The First Synthesis of Stilbene Dendrimers and their Photochemical *trans–cis* Isomerization

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Highly branched stilbene dendrimers underwent *trans–cis* isomerization in the excited singlet state within the lifetime of 10 ns.

Recently much attention has been focused on the synthesis and the function of dendritic macromolecules such as in enzymatic reactions.[1,2] However, only a limited number of photochemical reactions of dendritic compounds have been reported. For example, dendrimers having azobenzene as a core have been studied, where *trans*-azobenzene dendrimers underwent isomerization to give the *cis*–isomer on photoirradiation followed by the thermal reverse *cis*-to-*trans* isomerization.[3,4] The *cis–trans* isomerization can occur through either the inversion mechanism or the rotation mechanism in azobenzene derivatives. Since azobenzene does not emit fluorescence, the dynamic behaviors in the excited state could not be studied.

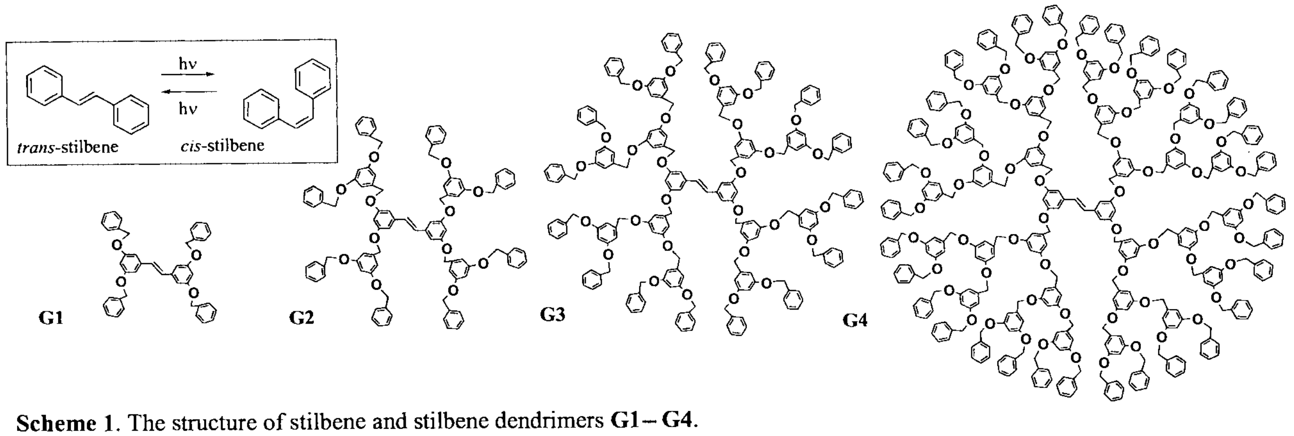
The photochemical *cis–trans* isomerization of arylethenes usually takes place in the excited state through the rotation around the C=C double bond.[5,6] We have prepared a series of arylethenes and found that their photochemical isomerization can be modified by introduction of an appropriate aryl substituent on ethylenic carbon inducing the diabatic mutual isomerization and the adiabatic one-way *cis–trans* isomerization depending on the energetic profiles of the aryl substituent.[7]

We now wish to report the first synthesis of a series of stilbene dendrimers G1–G4 (Scheme 1) and their photoisomerization behavior. The photoisomerization of C=C double bond could not occur by inversion mechanism which does not need large motion of the substituent on the double bond but can take place by the rotation around the double bond.[5,6] There are several advantages to study the dendrimers having the stilbene core, where the most prominent one must be that one could follow their dynamic behavior by fluorescence[8] as well as transient spectroscopy. Actually, the stilbene dendrimers exhibited fluorescence emission with moderately high quantum efficiency.

A series of dendrimers (G1–G4) have been prepared and their structures have been determined by NMR and TOFMS spectroscopy.[9] Figure 1 showed the absorption spectra of G1–G4 in tetrahydrofuran (THF) at room temperature. All the compounds exhibited the similar absorption spectra at 300–350 nm with the absorption maximum at 310 nm due to the stilbene core. However, the absorbance at 280 nm increased with increasing of the generation of the dendrimer due to the absorption of the benzylether group of the surrounding dendron.

The fluorescence emission has been observed for all the stilbene dendrimers with similar fluorescence maximum at 400 nm. The quantum yield of fluorescence emission is almost the same for G1–G3 with the value of ca. 0.6, while that of G4 is slightly higher than G1–G3 and is 0.71. The fluorescence excitation spectra are similar to the absorption spectra of the corresponding dendrimers indicating that not only the photon absorbed by stilbene core, but also that absorbed by surrounding dendron group could induce the fluorescence emission from the stilbene core. Since the surrounding dendron and the stilbene core have no π conjugation, one could explain the occurrence of the efficient energy transfer from dendron group to the stilbene core by dipole–dipole interaction to give the core fluorescence emission. The efficiency of the energy transfer process from dendron group to the core (Φ_{ET}) was estimated by comparing the fluorescence quantum yield by excitation at 280 nm (dendron excitation) with that by excitation at 310 nm (core stilbene excitation). Thus, Φ_{ET} was determined to be 0.81 and 0.34 for G3 and G4, respectively.

On irradiation with 330 nm light from the 150 W xenon lamp through the monochrometer, *trans*–isomers of G1–G4 underwent *trans*-to-*cis* isomerization as revealed by the change of the absorption spectra. A typical example for G1–G4 is shown in Figure 2. The photochemical isomerization on direct irradiation can proceed in the excited singlet state as well as in the



Scheme 1. The structure of stilbene and stilbene dendrimers **G1 – G4**.

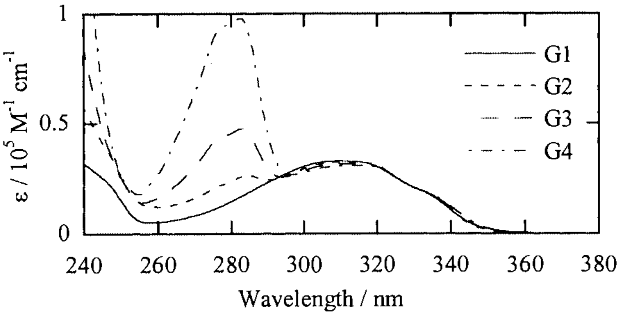


Figure 1. Absorption spectra of stilbene dendrimers G1–G4 in THF.

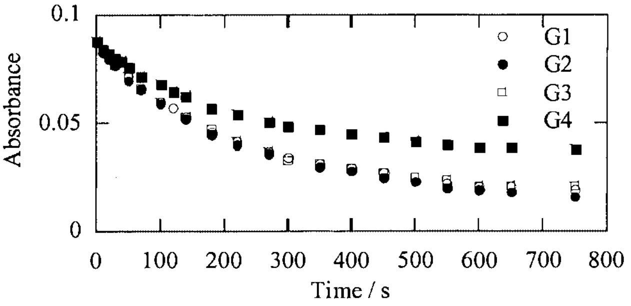


Figure 2. Change of absorbance at 330 nm for G1–G4 with irradiation at 330 nm under argon in THF.

triplet state. In order to clarify the mechanism of the *trans–cis* isomerization of stilbene dendrimers, we have studied the temperature effect on the fluorescence lifetime as well as the laser transient spectroscopy. All the dendrimers G1–G4 gave no detectable T–T absorption spectra indicating that the isomerization proceeds not in the triplet state but in the excited singlet state.

Stilbene dendrimers G1–G4 have a fluorescence lifetime of 9.3–9.7 ns at 23 °C and the lifetime changed with the temperature to give 10.8–11.3 ns at 0 °C and 7.7–8.0 ns at 50 °C in THF. Therefore, the *trans–cis* isomerization of G1–G4 should take place in the excited singlet state. The deactivation of the stilbene usually takes place by the isomerization around the double bond in the excited singlet state (k_{iso}), fluorescence emission (k_f), and intersystem crossing to the triplet state (k_{isc}). Since the intersystem crossing to the triplet state could not be detected in G1–G4, one can assume that $k_{isc} << (k_{iso} + k_f)$. Thus, by using the fluorescence quantum yields and the fluorescence lifetimes determined at varying temperature, the temperature dependent k_{iso} values can be evaluated. The Arrhenius plot gave the activation energy E_a and the frequency factor A for the isomerization in the excited singlet state. The E_a and A values are almost the same for G1–G3 as 2.6 kcal mol^{-1} and 4×10^9 s^{-1}, respectively, but those for G4 are considerably different and are 4.3 kcal mol^{-1} and 4×10^{10} s^{-1}, respectively. These results indicate that the mechanism of *trans–cis* isomerization of G4 might be quite different from that of G1–G3.

The isomerization of the one bond rotation around the central double bond needs considerably large volume change in G4 which does not seem to take place within the singlet lifetime. With regard to the *cis–trans* isomerization in highly condensed media at low temperature or in protein, Liu and Hammond postulated quite interesting mechanism called Hula–Twist (H–T) mechanism,[10] where isomerization takes place not by the one-bond rotation around the double bond but by the concomitant twist of the double bond and the adjacent single bond to accomplish the double bond isomerization.

In the H–T mechanism, highly congested substituent slides to the isomer along the reaction coordinate. Therefore, the H–T mechanism does not need a large motion of internal rotation and we may explain the relatively efficient *trans–cis* photoisomerization in G4 by this mechanism. The H–T mechanism was observed in the isomerization of the vitamin D derivatives at 77 K[11] and the mechanism seems to be applied to the isomerization in glassy solvent at low temperature or in largely congested environment such as in protein. The present finding indicates that isomerization by H–T mechanism can occur at room temperature in fluid solution.

In summary, we have successfully prepared a series of stilbene dendrimers exhibiting fluorescence emission with considerably high quantum efficiencies. In addition, we have found that even the G4 stilbene dendrimer with the molecular weight as high as 6548 can undergo isomerization around the double bond within the lifetime of its excited singlet state as revealed by fluorescence spectroscopies. To the best of our knowledge this is the first clear experiment that photochemical isomerization of the C=C double bond in molecular weight of over 6000 can take place efficiently within 10 ns time scale.

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9 G1: ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 5.07 (8H, s, CH_2), 6.56 (2H, s, Stilbene-C_6H_3-4,4'), 6.75 (4H, s, Stilbene-C_6H_3-1,1',5,5'), 6.98 (2H, s, olefin), 7.27–7.46 (20H, m; C_6H_5). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 70.16, 101.77, 105.95, 121.05, 127.62, 128.10, 128.69, 136.92, 139.27, 160.26. G2: MALDI-TOFMS. Found: m/z 1476.5. Calcd for $C_{98}H_{84}O_{12}Na$: $[M+Na]^+$, 1476.7. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 4.99 (4H, s, CH_2), 5.02 (4H, s, CH_2), 6.56–6.75 (18H, m, inner C_6H_3), 6.98 (2H, s, olefin), 7.21–7.43 (40H, m, outer C_6H_5). G3: MALDI-TOFMS. Found: *m/z* 3175.1. Calcd for $C_{210}H_{180}O_{28}Na$: $[M+Na]^+$, 3174.7. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 5.07 (56H, m, CH_2), 6.45–6.73 (42H, m, Ph), 6.97 (2H, s, olefin), 7.22–7.38 (80H, m, Ph). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 70.08, 101.90, 106.15, 127.64, 128.08, 128.66, 136.76, 139.49, 160.45. G4: MALDI-TOFMS. Found: *m/z* 6557.8. Calcd for $C_{434}H_{372}O_{60}Li$: $[M+Li]^+$, 6554.7. ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 4.71–5.01 (120H, m, CH_2), 6.39–6.68 (90H, m, inner C_6H_3), 6.91 (2H, s, olefin), 7.12–7.42 (160H, m, outer C_6H_5).
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