The Photochemical Specific Isomerization of Dendritic Stilbenes

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The photochemical properties of stilbene dendrimers **1**–**3** in THF, as well as the corresponding potassium salts (water-soluble stilbene dendrimers = WSDs) **4**–**6** in aqueous solution were studied. Unlike the stilbene dendrimers **1**–**3**, the environment of the core moiety in WSDs **4**–**6** depended on the generation. The first generation WSD **4** suffers from the water atmosphere around the stilbene core, as can be understood by the molecular structure. The largest Stokes shift observed in **4** among WSDs indicated that the dipole moment changed considerably upon photoexcitation. The Stokes shift tended to become smaller in higher generations. This means that the surrounding dendron should block the water molecule from reaching the stilbene core. The core stilbene in G3 WSD **6** may have an environment almost free of water, based on the observation of a similar Stokes shift of that of stilbene dendrimer **3**, only soluble in organic solvents in which the core stilbene has a hydrophobic environment. These findings can be extended to the preparation of water soluble organic molecules with hydrophobic interiors with a photoresponsive chromophore at the core as a single molecule. Most interestingly, **6** underwent a photochemical one-way *trans*-to-*cis* isomerization. In addition to the photochemical studies of **1**–**6**, the fluorescence properties of G3 dendrimer **3** were compared to those of the other series of stilbene dendrimer **7**, which have no carboxylate groups at the periphery.

Dendrimers have a well defined molecular structure and can be used to make new materials.[1–3] Among them, photochemical reactions and the approach to amplify structural changes of the chromophore with a small molecular weight to a large structural change of the whole molecule would be interesting. In this respect, we have prepared several dendrimers having a photoresponsive molecular structure.[4–7] Stilbene dendrimers having benzyl ether type dendron groups at the meta-position of the phenyl ring of the core stilbene underwent mutual photoisomerization between *cis*- and *trans*-isomers.[6] The *trans*-to-*cis* photoisomerization proceeds through the deactivation from the excited singlet state perpendicular conformation, as revealed by the temperature effect on the fluorescence lifetime. In addition, transient grating experiments were done to observe the deactivation processes indicated that part of the isomerization takes place in the excited triplet state after intersystem crossing. Molecular oxygen quenched the excited singlet state of the core stilbene, which has a fluorescence lifetime of ca. 10 ns, and was reduced in the presence of oxygen to 3–5 ns depending on the generation. We have observed a relation between the oxygen quenching of the core stilbene and the acceleration of the *trans*-to-*cis* isomerization in tristyrylbenzene dendrimers having an excited singlet lifetime state as long as 20 ns.[8] Furthermore, the fluorescence properties and the isomerization behavior of stilbene dendrimers having polyphenylene type dendron groups have been reported.[9,10]

The azobenzene dendrimers, which usually do not have any fluorescence, were prepared and their photochemical isomerization,[11,14] and unusual energy accumulation of the infrared light,[12] and some thermodynamic parameters were reported.[13]

The above dendrimers can be dissolved only in organic solvents. However, the photochemical properties of the dendrimers in water are of interest from the view point of mimicing photoresponsive biomaterials. We have already reported the synthesis and photochemical behavior of water soluble stilbene dendrimers (WSDs).[15,16] Very interestingly, the third generation WSD exhibited one-way *trans*-to-*cis* isomerization upon photoirradiation. In the previous communication, we reported only the qualitative behavior of this one-way *trans*-to-*cis* photoisomerization. We have determined the quantum yield of the isomerization as well as the fluorescence quantum yields and fluorescence lifetimes. On the basis of theses results an unusual *trans*-to-*cis* one-way isomerization is discussed. In addition, the present paper aims to report a full account of the photochemical properties of water soluble stilbene dendrimers (WSDs). Furthermore, the photochemical properties of the methyl ester of the peripheral carboxylate group were reported.

Experimental

Material and Solvents. The synthesis and characterization of *trans*-isomers of stilbene dendrimers (**1**–**6**, Fig. 1), and corresponding *cis*-isomers (*cis*-**1**–*cis*-**6**) were already reported in the previous paper.

Measurement. Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with a Horiba NAES-1100 time resolved spectrofluorometer. The quantum yields of fluorescence emissions were determined by using naphthalene ($\Phi_f = 0.23$) as a standard. A correction in the difference in refractive index among the solvents was made for each sample. The absorbance of the sample solution at the excitation wavelength was adjusted to less than 0.1, and the inte-

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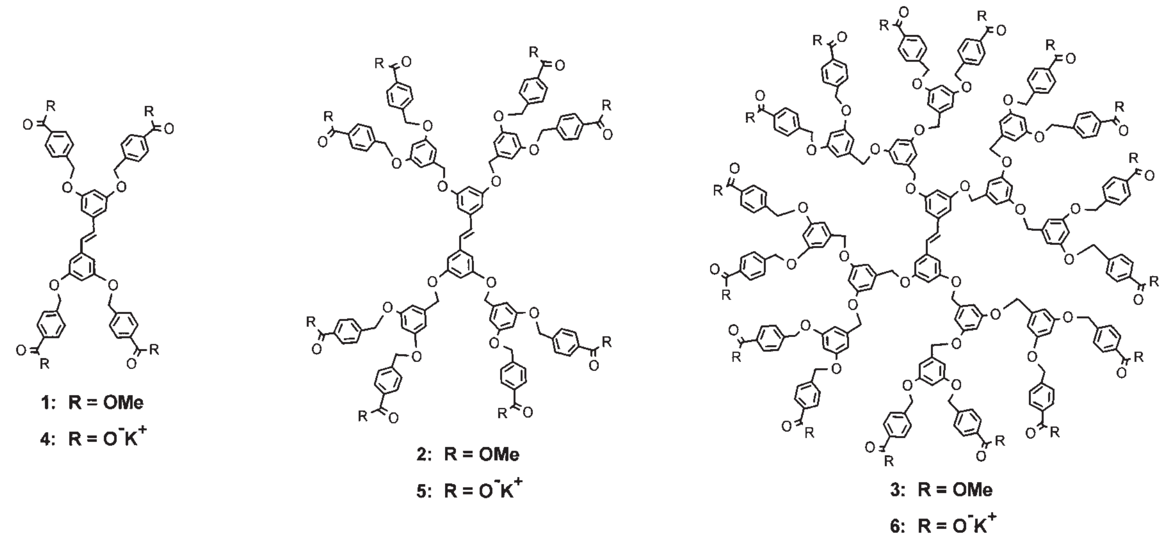


1: R = OMe
4: R = O^-K^+

2: R = OMe
5: R = O^-K^+

3: R = OMe
6: R = O^-K^+

Fig. 1. Structures of *trans*-isomers of stilbene dendrimers **1**–**3** and water-soluble stilbene dendrimers (WSDs) **4**–**6**.

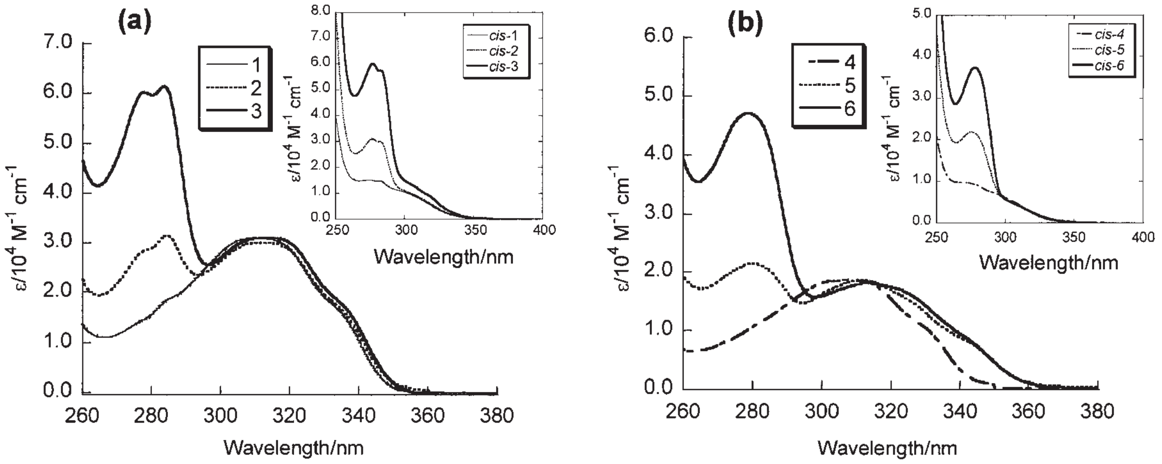


Fig. 2. UV absorption spectra of (a) stilbene dendrimers **1**–**3** in THF solution and (b) WSDs **4**–**6** in 2×10^{-3} M KOH aqueous solution. Inset in Fig. 2a shows the absorption spectra of *cis*-**1**–*cis*-**3** in THF solution. Inset in Fig. 2b shows the absorption spectra of *cis*-**4**–*cis*-**6** in 2×10^{-3} M KOH aqueous solution.

gration of the fluorescent spectra over all wavenumbers was plotted against absorbance at the excitation wavelength. The slope of these plots gives the relative value of the fluorescence quantum yield, and the quantum yield of fluorescence emission was then determined. The quantum yield of the *trans*-to-*cis* isomerization of *trans*-isomer **1** was determined upon irradiation at 313 nm from a 150 W xenon lamp through a monochrometer. The sample solution was deaerated by bubbling argon, and irradiated for 20 min to keep the conversion within 8%. The light intensity was determined by tris(oxalato)ferrate(III) actinometry. The concentration of each isomer was determined by high-performance liquid chromatography through a column (Kanto RP-18) eluting with methanol–water = 92:8. The quantum yield of other dendrimers was determined by comparison of the rate of absorbance change of the optically matched solution at 330 nm with that of *trans*-**1** under the same irradiation conditions.

Results

Absorption Spectra. Figures 2a and 2b show the absorption spectra of the *trans*-isomer of stilbene dendrimers **1**–**3** in THF and the corresponding potassium salts **4**–**6** (WSDs **4**–**6**) in 2×10^{-3} M KOH aqueous solution (pH 10.5), respectively. The inset in Figs. 2a and 2b shows the *cis*-isomers of **1**–**3** and **4**–**6**, respectively. In all spectra, the increase in the absorption maximum at 277–280 nm with increasing generations for each compound indicates increments of the benzyl ether group. All *trans* form dendrimers exhibited absorption at 300–360 nm with $\lambda_{\max}$ at 310–315 nm due to the *trans*-stilbene cores, whereas a much smaller absorption coefficient at 300–360 nm was observed for *cis*-isomers. In Fig. 2a, the π–π^* absorption band of the stilbene moiety appeared in almost the same region among **1**–**3**, while, as shown in Fig. 2b, the absorption band of the *trans*-stilbene moiety in WSDs **4**–**6** appeared in different regions between the lower and the higher generations of dendrimer. The penetration of water into the core stilbene tends to become difficult with increasing generations of the dendrimer. Thus, the core stilbene in **6** must have a more hydrophobic environment with increasing generation. The third generation of WSD **6** showed almost the same absorption spectra with that of the stilbene dendrimers **1**–**3** soluble in organic solvents.

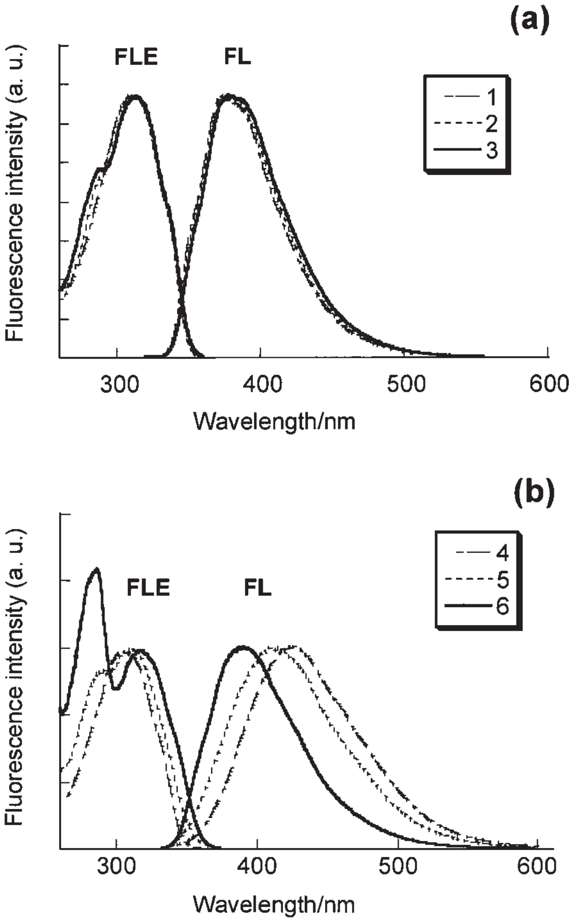


Fig. 3. Fluorescence (FL) and fluorescence excitation spectra (FLE) of **1**–**3** in THF solution (a) and **4**–**6** in 2×10^{-3} M KOH aqueous solution (b). The spectra were measured with the absorption maximum to be <0.1 and were normarized.

Fluorescence. All *trans*-isomers of **1**–**6** fluorescenced and all *cis*-isomers did not show any fluorescence at room temperature. The fluorescence spectra of the *trans*-isomers of **1**–**3** are shown in Fig. 3a. The fluorescence maximum slightly shifted to a longer wavelength at higher generations to give $\lambda_{\max} = 376$, 380, and 387 nm, respectively, for **1**, **2**, and **3**. The fluorescence lifetime under an argon atmosphere was determined to be 4.6, 6.8, and 6.3 ns for **1**, **2**, and **3**, respectively. These values are shorter than those observed for the benzyl ether type stilbene dendrimers without methoxycarbonyl groups at the periphery. Thus, the peripheral methoxycarbonyl groups may exhibit some effects in decreasing the fluorescence lifetime. The fluorescence quantum yield of **1** (0.27) is slightly lower that that for **2** (0.39) and **3** (0.40). The fluorescence excitation spectra of the core stilbene at 300–360 nm is almost the same as the absorption spectra, but the spectral profile of the fluorescence excitation spectra of *trans*-**2** and **3** at 280 nm are quite different from those of the absorption spectra. These results show that the energy transfer from the dendron group to the core stilbene scarcely takes place.

The fluorescence and fluorescence excitation spectra of WSDs **4**–**6** in aqueous solution are shown in Fig. 3b. The fluorescence maximum shifted to shorter wavelengths with increasing generations, from 426 nm for **4** to 389 nm for **6**. The fluorescence excitation spectra were similar to those of the absorption spectra. The considerably large peak at 280 nm in **5** and **6** due to the absorption of the dendron groups in the fluorescence excitation spectra indicates the occurrence of an efficient energy transfer from the peripheral dendron groups to the core stilbene. One can estimate the energy transfer efficiency by comparing the absorption spectra and the fluorescence spectra of the dendron part and the stilbene part. Thus, the energy transfer efficiency for **5** is as high as 49% and 31% for **6**. The fluorescence quantum yield for WSDs **4**–**6** depended on the generation; 0.21, 0.05, and 0.17 for **4**, **5**, and **6**, respectively.

The *trans*-isomer of **4** gave a fluorescence lifetime of 15 ns with single exponential decay. However, the fluorescence decay curves did not fit a single exponential function, but rather fit two exponential functions to give 2.1 and 11.1 ns for **5** and 3.7 and 11.2 for **6**. These results indicate that the structure and environment are not uniform in **5** and **6**.

Photoisomerization and Photocyclization. On irradiation with 330 nm light under argon, the *trans*-isomers of stilbene dendrimers **1**–**3** and WSDs **4**–**6** underwent isomerization around the double bond to give the corresponding *cis*-isomer (Fig. 4). The isomer ratio at the photostationary state ($[t]/[c])_{pss}$ was determined to be 33/67, 24/76, and 8/92 for **1**, **2**, and **3**, respectively (Table 1). Thus, with increasing generations of the stilbene dendrimer, the *cis*-isomer composition in the photostationary state increased. A similar tendency was observed for the other series of stilbene dendrimers, as well as WSDs **4**–**6**: the photostationary state *trans*-to-*cis* isomer ratio $([t]/[c])_{pss}$ was 6:94, 1:99, and 0:100 for **4**, **5**, and **6**, respectively, in water at pH 10.5. The quantum yield of the *trans*-to-*cis* isomerization was almost constant among stilbene dendrimers **1**–**3** in THF, 0.27 for **1** and 0.26 for both **2** and **3**, while the quantum yields of the *trans*-to-*cis* isomerization for WSDs **4**–**6** depended on the generation, and was determined to be 0.17, 0.47, and 0.15 for **4**, **5**, and **6**, respectively.

On UV irradiation, *cis*-**1** underwent a photocyclization reaction with a quantum yield (Φ_{cycl}) of 0.27 as well as *cis*-to-*trans* isomerization ($\Phi_{c \rightarrow t} = 0.09$). Since the photocyclization of 3,3′,5,5′-tetramethoxystilbene took place quite efficiently,[5] the cyclization was expected, especially in the lower generation dendrimer **1**. In the case of the higher generation dendrimer **3**, however, photocyclization did not take place, probably due to the bulky dendron groups. A photocyclization reaction in the *cis*-isomers did not take place for any WSDs **4**–**6**. The quantum yield of the *cis*-to-*trans* isomerization was determined to be 0.06 and 0.10 for **4** and **5**.

Discussion

The water soluble stilbene dendrimers studied in this paper have three major remarkable features. The most interesting feature is the one-way *trans*-to-*cis* isomerization giving 100% *cis*-isomer in the photostationary state in **6** (Scheme 1). Usually, stilbene undergoes a photochemical mutual isomerization to give a photostationary mixture of *trans*- and *cis*-isomers with prolonged irradiation. There are exceptions to this one-way isomerization. One of them is the photochemical one-way isomerization from *cis*-to-*trans* for stilbene-like compound with an anthracene ring instead of one of the phenyl rings. Thus, sty-

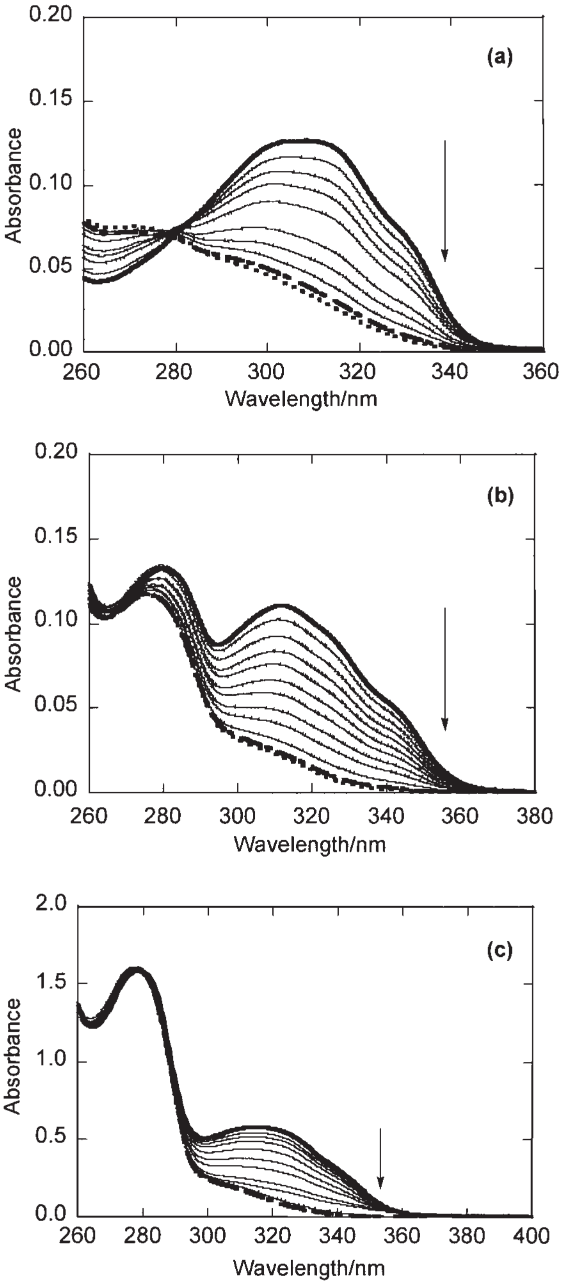


Fig. 4. Change of the absorption spectra of **4** (a), **5** (b), and **6** (c) on irradiation with 330 nm light in 2 × 10^{-3} M KOH aqueous solution; *trans*-isomer (solid line), *cis*-isomer (dotted line), and the irradiated sample at the photostationary state (dot–dash line).

rylanthracene undergoes one-way *cis*-to-*trans* isomerization with a considerably high quantum efficiency.[17] This one-way isomerization proceeds as an adiabatic process in the excited triplet state (partly in the excited singlet state). Another example of one-way isomerization is the *trans*-to-*cis* one-way isomerization for hydrogen bonded compounds.[18,19] In this case, only the *cis*-isomer forms intramolecular hydrogen bonds to accelerate the deactivation from the *cis*-form without undergoing isomerization to the *trans*-isomer.

The present compound does not have any hydrogen bonding at the core stilbene, or any substituent to change the potential energy surface to induce isomerization in a specific way. Thus, the occurrence of the one-way isomerization in **6** must be caused by the surrounding dendron groups. The dendron groups have carboxylate anions at the periphery with counter cations at the surface, which may induce an electric field. Thus, the change in the electric field may result in the one-way *trans*-to-*cis* isomerization in a very unusual way. Otherwise, the surrounding dendron groups may have a more congested environment for the *cis*-isomer than the *trans*-isomer due to the hydrophobic inner part and hydrophilic periphery. The *cis*-isomer seems to be unable to isomerize to the *trans*-isomer because of the higher congestion of the dendron groups inhibiting the structural change of the stilbene core within the excited lifetime.

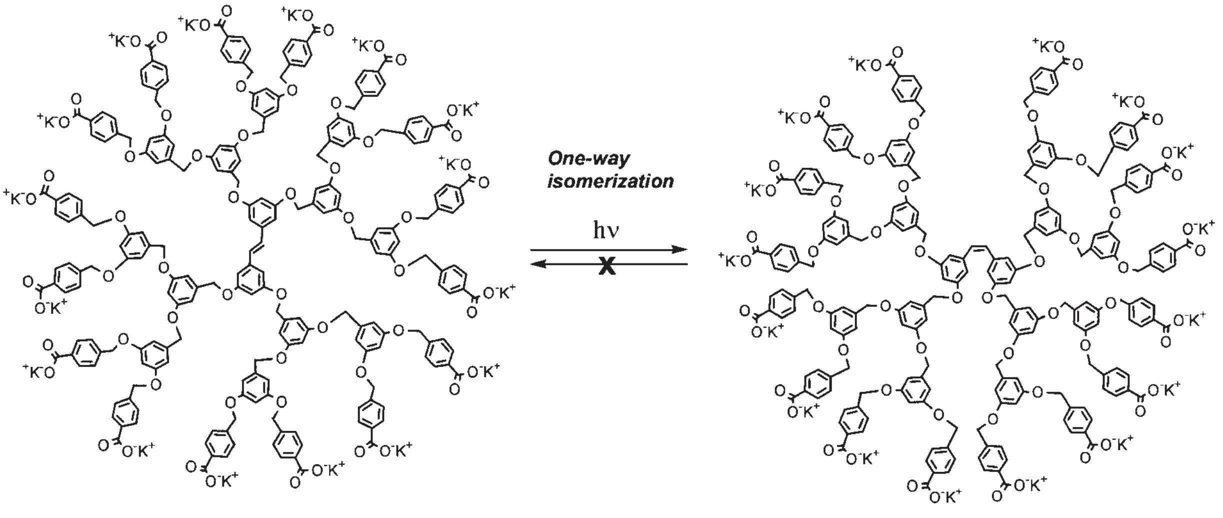
The second feature is the possibility of using the molecule as a photoresponsive unimolecular micelle. One can incorporate hydrophobic molecules inside **6**, and, upon photoirradiation, **6** undergoes a one-way *trans* → *cis* isomerization to give exclusively *cis*-**6**. *cis*-**6** should have a different structure from global **6**, and may dissociate from the hydrophobic molecules to behave as a kind of caged compound. In this respect, we are now trying to incorporate organic dyes to study the change in the properties of **6**, and incorporating dyes depending on the conformation of the double bond.

The third feature concerns the fluorescence properties. One can compare the fluorescence properties of *trans*-**3** and **6** and stilbene dendrimer without methoxycarbonyl groups (**7**) (Fig. 5). **7** exhibited a fluorescence lifetime of 10 ns, with the energy transfer taking place from the peripheral dendron groups to the core stilbene with an efficiency of 81%. The introduction of the methoxycarbonyl groups at the peripheral phenyl ring decreased the fluorescence lifetime of the stilbene core from 10 ns for **7** to 6.3 ns for **3**. The present finding is very interesting because the introduction of the methoxycarbonyl groups affected the fluorescence properties of the stilbene core. This might be the first finding of the substituent effect on the fluorescence lifetime of the dendrimer at the remote position. The considerably different profile of the fluorescence excitation spectra between **3** and **6** indicates a change in the molecular structure and/or size of the dendrimer depending on whether it is soluble in organic solvents or in water. In organic solvents such as THF, the solvent may penetrate into the dendrimer and, therefore, the dendrimer might have a flexible structure with a rather extended conformation of the dendron groups. However, in water soluble dendrimers, this penetration is difficult, and therefore, the dendrimer might assume a more compact conformation, with the carboxylate anion groups facing to the water surface. The water soluble dendrimers become more compact, and therefore the average distance between the benzyl ether dendrons and core stilbene for **6** should be shorter than that for the **3**.

The features of water soluble dendrimers should be observable in dendrimers **4**–**6**, having water soluble peripheral carboxylate anion groups and an inner hydrophobic group. Due to the above structure, the molecular structure of **5** and **6** becomes more compact, and therefore the average distance between the dendron group and core stilbene becomes shorter to accelerate the energy transfer from the dendron group to the core stilbene. In addition, due to the compact structure, a

Table 1. *trans/cis* Ratio at the Photostationary State (($[\mathrm{t}]/[\mathrm{c}])_{\mathrm{pss}}$), Quantum Yields of Photoisomerization ($\Phi_{\mathrm{t}\rightarrow\mathrm{c}}$ and $\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$) and Photocyclization ($\Phi_{\mathrm{cycl}}$), Fluorescence Quantum Yield (Φ_{f}), Fluorescence Lifetime (τ_{f}), Rate Constants for Quenching (k_{q}), Fluorescence Emission (k_{f}), Photoisomerization (k_{iso}), Nonradiative Deactivation (k_{d}), and Excited Singlet State Deactivation (k_{s}) of Dendrimers **1**–**6**

	$([\mathrm{t}]/[\mathrm{c}])_{\mathrm{pss}}$	$\Phi_{\mathrm{t}\rightarrow\mathrm{c}}$	$\Phi_{\mathrm{c}\rightarrow\mathrm{t}}$	Φ_{cycl}	Φ_{f}	τ_{f} /ns	k_{q} /10^{10} $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	k_{f} /10^{7} s^{-1}	k_{iso} /10^{7} s^{-1}	k_{d} /10^{7} s^{-1}	k_{s} /10^{7} s^{-1}
1	33:67	0.27	0.09	0.27	0.27	4.6	1.2	5.9	11.7	4.1	21.7
2	24:76	0.26			0.39	6.8	1.2	5.7	7.6	1.4	14.7
3	8:92	0.26	0.13	0	0.40	6.3	0.6	6.4	8.3	1.2	15.9
4	6:94	0.17	0.06	0	0.21	15.0	0.7	1.4	2.2	3.0	6.6
5	1:99	0.47	0.10	0	0.05	11.1/2.1					
6	0:100	0.15	—	—	0.17	11.2/3.7					



6 ***cis*-6**

Scheme 1.

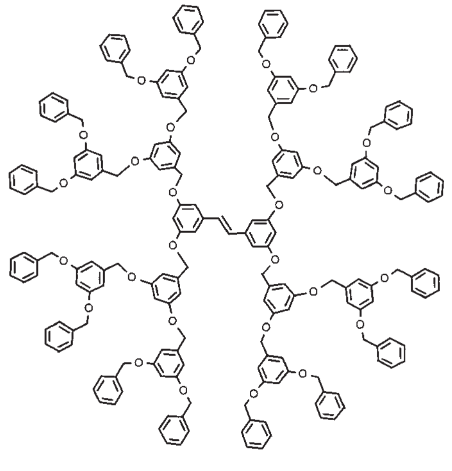


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Fig. 5. Structure of G3 stilbene dendrimer without carboxylate group at the periphery.

structural change to the *cis*-isomer might have a higher steric effect, inhibiting the *cis*-to-*trans* isomerization. The feature of dendrimers soluble in organic solvents (**1**–**3**) is the effect of the methoxycarbonyl groups at the periphery on the fluorescence lifetime of the core stilbene. Although the reason of this effect is not clear, this may be a specific quality of dendrimer structure and the substituents at the remote position in affecting the excited state properties of the inner aromatic group.

Conclusion

The environment of the stilbene dendrimers depended on the generation, especially in WSDs **4**–**6**. Thus, the first generation **4** suffers from the water atmosphere around the core stilbene, as can be understood by the molecular structure. The largest Stokes shift observed in **4** indicates that the dipole moment changed considerably with photoexcitation. With increasing generations, the Stokes shift tended to become smaller. This means that the surrounding dendron groups should block the water molecules from inside the core stilbene part. Finally, the core stilbene in **6** may have an environment almost free of water molecules, based on the observation of a similar Stokes shift for stilbene dendrimers soluble in organic solvents where the core stilbene has a hydrophobic environment. Furthermore, **6** underwent an unprecedented one-way *trans*-to-*cis* photoisomerization in water.

The above finding can be extended to prepare water soluble organic molecules with hydrophobic interiors and photoresponsive chromophores at the core as single molecules. There are several molecules which are soluble in water. However, as far as we are aware, the present stilbenoid molecules are the first clear report of preparing water soluble single molecules with a photoresponsive and hydrophobic interior to be used as a photoresponsive unimolecular micelle.

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