Photoresponsive Arylether Dendrimers with Azobenzene Core and Terminal Vinyl Groups

Ji-hye Lee, Daeock Choi,[*] Ji Eun Park, and Eun Ju Shin[*]

Department of Chemistry, Sunchon National University, Suncheon, Jeonnam 540-742, Korea. [*]E-mail: ejs@sunchon.ac.kr
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Photoresponsive arylether dendrimers **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (*n* = 1-3) with an azobenzene unit at the core and several vinyl groups (3,5-bis(but-3-enyloxy)phenyl groups or 3,4,5-tris(but-3-enyloxy)phenyl groups) at the periphery have been prepared. Their structures and reversible *trans-cis* isomerization behaviors have been investigated by ^{1}H-NMR, ^{13}C-NMR, MALDI-TOF-Mass, and UV-vis spectra. All six azobenzene-cored dendrimers carried out very fast *trans → cis* photoisomerization on irradiation of 350 nm light and reached to the photostationary state within 180 s. During the dark incubation, slow thermal back reversion from *cis* to *trans* form is observed for all six dendrimers and is completed within 3 days for **1a-1c** and 1 day for **2a-2c**. Isomerization efficiency decreases with increasing generation. However, the initial reaction rates of both *trans → cis* photochemical isomerization and *cis → trans* thermal isomerization increases significantly with increasing generation for dendrimers for **1a-1c** but only slightly for **2a-2c**.

Key Words : Azobenzene, Arylether dendrimer, Isomerization, Absorption spectrum

Introduction

Dendrimers are highly ordered, monodisperse, tree-like functional macromolecules, in which the position and number of functional component can be precisely controlled.[1] As the generation becomes higher, the structure of dendrimers changes from flat to spherical and interior void space increases. Dendritic compounds with diverse functional moieties have been reported in recent years.[1-18] Dendrimers with photoresponsive moiety at the core or the branch or the periphery may play an important role in nanotechnology including the preparation of functional nanomaterials such as nano-sized molecular electronic device, molecular photoswitch, sensor, and drug-delivery systems because light-driven simple geometrical change of core molecule or concurrent geometrical changes of many peripheral molecules may result in the large conformational change throughout the dendritic entity.[19-22]

Azobenzene is well known photochromic molecule to show clean reversible isomerization.[23-26] The more stable *trans*-azobenzene can be converted to the less stable *cis*-azobenzene by UV light irradiation. *Cis*-azobenzene can be converted back to *trans*-azobenzene by visible light irradiation or thermally in the dark. Intense investigation has been carried out for the dendrimer with a photoisomerizable azobenzene unit[19] in the core[27-29] or periphery.[30-32]

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.

Recently, we have studied the preparation and isomerization behavior of azobenzene-cored dendrons having the

mono-substituted photoisomerizable azobenzene and terminal vinyl groups.[33]

We now wish to report synthesis (Figures 1 and 2), and their photo- and thermal-isomerization behavior (Figure 3) of arylether dendrimers, which contain di-substituted, photoresponsive azobenzene in the core, and 3,5-bis(but-3-
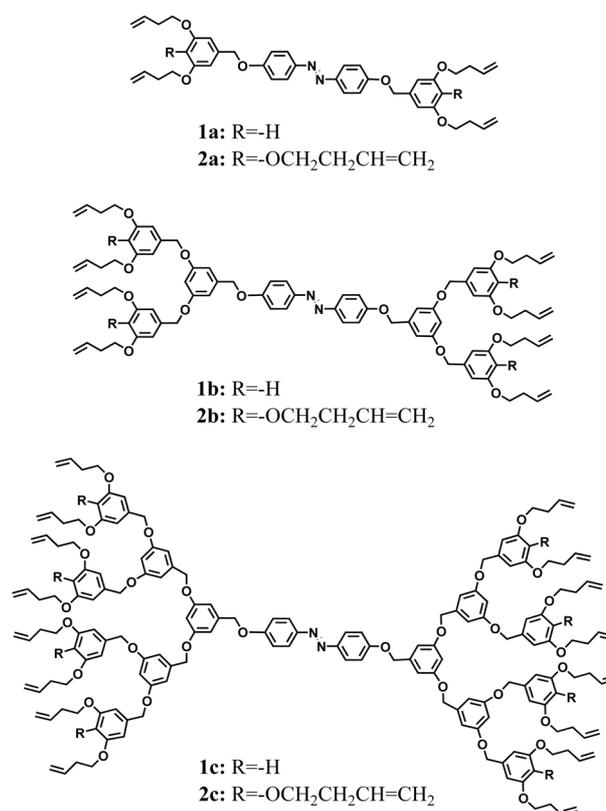

1a: R=-H
2a: R=-OCH₂CH₂CH=CH₂

1b: R=-H
2b: R=-OCH₂CH₂CH=CH₂

1c: R=-H
2c: R=-OCH₂CH₂CH=CH₂

Figure 1. Structures of **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (*n* = 1-3).
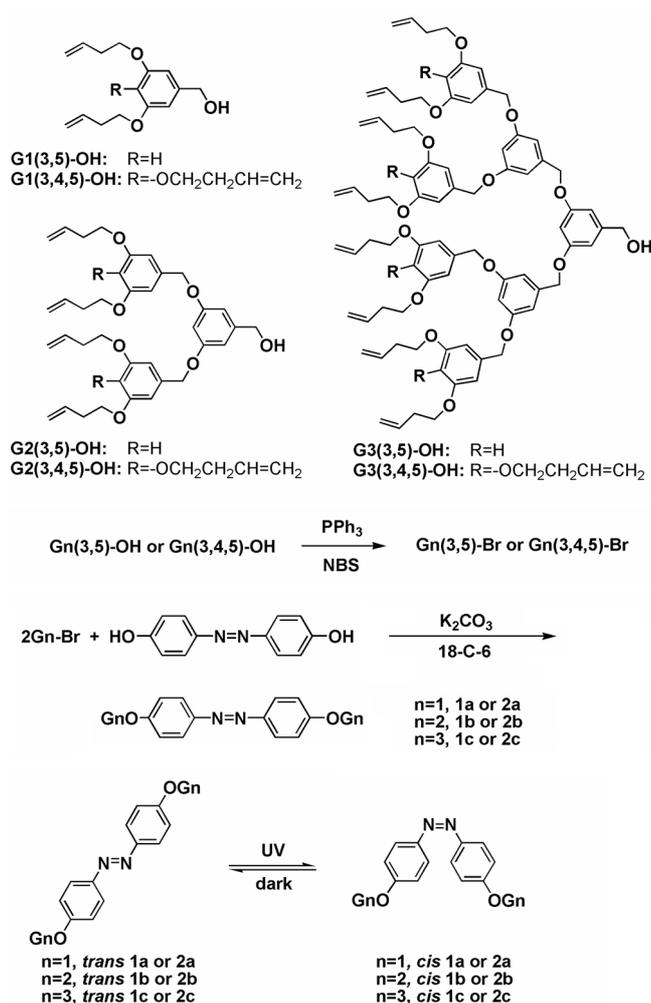
Figure 2. Synthesis of **1a-1c** and **2a-2c**.

enyloxy)phenyl groups or 3,4,5-tris(but-3-enyloxy)phenyl groups in the periphery, **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (n = 1-3) (Figure 1).

Experimental Section

Synthesis. The preparation of arylether dendrons **Gn(3,5)-OH** and **Gn(3,4,5)-OH** (n = 1-3) by Mitsunobu etherification reaction has been previously reported.[16,33]

Photoresponsive azobenzene-cored arylether dendrimers **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (n = 1-3) (Figure 1) of first, second, and third generations with 3,5-bis(but-3-enyloxy)phenyl groups or 3,4,5-tris(but-3-enyloxy)phenyl groups in the periphery have been synthesized by the Williamson ether synthesis reaction between 4,4'-dihydroxyazobenzene and corresponding **Gn-Br** (n = 1-3) (Figure 2).[16,33]

General procedure for synthesis of azobenzene-cored dendrimers 1a-1c and 2a-2c. Structures and synthetic procedure of azobenzene-cored dendrimers **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (n = 1-3) are shown in Figure 1 and Figure 2, respectively.

To a stirred solution of arylether dendrons **Gn(3,5)-OH** or

Gn(3,4,5)-OH (n = 1-3) in dichloromethane, NBS and PPh$_3$ were added successively at -5 ^{o}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$_3$ and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude **Gn(3,5)-Br** or **Gn(3,4,5)-Br** (n = 1-3) was used directly for the synthesis of azobenzene-cored dendrimers **Bis-azo-Gn(3,5) 1a-1c** and **Bis-azo-Gn(3,4,5) 2a-2c** (n = 1-3) without further purification.

Dendrimers **1a-1c** and **2a-2c** were synthesized by Williamson ether synthesis using 4,4'-dihydroxyazobenzene and corresponding crude **Gn(3,5)-Br** or **Gn(3,4,5)-Br** (n = 1-3). To a stirred solution of crude **Gn(3,5)-Br** or **Gn(3,4,5)-Br** (n = 1-3) in acetone, 4,4'-dihydroxyazobenzene and K$_2$CO$_3$ and 18-crown-6-ether 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 dendrimers **Bis-azo-Gn(3,5) 1a-1c** or **Bis-azo-Gn(3,4,5) 2a-2c** (n = 1-3).

For example, in the case of synthesis of first generation azobenzene-cored dendrimer **Bis-azo-G1(3,5) 1a**, to a stirred solution of **G1(3,5)-OH** (40 mg, 0.16 mmol) in dichloromethane (2 mL), NBS (50 mg, 0.28 mmol) and PPh$_3$ (74 mg, 0.28 mmol) were added successively at -5 ^{o}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$_3$ and brine solution. The combined organic extract was dried over magnesium sulfate and filtered. The solvent was evaporated and the crude product **G1(3,5)-Br** was dissolved in 3 mL of acetone.

To a stirred solution of crude **G1(3,5)-Br** (50 mg, 0.16 mmol) in 3 mL of acetone, 4,4'-dihydroxyazobenzene (34 mg, 0.16 mmol) and K$_2$CO$_3$ (44 mg, 0.32 mmol) and 18-crown-6-ether (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 32 mg (0.05 mmol, yield 31%, yellow solid) of first generation azobenzene-cored

dendrimer **Bis-azo-G1(3,5) 1a**.

1a: 31% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, 4H, J = 8.9 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.04 (d, 4H, J = 8.9 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.58 and 6.42 (m, 6H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.84-5.96 (m, 4H, -CH$_2$-C<u>H</u>=CH$_2$), 5.04-5.18 (m, 12H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH= C<u>H$_2$</u>), 3.99 (t, 8H, J = 6.7 Hz, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.48-2.53 (m, 8H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.7, 160.4, 147.2, 138.9, 134.4, 124.4, 117.2, 115.1, 105.9, 101.1, 70.2, 67.3, 33.6 ppm; MALDI-TOF MS m/z 673.63 (C$_{42}$H$_{46}$N$_2$O$_6$ requires 674.34).

1b: 25% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, 4H, J = 9.0 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.03 (d, 4H, J = 9.0 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.41-6.67 (m, 18H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.84-5.96 (m, 8H, -CH$_2$-C<u>H</u>=CH$_2$), 4.96-5.18 (m, 28H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH= C<u>H$_2$</u>), 3.99 (t, 16H, J = 6.7 Hz, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.50-2.55 (m, 16H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.7, 160.3, 147.2, 139.0, 134.4, 124.4, 117.4, 115.1, 106.4, 106.0, 101.7, 101.0, 70.1, 67.3 33.6 ppm; MALDI-TOF MS m/z 1377.4 (C$_{86}$H$_{94}$N$_2$O$_{14}$ requires 1378.67).

1c: 37% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, 4H, J = 8.8 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.08 (d, 4H, J = 8.8 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.45-6.78 (m, 42H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.89-5.96 (m, 16H, -CH$_2$-C<u>H</u>=CH$_2$), 4.99-5.22 (m, 60H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH= C<u>H$_2$</u>), 4.03 (t, 32H, J = 6.6 Hz, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.54-2.64 (m, 32H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 161.5, 161.4, 148.5, 140.4, 135.7, 125.7, 118.5, 116.4, 107.7, 107.2, 102.9, 102.3, 101.9, 71.4, 68.8, 34.9 ppm; MALDI-TOF MS m/z 2786.65 (C$_{174}$H$_{190}$N$_2$O$_{30}$ requires 2787.34).

2a: 51% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, 4H, J = 9.0 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.06 (d, 4H, J = 9.0 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.65 (s, 4H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.86-5.99 (m, 6H, -CH$_2$-C<u>H</u>=CH$_2$), 5.02-5.19 (m, 16H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH=C<u>H$_2$</u>), 4.00-4.07 (m, 12H, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.51-2.59 (m, 12H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.7, 153.1, 147.2, 138.0, 135.3, 134.6, 131.8, 124.4, 117.1, 116.3, 115.1, 106.5, 72.5, 70.5, 68.5, 34.6, 33.8 ppm; MALDI-TOF MS m/z 813.53 (C$_{50}$H$_{58}$N$_2$O$_8$ requires 814.42).

2b: 38% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, 4H, J = 8.9 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.05 (d, 4H, J = 8.9 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.57-6.70 (s, 14H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.85-5.99 (m, 12H, -CH$_2$-C<u>H</u>=CH$_2$), 4.93-5.19 (m, 36H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH= C<u>H$_2$</u>), 3.95-4.06 (m, 24H, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.48-2.59 (m, 24H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.7, 153.1, 147.2, 138.0, 135.3, 134.6, 131.9, 124.4, 117.0, 116.2, 115.1, 106.6, 106.4, 72.5, 70.5, 70.2, 68.5, 34.6, 33.8 ppm; MALDI-TOF MS m/z 1655.92 (C$_{102}$H$_{118}$N$_2$O$_{18}$ requires 1658.84).

2c: 43% yield; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, 4H, J = 8.9 Hz, azo-side aromatic H -N=N-<u>Ar</u>-O-), 7.05 (d, 4H, J = 8.9 Hz, oxy-side aromatic H -N=N-<u>Ar</u>-O-), 6.57-6.69 (s,

32H, aromatic H -O-CH$_2$-<u>Ar</u>-), 5.86-5.94 (m, 24H, -CH$_2$-C<u>H</u>=CH$_2$), 4.92-5.18 (m, 72H, -O-C<u>H$_2$</u>-Ar- & -CH$_2$-CH= CH$_2$), 3.99-4.05 (m, 48H, -O-C<u>H$_2$</u>-CH$_2$-CH=CH$_2$), 2.48-2.60 (m, 48H, -C<u>H$_2$</u>-CH=CH$_2$) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.7, 153.1, 147.2, 139.2, 138.0, 135.3, 134.6, 131.9, 124.4, 117.0, 116.3, 115.1, 106.6, 106.5, 101.6, 72.5, 70.5, 70.1, 68.5, 34.7, 33.8, 30.9 ppm; MALDI-TOF MS m/z 3342.59 (C$_{206}$H$_{238}$N$_2$O$_{38}$ requires 3347.68).

Spectroscopic measurements and photolysis. ^{1}H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-d_1. MALDI-TOF Mass spectra were measured on Applied Biosystem Voyager-DE'STR System 4407 Mass Spectrometer using 2,5-di-hydroxybenzoic acid in THF as a matrix. Absorption spectra were recorded on a Shimadzu UV-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 solution. Reaction progress of photoisomerization on UV irradiation and reverse thermal isomerization in the dark was monitored by change of absorption spectra.

Results and Discussion

Absorption spectra. The absorption spectra of azobenzene-cored dendrimers **Bis-azo-Gn(3,5)** (n = 1-3) **1a-1c** and azobenzene-cored dendrimers **Bis-azo-Gn(3,4,5)** (n = 1-3) **2a-2c** in dichloromethane are similar to one another. Their absorption maxima (see Table 1) appear at around 358 nm for *trans* isomers, around 282, 356, 443 nm for *cis*-**1a-1c**, and around 276, 356, and 443 nm for *cis*-**2a-2c**, due to the absorption of aryl ether dendrimer moiety, π-π^* and n-π^* absorption of azobenzene moiety, respectively. While the absorption intensities at 356 and 443 nm are similar for all six dendrimers, the absorbance is increased at 282 or 276 nm band on going from first generation dendrimer **1a** and **2a** to third generation dendrimers **1c** and **2c**.

Trans→cis **photochemical isomerization.** The absorption spectral changes of **1a-1c** in dichloromethane by 5 sec interval on irradiation at 350 nm were measured for monitoring the photoisomerization of azobenzene core (Figure 3). Absorption spectrum of **1a** is not changed any more after 180 sec irradiation. It is supposed that *trans*-**1a** converts

Table 1. Absorption spectral maxima, reaction efficiencies and rate constants for photoisomerization ($k_{t\to c}$) and thermal back isomerization ($k_{c\to t}$) of **1a-1c** and **2a-2c**

com-pound	λ_a^{trans}, nm	λ_a^{cis}, nm	A_0/A_∞ $t\to c$	A_∞/A_0 $c\to t$	$k_{t\to c}$, sec^{-1}	$k_{c\to t}$, min^{-1}
1a	359	284, 355, 445	3.57	4.05	1.9×10^{-2}	0.12
1b	358	282, 356, 443	2.38	2.44	2.8×10^{-2}	0.16
1c	358	282, 357, 442	2.51	2.56	3.5×10^{-2}	0.19
2a	358	356, 445	2.58	2.54	2.1×10^{-2}	0.31
2b	358	276, 355, 443	2.27	2.27	3.2×10^{-2}	0.42
2c	359	276, 357, 441	2.22	2.17	3.3×10^{-2}	0.38

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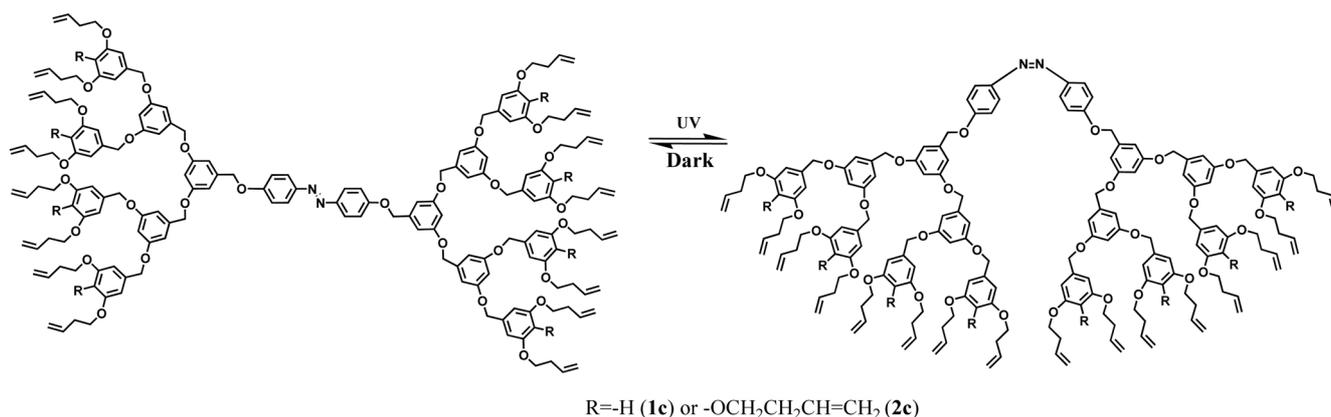R=-H (**1c**) or -OCH$_2$CH$_2$CH=CH$_2$ (**2c**)

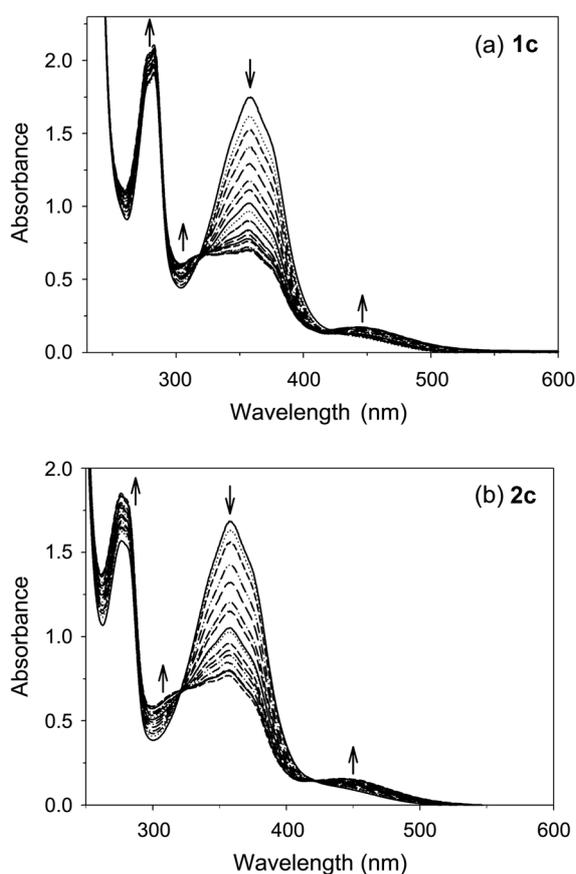**Figure 3**. Reversible isomerization of **1c** and **2c**.

Figure 4. Absorption spectral changes of **1c** (a) and **2c** (b) in dichloromethane with irradiation time (5 s interval) on irradiation at 350 nm by *trans→cis* photoisomerization.

Figure 5. Plot of ln[(A_∞–A_t)/(A_∞–A_0)] with 350 nm irradiation time for **1c**.

completely to the *cis* isomer in 180 sec. It takes 90 and 120 sec to reach to the photostationary state in the conversion of **1b** and **1c** from *trans* to *cis* isomer, respectively.

The absorption spectral changes of **2a-2c** in dichloromethane during 180 sec by 5 sec interval on irradiation at 350 nm were measured for monitoring the photoisomerization of azobenzene core. Irradiation of 120, 70, and 80 sec is required to reach to the photostationary state in the conversion of **2a**, **2b**, and **2c** from *trans* to *cis* isomer, respectively. Figure 4 shows the absorption spectral changes
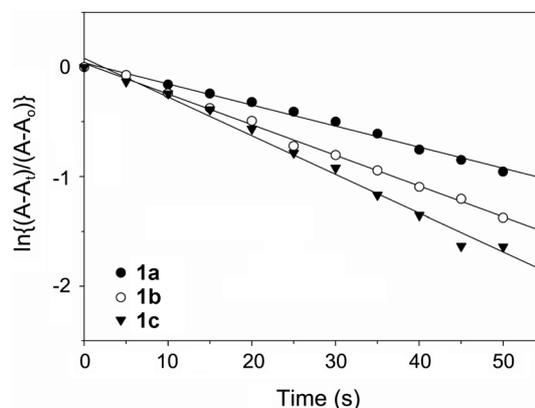
of **1c** and **2c** in dichloromethane by 5 sec interval on irradiation at 350 nm.

On 350 nm irradiation, absorption bands at 358 nm of dendrimers are very slightly blue-shifted and their intensities remarkably decrease while absorbance at 443 nm increases slightly, as azobenzene moiety at the core of dendrimers **1a-1c** and **2a-2c** converts photochemically from *trans* to *cis* form. All six azobenzene-cored dendrimers carried out very fast *trans→cis* photoisomerization on irradiation of 350 nm UV light and reached to the photostationay state within 180 sec. *Trans→cis* photoisomerization rates $k_{t\to c}$ are calculated from the absorbance changes with irradiation time *t* using the following equation.

$$\ln\frac{A_\infty - A_t}{A_\infty - A_0} = -k_{t \to c}t \ ,$$

where A_0, A_t, and A_∞ represent absorbances before irradiation, at irradiation time *t*, and at the photostationary state gained after the prolonged irradiation, respectively.

Plot of ln[(A_∞–A_t)/(A_∞–A_0)] with irradiation time for **1c** is shown in Figure 5.

As shown in Table 1, the initial reaction rates $k_{t\to c}$ of *trans→cis* photochemical isomerization increases significantly with increasing generation for dendrimers for **1a-1c** (isomerization rate **1a**<**1b**<**1c**) but only slightly for **2a-2c**
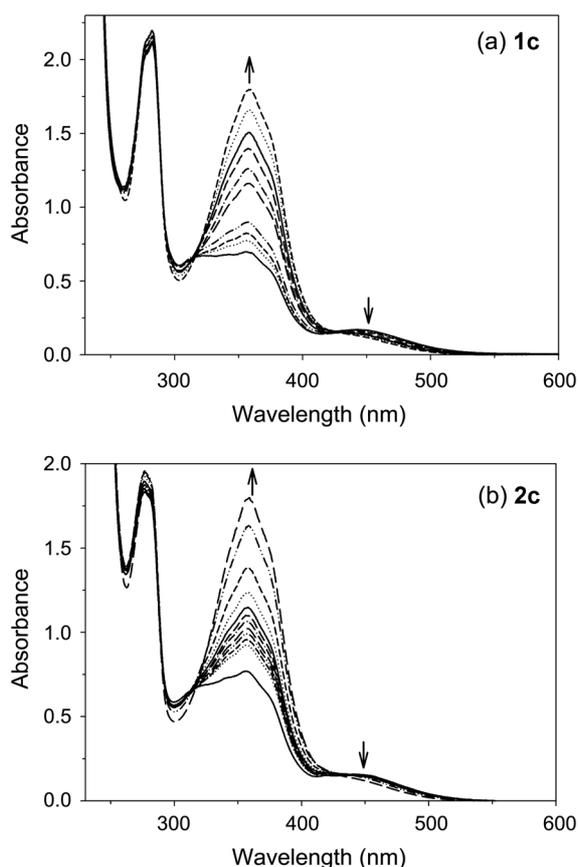
Figure 6. Absorption spectral changes of **1c** (a) and **2c** (b) in dichloromethane with incubation time in the dark by *cis*→*trans* thermal back isomerization after 350 nm irradiation for 120 sec (**1c**) or 180 sec (**2c**).

(isomerization rate **2a**<**2b**≈**2c**). Probably, higher steric restriction due to the enhancement of bulkiness in higher generation leads to faster *trans*→*cis* photoisomerization. *Trans*→*cis* photochemical isomerization rate is affected by generation of azobenzene-cored dendrimers, although not much altered by different dendrimer structure (isomerization rate **1a**≈**2a**).

Isomerization efficiency may be roughly estimated from A_0/A_∞ at 358 nm for *trans*→*cis* photoisomerization (see Table 1). Isomerization efficiency of **1a-1c** is more efficient than that of **2a-2c**. A_0/A_∞ tends to decrease with increasing generation. Efficiency of *trans*→*cis* photochemical isomerization decreases significantly with increasing generation for dendrimers **1a-1c** (isomerization efficiency **1a**>>**1b**≈**1c**) but only slightly for **2a-2c** (isomerization efficiency **2a**>**2b**≈**2c**). Photoisomerization is most efficient for least bulky **1a** and most inefficient for most bulky **2c**.

***Cis*→*trans* thermal isomerization.** Thermal reversion reactions of six azobenzene-cored dendrimers **1a-1c** and **2a-2c** are slow at room temperature and followed by absorption spectral changes in dichloromethane during incubation in the dark. Absorption spectral changes of **1c** and **2c** in dichloromethane with incubation time in the dark by *cis*→ *trans* thermal back isomerization after 350 nm irradiation are

shown in Figure 6. As the solution of **1a-1c** irradiated at 350 nm for enough time to complete *trans*→*cis* isomerization (70-180 sec) in dichloromethane were kept in the dark, slow thermal back reversion from *cis* form to *trans* form through thermal isomerization takes 3 days, much slower than **2a-2c** occurred in 1 day.

The absorption spectral changes of **1a-1c** in dichloromethane during the dark incubation for 3 days were measured for monitoring thermal isomerization of azobenzene core (Figure 3). Absorption spectra of **1a-1c** are completely recovered to the original spectra of corresponding *trans* isomers after 3 days dark incubation. Thermal back isomerization reactions of *cis*-**1a-1c** to *trans*-**1a-1c** are supposed to be completed in 3 days.

The absorption spectral changes of **2a-2c** in dichloromethane during the dark incubation were measured for monitoring the thermal back isomerization of azobenzene. Dark incubation of 27 hrs is required for complete recovery from *cis* to *trans* isomer in the conversion of **2a**, **2b**, and **2c**, respectively.

During the dark incubation, absorption bands at 356 nm of dendrimers are very slightly red-shifted and their intensities remarkably increase while absorbance at 443 nm decrease slightly, as azobenzene moiety at the core of dendrimers **1a-1c** and **2a-2c** reverts thermally from *cis* to *trans* form. *Cis*→*trans* reverse thermal isomerization rates $k_{c \to t}$ are calculated from the absorbance changes with dark incubation time t using the above equation.

As shown in Table 1, the initial reaction rates $k_{c \to t}$ of *cis*→*trans* thermal isomerization increases with increasing generation for dendrimers for **1a-1c** and **2a-2c** (isomerization rate **1a**<**1b**<**1c**<<**2a**<**2b**≈**2c**). This result is similar to the case of *trans*→*cis* photochemical isomerization. Probably, higher steric restriction due to the enhancement of bulkiness in higher generation and **2a-2c** leads to faster *cis*→*trans* thermal isomerization than in lower generation and less sterically crowded **1a-1c**. *Cis*→*trans* thermal isomerization rate is affected by not only structure but also generation of azobenzene-cored dendrimers.

Isomerization efficiency may be roughly estimated from A_∞/A_0 at 358 nm for *cis*→*trans* reverse isomerization (see Table 1). Isomerization efficiency of **1a-1c** is more efficient than that of **2a-2c**. A_∞/A_0 tends to decrease with increasing generation. Efficiency of *cis*→*trans* thermal isomerization decreases significantly with increasing generation for dendrimers **1a-1c** (isomerization efficiency **1a**>>**1b**≈**1c**) but only slightly for **2a-2c** (isomerization efficiency **2a**>**2b**≈ **2c**), similar to the case of *trans*→*cis* photochemical isomerization. *Cis*→*trans* thermal isomerization as well as *trans*→*cis* photochemical isomerization is most efficient for least bulky **1a** and most inefficient for most bulky **2c**.

For, photoresponsive benzyl arylether dendrimers with azobenzene unit at the core, efficiency and rate of both *trans*→*cis* photochemical isomerization and *cis*→*trans* thermal isomerization could be controlled by both dendrimer structure and generation of azobenzene-cored dendrimers.

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