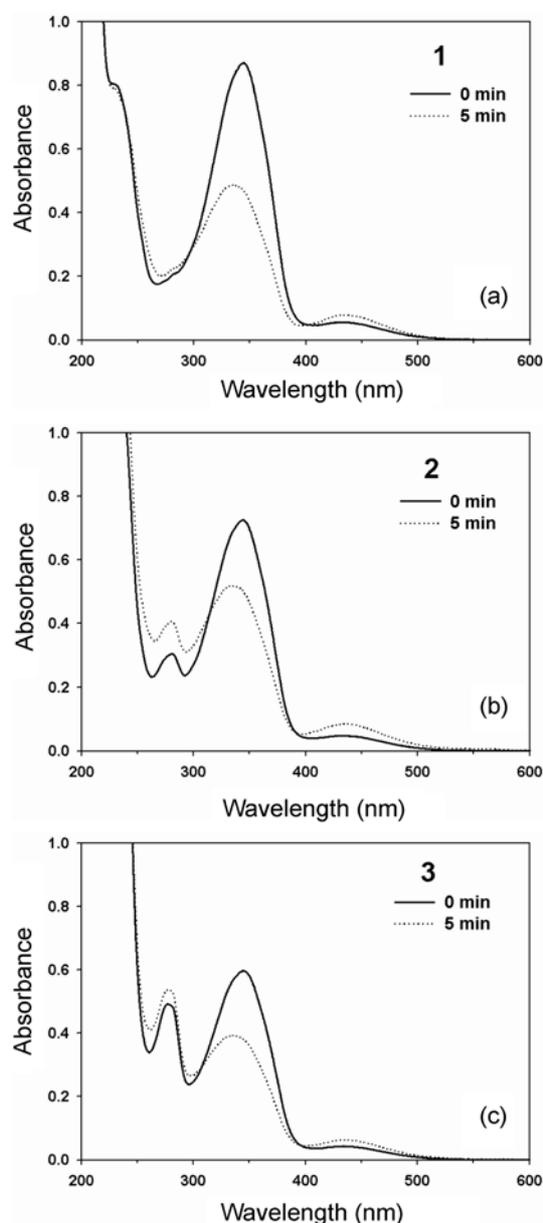


**Figure 3.** Absorption spectra of azobenzene-cored dendrons **1-3** in dichloromethane (a) and methanol (b).

2401PC spectrophotometer. Photoirradiation was carried out in a Rayonet RPR 100 photochemical reactor equipped with 20 Southern Ultraviolet 3500 Å lamps using pyrex reaction tube in dichloromethane or methanol solution. Photoisomerization reaction progress was monitored by change of absorption spectra.

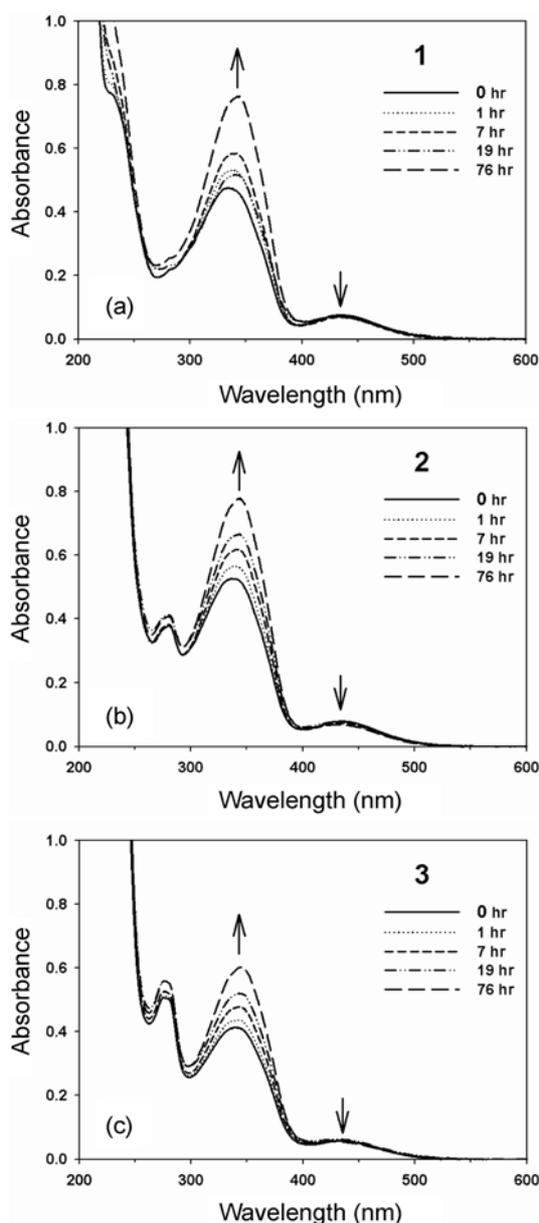
### Results and Discussion

Photoresponsive azobenzene-cored dendrons **1-3** of the



**Figure 4.** Absorption spectral changes of azobenzene-cored dendrons **1** (a), **2** (b), and **3** (c) in methanol upon 350 nm irradiation for 5 min.

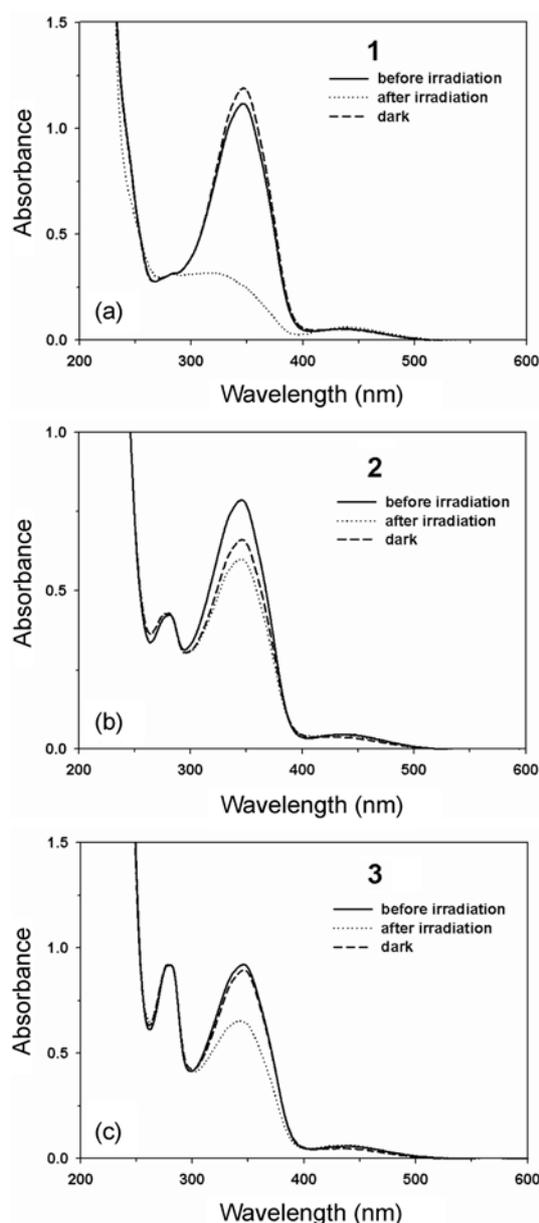
first, second, and third generation were prepared by the Williamson ether synthesis reaction between 4-hydroxyazobenzene and corresponding **Gn-Br** ( $n=1-3$ ) with a good or moderate yield (Scheme 1 and 2, see Experimental Section). Azobenzene-cored dendrons **1-3** are characterized by  $^1\text{H}$  NMR (Figure 1),  $^{13}\text{C}$  NMR (Figure 2), and MALDI-TOF Mass spectral data. In  $^1\text{H}$  NMR spectra, absorption peaks of azobenzene moiety having higher chemical shift than 7.0 ppm decreases as the generation increases from first to third. As for  $^{13}\text{C}$  NMR spectra, azobenzene peaks at 162.9, 153.7, 148.0, 132.6, 131.1, 126.3, 124.0, 117.2 ppm decrease relative to terminal vinyl peaks at 136.7 and 118.7 ppm and other remaining peaks, on going from first generation to third generation.



**Figure 5.** Absorption spectral changes of azobenzene-cored dendrons **1** (a), **2** (b), and **3** (c) in methanol, kept in the dark with time after irradiation at 350 nm for 5 min.

The absorption spectra of dendrons **1-3** in dichloromethane and methanol are represented in Figure 3 and similar to one another. Their absorption maxima appear at 280, 344 and 436 nm, due to the absorption of dendron groups,  $\pi-\pi^*$  and  $n-\pi^*$  absorption of azobenzene moiety, respectively. As shown in Figure 3, while the absorption intensities at 344 and 436 nm are similar for all three dendrons **1-3**, the absorbance is increased at 280 nm on going from first generation dendron **1** to third generation dendron **3**.

The absorption spectral changes of **1-3** in methanol on irradiation at 350 nm are shown in Figure 4. On 350 nm irradiation, absorption bands at 344 nm of dendrons are slightly blue-shifted and their intensities decrease and



**Figure 6.** Absorption spectral changes of azobenzene-cored dendrons **1** (a), **2** (b), and **3** (c) in dichloromethane upon 350 nm irradiation for 5 minutes and kept overnight in the dark after irradiation.

absorption bands at 436 nm increase, as azobenzene moiety in dendrons **1-3** converts photochemically from *trans* form to *cis* form. These azobenzene-cored dendrons **1-3** carried out very fast *trans*  $\rightarrow$  *cis* photoisomerization on irradiation of 350 nm light and reached to the photostationary state within 10 sec. All three azobenzene-cored dendrons **1-3** accomplished efficient *trans-cis* photoisomerization. *Trans*  $\rightarrow$  *cis* photoisomerization rates are similar for first, second, and third generation dendrons and are almost not perturbed by dendritic environment.

Thermal reversion of three azobenzene-cored dendrons **1-3** is followed by absorption spectral changes of **1-3** in methanol during incubation in the dark, shown in Figure 5. After the dark incubation, slow thermal back reversion to

*trans* form is observed for all three dendrons and is completed after 3 days. Thermal reversion of azobenzene moieties for dendrons **1-3** from *cis* form to *trans* form is very slow at room temperature and the rate of thermal reversion is similar to three azobenzene-cored dendrons **1-3**. *Trans* → *cis* photoisomerization and *cis* → *trans* thermal reversion rates are similar for first, second, and third generation dendrons and are not perturbed by dendritic environment even if *trans-cis* geometrical change of core molecule may result in the large conformational change throughout the dendritic entity.

Figure 6 shows the absorption spectral changes of **1-3** in dichloromethane on irradiation at 350 nm for 5 minutes and after dark incubation of irradiated solution. Absorption bands at 344 nm of dendrons decreases and 436 nm absorption band increases on irradiation, due to *trans* → *cis* photoisomerization of azobenzene moiety of dendrons **1-3**. Contrary to the case in methanol, *trans* → *cis* photoisomerization reactions are influenced by dendritic environment. While first generation dendron **1** shows very efficient *trans* → *cis* photoisomerization judging from drastic decrease of absorbance at 344 nm, second and third generation dendrons **2** and **3** show less efficient photoisomerization than **1**. Absorbances at 344 nm after irradiation are larger for dendron **2** and **3** than dendron **1**. Isomer composition at the photostationary state, [cis]/[trans] is very high for dendron **1**, while isomer ratios at the photostationary state, [cis]/[trans] are small for dendron **2** and **3**. It means that dendron **1** accomplishes more efficient *trans* → *cis* photoisomerization than dendron **2** and **3**.

As the irradiated solution of **1-3** in dichloromethane were kept in the dark, complete reversion from *cis* form to *trans* form occurred in 1 day through thermal isomerization, much faster than in methanol *Trans* → *cis* photoisomerization and *cis* → *trans* thermal reversion reactions of **1-3** in dichloromethane, especially for **1**, took place more efficiently than those in methanol. There should be probably steric restriction against isomerization due to the enhancement of bulkiness by the efficient solvation of polar methanol in the interior of dendron through hydrogen bonding between oxygen atom of dendron and methanol. Thermal *cis* → *trans* back reversion in methanol are slower than in dichloromethane as in the case of *trans* to *cis* photoisomerization. This means that the photoisomerization rate could be controlled by solvents as well as the temperature.

In summary, azobenzene-cored dendrons **1-3** having the photoisomerizable azobenzene core and terminal vinyl groups allowing the easy modification of periphery have been prepared. On 350 nm irradiation, efficient *trans* → *cis* photoisomerization rates are similar for first, second, and

third generation dendrons, reached to the photostationary state within 10 sec. First, second, and third azobenzene-cored dendrons **1-3** carried out very fast *trans* → *cis* photoisomerization on irradiation of 350 nm light and are dependent of dendritic environment and solvent. After the dark incubation, slow thermal back reversion to *trans* form is observed for all three dendrons and is completed after 1 day in dichloromethane and 3 days in methanol. Thermal isomerization reactions of dendrons **1-3** in polar methanol solvent are less efficient than in dichloromethane.

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