Click-Together Azobenzene Dendrons: Synthesis and Characterization

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ABSTRACT: We synthesized 1,2,3-triazole-linked azobenzene dendrons of four generations. No protection−deprotection approach was needed during the generation development via click reaction. The photoisomerization of azobenzene dendrons was studied using UV–vis spectra. The *cis* isomers of these dendrons were more stable than *trans* isomers in the dark; however, the *cis* isomers could be quickly converted to *trans* forms under visible light exposure in seconds. The *trans* form could change to *cis* form reversibly by UV irradiation as well.

Introduction

Macromolecular systems containing photoresponsive units such as azobenzene have attracted a strong interest for their *cis–trans* photoisomerization phenomena which make many novel optical applications possible, such as reversible optical information storage media,[1] optical switches,[2] control in LC molecules, etc.[3] Many of the systems reported in the literature focus on the incorporation of azobenzene molecules into a linear polymer chain as substituents.[4] Among these azobenzene polymers, aminoazobenzenes or the azobenzenes with electron-donor and electron-acceptor substituents are of high interest due to improved spectral properties, photoinduced orientation, and birefringence.[5]

In contrast to linear systems, dendrimers (including dendrons) have attracted increased attention because of their unidisperse perfect highly branched structures that lead to their globular, void-containing shapes, high solubility, and low viscosity compared to those of linear analogues. The incorporation of a photochromic moiety in dendrimers is very interesting because of the possibility of creating new light-sensitive materials, storage, and optical devices. The periphery of a dendrimer, for example, poly(propyleneimine) dendrimer,[6] poly(amidoamine) dendrimer,[7] and carbosilane dendrimer,[8] have been chemically modified with azobenzene groups, resulting in functioned dendrimers with intriguing photoswitchable properties. Some dendrimers with photochromic azobenzene cores have also been synthesized, whose reversible *cis*/*trans* isomerization has been studied.[9]

However, to our knowledge, only two classes of dendrimers or dendrons with all-azobenzene repeating units have been reported,[10,11] that is, the dendrons of poly(aminoethylbenzoic ester) prepared by Yokoyama and co-workers[10] and poly(benzyl ester) dendrimers prepared by Wang and Advincula.[11] These dendrimers with the azobenzene groups throughout the architecture show a novel advantage for nonlinear optical materials and are "intelligent" macromolecules whose molecular shapes and sizes can be changed upon irradiation with UV light. Although dendrimers with throughout azobenzene units are of high interest due to their unique structures and properties, it is tedious to prepare dendrimers using the traditional group protection−deprotection approach. To solve this problem, it requires efficient and versatile chemistry for the preparation of well-defined azobenzene dendrimers.

Very recently, the Huisgen 1,3-dipolar cycloaddition between azides and alkynes to yield triazoles, which is often referred to simply as the "click reaction", has emerged as an efficient covalently linking technique, characterized by extraordinary reliability and functional group tolerance.[12] The reaction has recently been widely utilized to functionalize surfaces, polymers, etc. It is also proved to be an efficient approach for the generation of diverse dendritic structures of high purity and in excellent yield.[13] Click chemistry is attractive for the synthesis of dendrimers, lying on two points: (1) azides and alkynes are clicked together, and no protection−deprotection approach is needed; (2) a 1,2,3-triazole group is a possible ligand for metal ions and is found to be a proton transport facilitator,[14] which can enable new functions for the dendrimers. "Click" dendrimer has been synthesized,[15] and recently, Tang et al. conveniently attach highly polar azo chromophore moieties to disubstituted polyacetylene through "click" reaction.[16] But triazole-linked azobenzene dendrimers have not been reported yet.

In this paper, we described the details of the growth of dendrons divergently with triazole linkages between each generation, established via repetitive click reactions between alkyne and azide moieties. Ultimately, the resulting azo dendrons contain the carboxyl group in the core, the azobenzene chromophores, and triazole units in the architectures. Perfect dendrimers can be synthesized from these dendrons by convergent routes.[17] However, these dendrons with central carboxylic acid groups seem more suitable for future design of "intelligent" devices, for example, by surface modification or linear−coil self-assembly with photoswitchable properties.[18]

Experimental Section

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker 300 NMR instrument, using tetramethylsilane (TMS) as an internal reference. FT-IR spectra were recorded on a Vector-22 FT-IR instrument.

UV–vis absorption spectra were measured on a Shimadzu UV-2401PC spectrometer. UV irradiation was carried out with 5 W UV lamp with wavelength at 302 nm. Irradiation by visible light was performed using a 23 W Philips day light bulb (>400 nm).

A Micromass GCT orthogonal time-of-flight mass spectrometer (EI-TOF MS; Manchester, UK) was used to analyze samples with low molecular masses. Average mass accuracy usually was less than 0.001 Da. Samples were introduced to the source by direct insert probe. Electron impact (EI, 70 eV) analysis is routinely run on this instrument.

A Finnigan LCQ Advantage MAX LC/MS/MS ion trap mass spectrometer (ESI-MS; Thermo Finnigan, San Jose, CA) was used in the electrospray ionization (ESI) mode. The spray voltage was

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2.4 kV with a current of about 20 mA. Samples were introduced to the source by direct insert probe.

Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Bruker Daltonics BIFLEX MALDI-TOF mass spectrometer (MALDI-TOF MS; Bruker Daltonics, Germany) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode.

Synthesis of *N,N*-Bis(2-hydroxyethyl)aniline (1). A round-bottom flask was charged with aniline (9.3 g, 0.1 mol) and 2-chlorohydrin (20.0 g, 0.25 mol) and then refluxed while 10% water solution of sodium hydroxide (80 mL) was slowly added. The reaction was monitored by thin layer chromatography (TLC). After the reaction has completed, the mixture was cooled to room temperature. The oil layer was gathered, and the water layer was further extracted with ether (3 × 50 mL). The organic layers were combined, and the solvents were removed by rotary evaporation. The crude product was distilled under a pressure of 15 mmHg at 228 °C to give compound **1** (15.6 g, 86% yield). ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 7.21 (m, 2H, *m*-Ar*H*), 6.68 (m, 3H, *o*-, *p*-Ar*H*), 4.01 (s, 2H, O*H*), 3.78 (t, 4H, OCH_2), 3.52 (t, 4H, NCH_2). EI-TOF MS: calcd for $(C_{10}H_{15}NO_2)^+$: *m/z* 181.1103; found: *m/z* 181.1096.

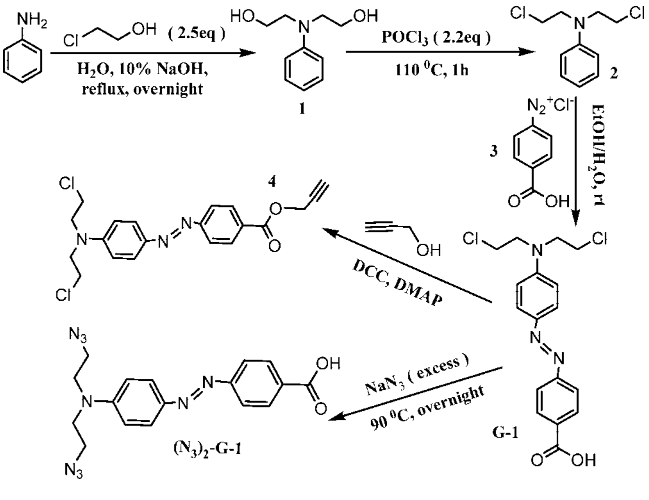
Synthesis of *N,N*-Bis(2-chloroxyethyl)aniline (2). **1** (7.6 g, 42.5 mmol) was slowly added into phosphorus oxychloride (8.36 mL) with ice bath. After the addition was completed, the mixture was heated at 110 °C for 1 h. After being cooled to room temperature, the solution was then poured into ethyl acetate (50 mL). After repeatedly washed with water and dried over anhydrous magnesium sulfate, the crude product was purified by silica gel chromatography eluted with petroleum ether/ ethyl acetate (9/1) to give compound **2** (7.83 g, 85.6% yield). ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 7.20 (m, 2H, *m*-Ar*H*), 6.65–6.71 (m, 3H, *o*-, *p*-Ar*H*), 3.66 (m, 4H, NCH_2), 3.56 (m, 4H, ClCH_2). EI-TOF MS: calcd for $(C_{10}H_{15}Cl_2N)^+$: *m/z* 217.0425; found: *m/z* 217.0426.

Synthesis of 4-Carboxy-4′-[bis(2-chloroethyl)amino]azobenzene (G-1). The diazonium salt (compound **3**) as prepared by adding a solution of sodium nitrite (2.166 g, 31.4 mmol) in water (15 mL) to a solution of *p*-aminobenzoic acid (4.242 g, 31 mmol) in water (60 mL) containing concentrated hydrochloric acid (9 mL) was added to a solution of **2** (6.600 g) in ethanol (225 mL). After 1 h at room temperature, red precipitates were collected and washed several times with water. The crude product was purified by recrystallization from 2-methoxyethaol to give compound **G-1** (9.125 g, 82% yield). IR: 3448, 3300–3000, 3066, 2960, 2926, 2850, 1681, 1598, 1510, 1421, 1393, 1347, 1316, 1248, 1137, 921, 867, 829 cm^{-1}. ^{1}H NMR (300 MHz, δ ppm, DMSO-d_6): 13.07 (s, 1H, COO*H*), 8.08 (d, 2H, *o*-Ar*H* to COO), 7.87 (d, 2H, *m*-Ar*H* to COO), 7.85 (d, 2H, *m*-Ar*H* to NCH_2), 6.99 (d, 2H, *o*-Ar*H* to NCH_2), 3.89 (d, 4H, NCH_2), 3.84 (d, 4H, NCH_2CH_2). EI-TOF MS: calcd for $(C_{17}H_{17}Cl_2N_3O_2)^+$: *m/z* 365.0698; found: *m/z* 365.0738.

Synthesis of Propynyl Ester of G-1 (4). To a solution of **G-1** (3.662 g, 10.0 mmol) in THF (50 mL) was added propynol (80% in toluene) (0.701 g, 10.0 mmol), 4-(dimethylamino)pyridine (DMAP) (0.244 g, 2.0 mmol), and dicyclohexylcarbodiimide (DCC) (2.120 g, 10.3 mmol) in dichloromethane (50 mL). The mixture was stirred at room temperature for 2 days. The reaction mixture was filtered to remove the precipitated dicyclohexylurea and was vacuum-dried. The crude product was purified by silica gel chromatography eluted with petroleum ether/ethyl acetate (10/1) to give compound **4** (2.526 g, 62.5% yield). IR: 3440, 3300–3000, 2956, 2920, 2850, 1717, 1623, 1599, 1543, 1510, 1395, 1392, 1363, 1346, 1288, 1261, 1134, 1090, 1024, 801 cm^{-1}. ^{1}H NMR (300 MHz, δ ppm, $CDCl_3$): 8.10 (d, 2H, *o*-Ar*H* to COO), 7.84 (q, 4H, *m*-ArH to COO, *m*-Ar*H* to NCH_2), 6.70 (d, 2H, *o*-Ar*H* to NCH_2), 4.88 (d, 2H, CH_2−C≡CH), 3.79 (t, 4H, NCH_2), 3.64 (t, 4H, NCH_2CH_2), 2.47 (t, 1H, C≡C*H*). EI-TOF MS: calcd for $(C_{20}H_{19}Cl_2N_3O_2)^+$: *m/z* 403.0854; found: *m/z* 403.0878.

Synthesis of 4-{4-[Bis(2-azidoethyl)amino]phenylazo}benzoic Acid, $(N_3)_2$-G-1. A round-bottom flask was charged with NaN_3 (0.103 g, 1.584 mmol), DMSO (3 mL), and compound **G-1** (0.182 g, 0.495 mmol). The reaction was allowed to stir in a 90 °C oil bath overnight, and then the solution was poured into dilute HCl solution under agitation. The precipitate was collected and washed several times with water and then dried under vacuum: yield 0.184 g (98%). IR: 3436, 3300–3000, 2956, 2920, 2850, 2099, 16828, 1597, 1549, 1511, 1417, 1394, 1369, 1349, 1293, 1263, 1136, 1108, 1024, 865, 820 cm^{-1}. ESI-MS: calcd for $(C_{17}H_{17}N_9O-H)^-$: *m/z* 378.14; found: *m/z* 378.18.

Scheme 1. Synthesis of the First Generation Dendron (G-1)



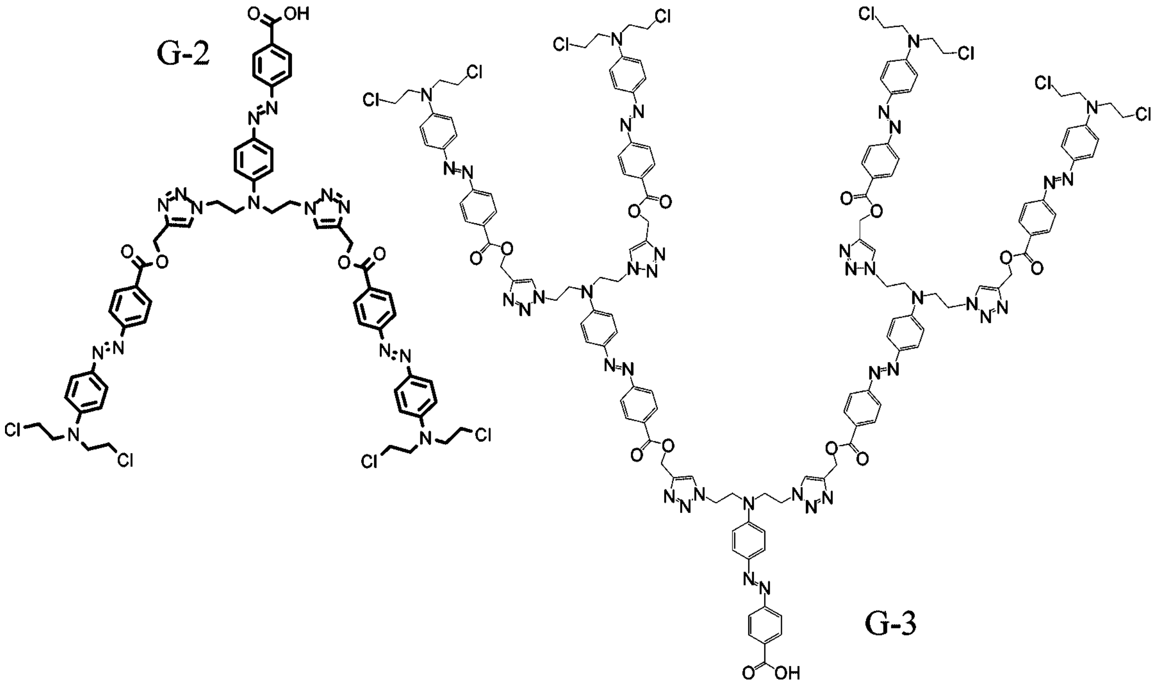
Synthesis of G-2. A round-bottom flask was charged with **$(N_3)_2$-G-1** (0.160 g, 0.422 mmol), DMSO (2 mL), and **4** (0.360 g, 0.886 mmol), followed by sodium ascorbic acid (0.042 g, 0.212 mmol) and $CuSO_4 \cdot 5H_2O$ (0.021 g, 0.084 mmol). The reaction was allowed to stir at room temperature for 2 days. The reaction was precipitated into dilute HCl solution, and then the solid was washed several times with water and then vacuum-dried. The crude product was dissolved in THF and eluted on a silica gel column with dichloromethane to remove excess monomer **4**, and then the eluent was changed to tetrahydrofuran/dichloromethane (2/8): isolated yield 0.541 g (90%). IR: 3444, 3300–3000, 3066, 2956, 2920, 2850, 1708, 1595, 1508, 1386, 1348, 1265, 1236, 1136, 1087, 862, 819 cm^{-1}. ^{1}H NMR (300 MHz, δ ppm, DMSO-d_6): 8.30 (s, 2H, triazole), 8.02 (d, 6H, *o*-Ar*H* to COO), 7.81 (q, 8H, *m*-Ar*H* to NCH_2 and COO in **G-2**), 7.75 (d, 4H, *m*-Ar*H* to NCH_2 and COO in **G-1**), 6.94 (d, 4H, *o*-Ar*H* to NCH_2 in **G-2**), 6.79 (d, 2H, *o*-Ar*H* to NCH_2 in **G-1**), 5.39 (s, 4H, COOCH_2), 4.59 (t, 4H, triazole−C$H_2$$CH_2$N), 3.87−3.82 (broad q, 20H, NCH_2CH_2Cl, triazole−CH_2CH_2N). ^{13}C NMR (75 MHz, δ ppm, DMSO-d_6): 164.9, 155.1, 150.1, 143.4, 141.9, 130.3, 129.5, 125.3, 121.9, 111.9, 58.0, 51.8, 49.8, 46.6, 40.9. ESI-MS: calcd for $(C_{57}H_{56}N_{15}O_6 + H)^+$: *m/z* 1186.33; found: *m/z* 1186.19.

Synthesis of G-3 and G-4. Details are given in the Supporting Information.

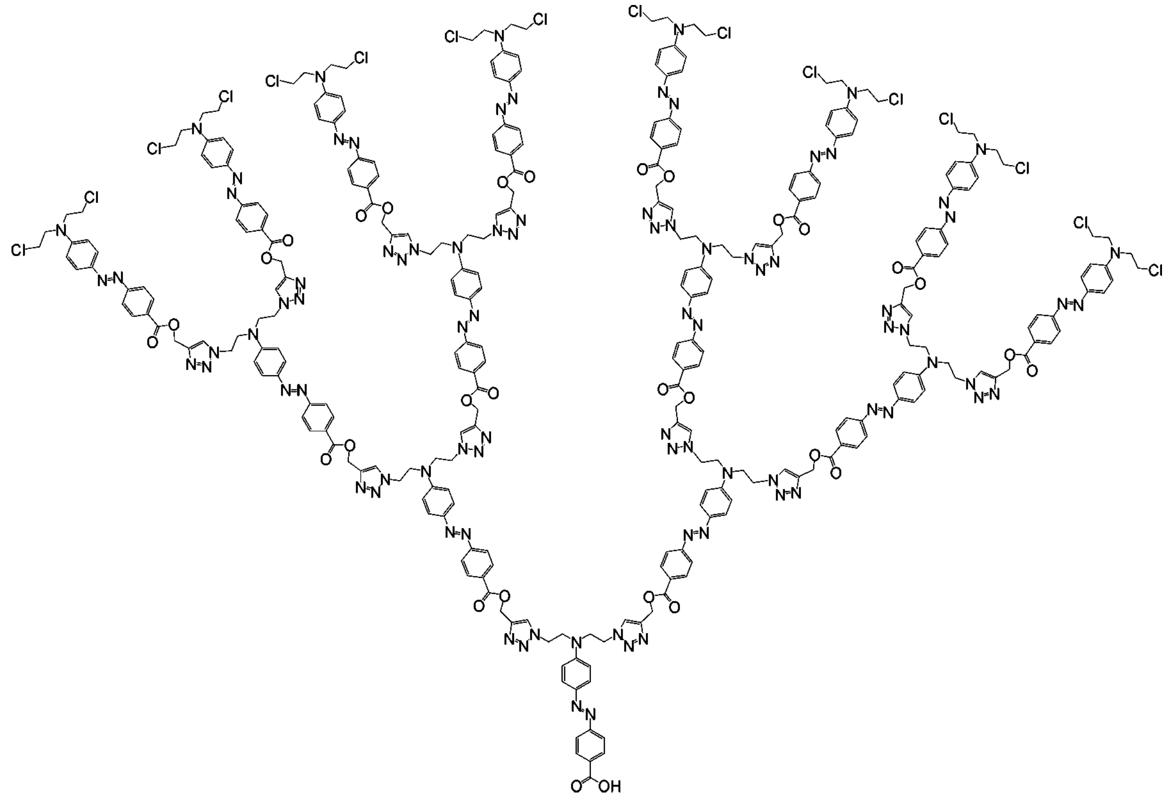
Results and Discussion

Syntheses of Triazole-Bridged Azobenzene Dendrons. The first generation azobenzene dendron, **G-1**, designed to present two chloride groups available for quantitative formation of the desired azido groups, was synthesized by the azo coupling reaction, as illustrated in Scheme 1. After esterification of **G-1** with propynol, the compound **4** was crafted to contain two chloroethyl groups and one alkyne group available to participate in click reactions during the generation growth steps. After azido substitution of the chloride groups of **G-1**, **$(N_3)_2$-G-1** was formed. Click reactions between azides of **$(N_3)_2$-G-1** and the alkyne of compound **4** resulted in the second generation **G-2**, whose structure is illustrated in Scheme 2. Dendrimer growth then proceeded via an iterative sequence that involved click reactions between the growing azide-terminated dendrons with the alkyne-functionalized compound **4**, until the fourth generation dendron (**G-4**) was obtained (Scheme 3). No protection and deprotection chemistry was needed during generation

Scheme 2. Structures of G-2 and G-3



Scheme 3. Structure of G-4



development. The click reaction were conducted in the presence of Cu(I) generated in situ from $CuSO_4 \cdot 5H_2O$ and sodium ascorbic acid, to give only 1,4-disubstituted 1,2,3-triazoles rather than a mixture with the corresponding 1,5-disubstituted isomer.

The structure of each generation dendron was thoroughly characterized by NMR spectroscopy. The triazole proton of **G-2** in DMSO-d_6 gave rise to a single peak at 8.30 ppm in 300 MHz ^1H NMR. However, in higher generations, triazole protons located at different layers caused small changes in chemical shifts. The resonant peaks of the azobenzene units in **G-2**, **G-3**, and **G-4** were apparent in region 8.02–6.68 ppm, contrasted to region 8.10–6.95 ppm for that in G-1. Separate resonances were observed apparently at 6.95 and 6.68 ppm for the o-Ar*H* to NCH_2 of azobenzene groups respectively at exterior and interior of dendrimers. New resonances caused by the formation of triazoles were observed at about 8.29 ppm and around 4.59 ppm for triazole proton and triazole$-CH_2CH_2N$, respectively, as the second, third, and fourth generation dendrimers formed. The relative integration ratios of triazole$-CH_2CH_2N$ (4.59 ppm) vs triazole$-CH_2CH_2N$ and NCH_2CH_2Cl (in region 3.88–3.82 ppm)

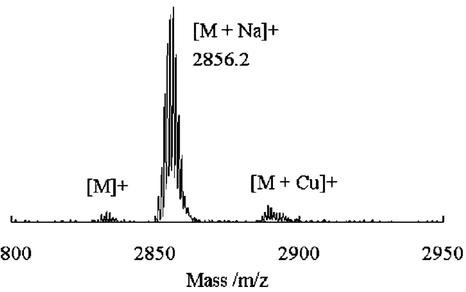


Figure 1. MALDI-TOF mass spectrum of **G-3**.

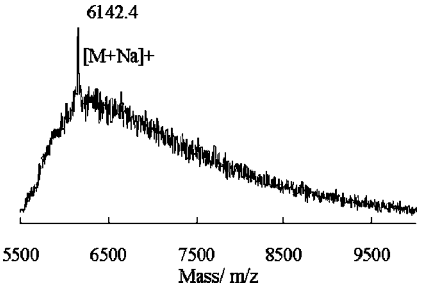


Figure 2. MALDI-TOF mass spectrum of **G-4**.

Table 1

	G-1	G-2	G-3	G-4
MW	365.1	1185.3	2831.4	6118.2
no. of azo	1	3	7	15
$\lambda_{\pi-\pi^*}$, nm	364.5	363.2	362.9	361.5
$\lambda_{n-\pi^*}$, nm	419.9	426.2	424.6	425.2
$\epsilon_0^{n\to\pi^*}$, M^{-1} cm^{-1}	15000	13100	13800	15600
$A^{trans\to cis}{}_{PSS}/A_0$	0.93	0.85	0.84	0.83
τ_1,[a] s	5.06	2.87	3.47	3.83
τ_2,[a] s	31.0	21.8	21.8	25.6

[a] τ_1, kinetic time for *cis* → *trans* transition and τ_2 for *trans* → *cis* transition under the conditions of this work.

were a useful diagnostic tool for charactering the generation progression of the dendrons. The ratios increased as the generation of dendrons grew, such as with 4:20 for **G-2**, 12:44 for **G-3**, and 28:92 for **G-4**.

The exact molecular weights (MW) of dendrons were measured by mass spectroscopy. The MALDI-TOF mass spectrum measured for dendrimers **G-3** and **G-4** showed the expected $[M + Na]^+$ ion at $m/z = 2856.2$ and 6142.4, respectively (Figures 3 and 4, respectively), while the ESI-MS measured for **G-2** showed the M^+ ion at 1188.19. The MWs of all dendrons are summarized in Table 1. All the experimental results were in good agreement with the expected molecular weights for the structures.

Photoisomerization. Azobenzene undergoes mutual isomerization between the *cis* and *trans* isomers. Though the *trans* form of the azobenzene molecule is thermodynamically more stable and therefore the *cis* form obtained by photoisomerization will return to the *trans* form in the absence of the actinic light, however, some reverse cases have also been reported; for example, the *cis* forms in an amido azobenzenesulfonate and a dumbbell-shaped azobenzene with bulky substituents were surprisingly stable in the dark.[19]

UV–vis spectroscopy was used to characterize the photoisomerization of the azobenzene dendrons synthesized in this work. Figure 3 shows the UV–vis spectra of **G-4** in THF solutions after exposure to varying conditions of UV irradiation at 302 nm (Figure 3a) or visible light (Figure 3b). The absorption band at about 361.5 nm is attributed to the $\pi \to \pi^*$ transition in *trans* isomer and the band at 425 nm to the $n \to \pi^*$ transition in *cis* isomer. The $n \to \pi^*$ band in the azodendrimers synthesized is much stronger than that in a simple azobenzene molecule due to the hyperchromic effect of amine groups. In Figure 3a, the sample solution having stored in the dark for 20 h (exposure time = 0 with absorbance of A_0) gained the curve with the characteristic of pure *cis* isomer. However, exposure to visible light caused the *cis* → *trans* isomerization, resulting in a progressive increase in the intensity of the 361.5 nm absorption band and a progressive decrease in the 460 nm absorption band, with a photostationary state (PSS) reached after about 10 s. UV irradiation at 302 nm caused a reverse isomerization (*trans* to *cis*) as noted by the decrease of the 361.5 nm band and increase of the 425 nm band, with a photostationary state reached after about 2 min (Figure 3b). The sample could also reach its initial state as the *cis* form in 20 h at darkness though a thermal isomerization process. We used the ratio of $A^{trans\to cis}{}_{PSS}/A_0$ to characterize the UV isomerization efficiency of different dendrons, where $A^{trans\to cis}{}_{PSS}/A_0$ is the absorbance at the photostationary state of UV induced *trans*-to-*cis*isomerization process, and A_0 is the absorbance maximum of the sample in 20 h in darkness. The results are listed in Table 1. For **G-4**, the photoisomerization efficiency was about 0.83. The *cis* form of the azobenzene dendron was more stable than the *trans* form in the dark. Qualitatively, similar results have been obtained for all the dendrons. As the generations of dendrons increased, the band due to the $\pi \to \pi^*$ transition shifted to a shorter wavelength; however, the band due to the $n \to \pi^*$ transition appeared at longer wavelength. The *trans*-to-*cis* photoisomerization efficiency was getting lower as the generations of dendrons increased, perhaps due to hindrance of condensed structures (Table 1).

Figure 4 shows the UV irradiation and visible light exposure time dependences of the absorbance at 460 nm for **G-4** in a dilute solution. The ordinate was normalized by the value of absorbance at zero time in the dark (A_0). The absorbance value at 460 nm exponentially decayed with increasing visible light exposure time during the *cis* → *trans* transition or exponentially increased with UV irradiation time during the *trans* → *cis* transition. The photoisomerization proceeded on the first-order reaction. Hence, the experimental results were fitted by

$$\frac{A(t)}{A_0} = I \exp\left(-\frac{t}{\tau}\right) + I_0 \qquad (1)$$

The *cis* → *trans* transition in **G-4** showed τ_1 of 3.8 s; however, τ_2 for *trans* → *cis* transition is about 25.6 s under the conditions of this work. The τ_1 and τ_2 values of other dendrons are listed in Table 1.

In summary, we have synthesized 1,2,3-triazole-linked azobenzene dendrons of four generations by click reaction. No protection−deprotection approach was needed in the synthesis via click reaction. Furthermore, the 1,2,3-triazole group could enable more novel functions for the dendrons. The isomerization was studied using UV–vis spectra. These dendrons had much strengthened $n \to \pi^*$ absorbance that facilitated photoactivated *cis* → *trans* transition. The *cis* isomers of these dendrons were more stable than *trans* isomers in the dark; however, the *cis* isomers could be quickly converted to *trans* forms under visible light exposure in seconds. The *trans* form could change to *cis* form by UV irradiation as well. Both *cis* → *trans* and *trans* → *cis* phototransition processes obeyed the first-order kinetics. The differences of characteristic kinetic times and photoisomerization efficiency between **G-1** and **G1**, **G-2**, and **G-3** were legible, perhaps due to the introduction of triazole linkages.

The *cis* forms of these dendrons were stable in the dark, however, and showed very short photoactivated lifetime of *cis* forms. Therefore, it might be possible to make fast digital nanoscale switches based on our findings. Azobezene with short *cis* lifetime and strengthened $n \to \pi^*$ absorbance thus facilitated

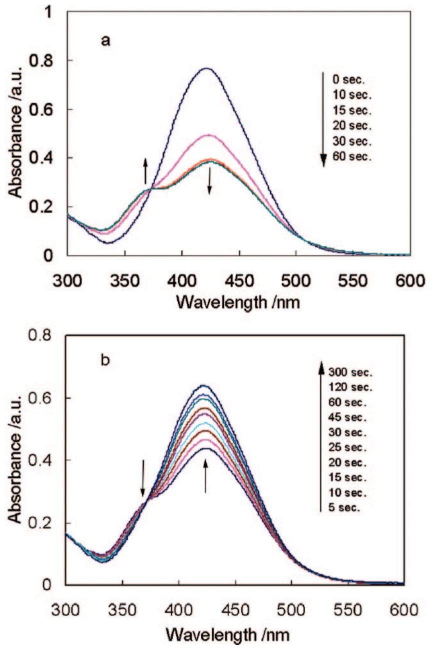


Figure 3. UV–vis spectra of **G-4** in a THF solution with a concentration of 0.02 g/mL. (a) Absorbance changes with visible light exposure time. At exposure time of zero (the highest curve), the sample has been in dark for 20 h. (b) Absorbance of the sample that has reached the photostationary state in (a) changes with UV irradiation (302 nm) time.

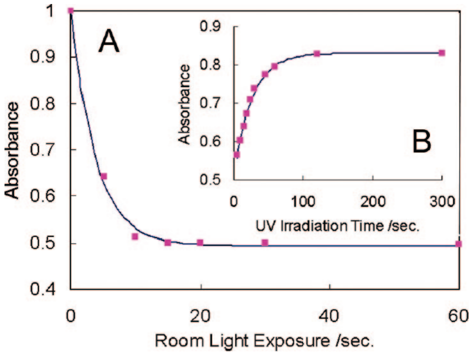


Figure 4. (A) Dependence of absorbance at 460 nm for **G-4** in a dilute solution on the visible light exposure time during the *cis* → *trans* transition process. (B) Dependence of absorbance on the UV irradiation (302 nm) time during the *trans* → *cis* transition process. The absorbance ordinates were normalized by the value of absorbance at zero time in the dark. The solid lines are fitting curves according to the first-order kinetics.

cis → *trans* photoisomerization process were good candidates for photoinduced birefringence.

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Supporting Information Available: Experimental details in the synthesis of **G-3** and **G-4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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