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Photoisomerization and Fluorescence Properties of *para*-Substituted Benzyl Ether-Type Stilbene Dendrimers

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Stilbene dendrimers were prepared by coupling 4,4′-dihydroxystilbene with first, second, third, or fouth generation benzyl ether-type dendrons. Despite a short lifetime of the core structure (<1 ns), all the generations of stilbene dendrimers underwent photoisomerization with the same efficiency as that of 4,4′-dimethoxystilbene.

The movement of a large molecular weight molecules is related to signal transmission, such as vision. In this system, the isomerization of a retinal chromophore induces a structural change in the protein. We have been studying a series of stilbene dendrimers, which have large molecular weight and undergo photoisomerization with considerably high efficiency.[1] Photoisomerization of stilbene dendrimers takes place within the singlet lifetime of stilbene followed by a structural change in a part of the dendron to give a stable conformation.

In the course of our studies, we have found that the stilbene dendrimers, in which a series of benzyl ether-type dendrons are substituted at the *meta* position of stilbene, (*m*-G*n*; $n =$ 1, 2, 3, and 4), underwent photoisomerization with almost the same efficiency as that of 3,3′,5,5′-tetramethoxystilbene (*m*-G0).[2,3] For example, *m*-G4 with a molecular weight over 6500 underwent *trans–cis* isomerization in the singlet excited state within 10 ns.[2] According to these results, the photoisomerization of *m*-G4 is supposed to take place via a volume conserving mechanism such as Hula-twist mechanism,[4,5] in which the C=C double bond and the adjacent single bond rotate simultaneously. If the photoisomerization of stilbene dendrimers takes place via a conventional one-bond rotation mechanism, isomerization would be accompanied by a large structural change in dendrons.

The movement of the dendrons is expected to be much slower than that of the stilbene core because of the large difference in molecular weight and steric hindrance. The singlet lifetime (350 ps)[6] of *trans*-4,4′-dimethoxystilbene, which is indicated as *trans*-G0 in Fig. 1, is much shorter than that of 3,3′,5,5′-tetramethoxystilbene (10 ns).[2] Therefore, the dendron could influence the photoisomerization of *para*-substituted stilbene G0–G4 (Fig. 1) more strongly than that of *meta*-substituted stilbene, because a dendron may not keep up with the movement of photoisomerization of the stilbene core with a short singlet lifetime of hundreds of picosecond for *para*-substituted stilbene.

All the generations of *para*-substituted stilbene dendrimers G0–G4 were synthesized by a coupling reaction between *trans*-4,4′-dihydroxystilbene and the corresponding benzyl-type dendritic bromide in the presence of K_2CO_3 and 18-crown-6 in 2-butanone.[2,7] *trans*-G0, *trans*-G1, and *trans*-G2 were purified by recrystallization, and *trans*-G3 and *trans*-G4 were purified by gel permeation column chromatography. The molecular weight of *trans*-G3 was measured by MALDI-TOF-MS. However, the mass peak for *trans*-G4 could not be found in the MS. HPLC analysis by using a gel permeation column (Column TOSOH, G-2500H HR; eluent, chloroform) gave the retention time of 9.46 and 8.75 min for *trans*-G3 and *trans*-G4, respectively. In addition, ^{1}H NMR, absorption, fluorescence, and fluorescence excitation spectra support the structure of *trans*-G4.

Figure 2 shows absorption spectra of *trans*-G1, -G2, -G3, and -G4 compared with that of *trans*-4,4′-dimethoxystilbene (G0) in THF under argon atmosphere. An absorption band appeared in the wavelength region from 300 to 340 nm with a maximum of 328 nm for G1 to G4 is similar to that of G0, and therefore, the absorption band is assigned to the core stilbene. On the other hand, the molar extinction coefficient at 284 nm increased with each generation of the dendrimer, and therefore, the band was assigned to the benzyl ether-type dendron group.

Stilbene dendrimers, G1–G4, underwent *trans–cis* isomerization upon irradiation at 330 nm in THF solution under argon atmosphere. Figure 3 shows the absorption spectral changes for *trans*-G4 on irradiation at 330 nm in THF solution, and the absorbance changed at 328 nm (the absorption maximum) for *trans*-G0–G4 with irradiation time. The absorbance at 328 nm decreased upon irradiation with an isosbestic point in the absorption spectra at around 278 nm to give a photostationary state.

The quantum yield of *trans*-to-*cis* isomerization of G0 was determined to be 0.32 in THF by HPLC analysis and by using tris(oxalate)ferrate actinometry. In addition, the quantum yield of *trans*-to-*cis* isomerization of G1, G2, G3, and G4 was determined to be 0.46, 0.37, 0.36, and 0.36, respectively. These results showed that the introduction of dendron substituents scarcely affects the efficiency of photoisomerization.

Figure 4 shows fluorescence and fluorescence excitation spectra of *trans*-G1, -G2, -G3, and -G4 compared with that of G0 in THF under argon atmosphere. The spectral shape and the maximum wavelength of the *trans*-form of dendrimers upon irradiation at 330 and 280 nm were the same as those of the *trans*-G0, indicating that the fluorescence emission was observed from the excited singlet state of the stilbene core. The quantum yield of fluorescence emission upon irradiation at 330 nm was 0.34, 0.41, 0.41, 0.46, and 0.47 for *trans*-G0, -G1, -G2, -G3, and -G4, respectively. The result showed that the introduction of a dendron group slightly increased the fluorescence quantum yield.

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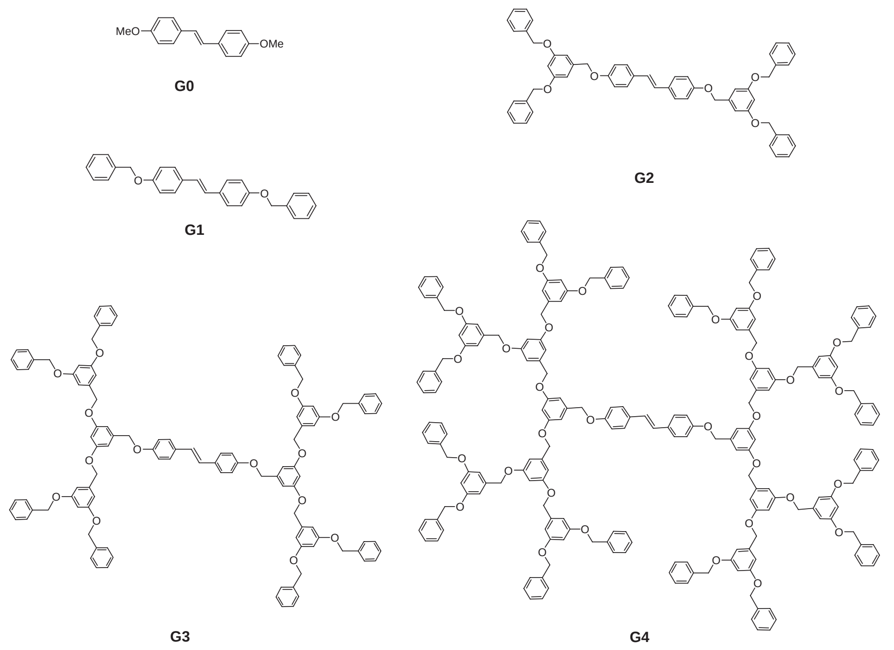

Fig. 1. Structures of stilbene dendrimers-substituted dendron at *para* position of stilbene.

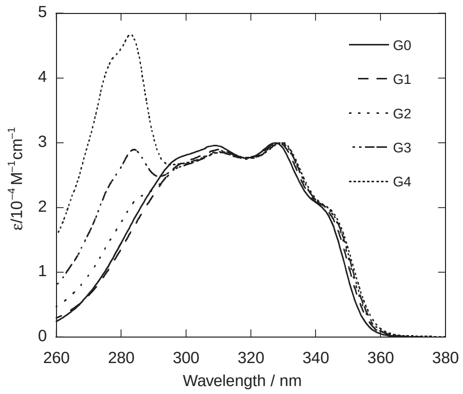

Fig. 2. Absorption spectra of *trans*-G0, -G1, -G2, -G3, and -G4 in THF under argon atmosphere.

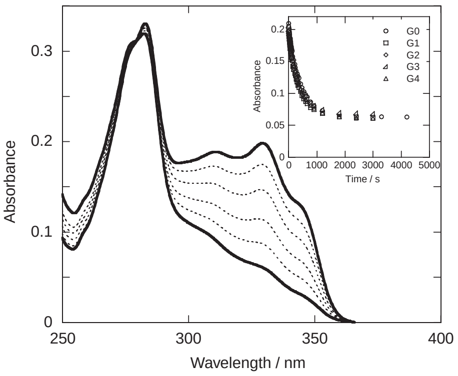

Fig. 3. Change in the absorption spectrum of *trans*-G4 upon irradiation at 330 nm in THF under argon atmosphere. Inset shows the change in the absorbance at 330 nm of the optically matched THF solutions of G0, G1, G2, G3, and G4 upon irradiation at 330 nm.

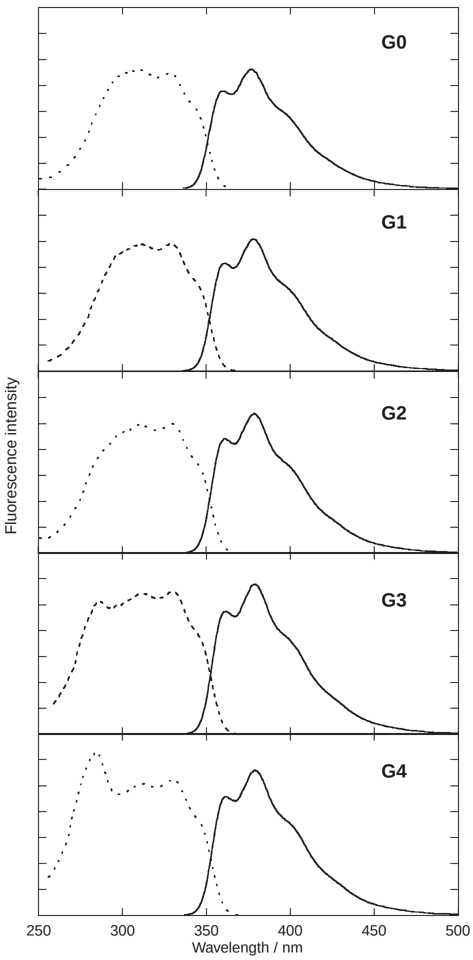

Fig. 4. Fluorescence spectra and fluorescence excitation of *trans*-G0, -G1, -G2, -G3, and -G4 in THF under argon at room temperature.

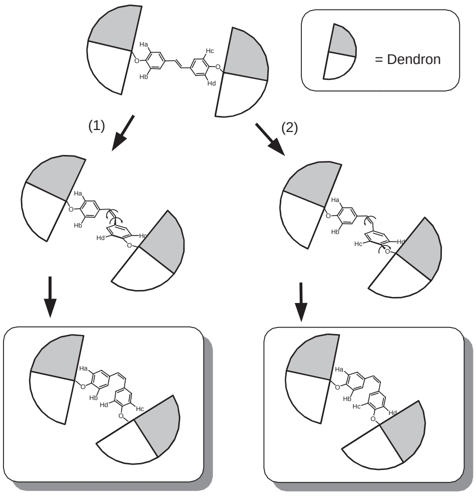

Fig. 5. Postulated mechanism of *trans–cis* isomerization in *para*-substituted stilbene dendrimer.

The dendrimers, *trans*-G1, -G2, -G3, and -G4, did not exhibit the fluorescence emission attributed to the dendrons even upon irradiation at 284 nm, where the dendron group mainly absorbed the light.[8,9] The efficiency of the singlet energy transfer from a dendron to a stilbene core can be estimated from the normalized fluorescence excitation spectrum and absorption spectrum. Thus, the quantum yield of energy transfer (Φ_{ET}) from a dendron to stilbene core was calculated to be 1, 0.65, and 0.57 for *trans*-G2, -G3, and -G4, respectively. The value of Φ_{ET} was related by the distance between peripheral dendron group and a stilbene core, and energy transfer showed to take place by the Förster mechanism.

The singlet lifetime of *trans*-3,3′,5,5′-tetramethoxystilbene depends on the presence of oxygen, temperature, and solvent, probably due to the long singlet lifetime of ca. 10 ns.[2] In this case, temperature affects the rate constant of *trans–cis* isomerization in the excited singlet state having activation barrier.[10] We tried to determine the fluorescence lifetime of *trans*-G0–G4, but the lifetime was out of range of the detection limit (1 ns) of our single photon counting apparatus (Horiba NAES-1100). These results indicate that the fluorescence lifetime of the stilbene core was scarcely affected by the dendron group, and the dendrimers underwent *trans–cis* isomerization within the singlet lifetime of hundreds of picosecond. A bulky dendron group may affect the isomerization due to the steric hindrance. However, the stilbene dendrimers G0–G4 underwent photoisomerization with a high quantum yield of 0.3 as mentioned above. This means that the isomerization should take place not by a one-bond rotation but by a concomitant twisting of the single bond and the double bond.

According to these results, the *para*-substituted stilbene dendrimers seem to undergo *trans–cis* photoisomerization by a Hula-twist mechanism (Path (1) in Fig. 5). Another possible explanation is that *trans–cis* photoisomerization of *para*-substituted stilbene dendrimers, G1–G4, could take place simultaneously with a rotation of the ether bond at the *para* position of the sitilbene due to higher symmetry than *m*-G*n* (Path (2) in Fig. 5). In any case, photoisomerization of stilbene dendrimers should take place concomitant rotations of the C=C double bond and a single bond.

In conclusion, benzyl ether-type dendrons slightly affected the movement of a core molecule, indicating the occurrence of a volume conserving isomerization mechanism. Thus, the *trans–cis* isomerization takes place within subnano-second time scale within the interior of the dendrimers. These results will open a way to develop the photoresponsive macromolecules based on *trans–cis* isomerization of olefins and to show how large molecules move.

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7 *trans*-G1: ^{1}H NMR (400 MHz, DMSO): δ 5.08 (4H, s), 6.96 (4H, d, $J = 8.8$ Hz), 7.00 (2H, s), 7.25–7.49 (14H, m). Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68, H, 6.16%. Found: C, 85.01, H, 6.30%. *trans*-G2: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (4H, s), 5.02 (8H, s), 6.55 (2H, t, $J = 2.4$ Hz), 6.67 (4H, d, $J = 2.0$ Hz), 6.90–6.92 (6H, m), 7.26–7.43 (24H, m). Anal. Calcd for $C_{56}H_{48}O_6$: C, 82.33, H, 5.92%. Found: C, 82.03, H, 6.22%. *trans*-G3: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (4H, s), 4.99 (8H, s), 5.02 (16H, s), 6.54 (2H, t, $J = 2.2$ Hz), 6.56 (4H, t, $J = 2.2$ Hz), 6.62–6.69 (12H, m), 6.89 (4H, d, $J = 10.4$ Hz), 6.93 (2H, s), 7.26–7.44 (44H, m). MALDI-TOF-MS Calcd for $C_{112}H_{96}O_{14}$ $[M]^+ = 1664.7$; Found 1664.2. *trans*-G4: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.88–4.97 (28H, m), 5.04 (32H, s), 6.49–6.57 (14H, m), 6.55 (4H, d, $J = 8.8$ Hz), 6.59–6.71 (28H, m), 6.89 (2H, s), 7.26–7.41 (84H, m).

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