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Synthesis and photochemical properties of polyphenylene dendrimers with photoreactive stilbene core

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Abstract—Photoresponsive polyphenylene dendrimers *trans*-**1** and **2** were synthesized for the first time, and their photochemical reaction as well as excited state properties were studied. *trans*-**1** and **2** exhibited fluorescence emission with considerably high quantum efficiency. Furthermore, they underwent photochemical isomerization to the *cis*-isomers. Thus, polyphenylene dendrimer *trans*-**2** with the molecular weight as high as 4700 and with weak conjugation throughout the molecule was found to undergo *trans–cis* photoisomerization within its excited state lifetime. © 2002 Elsevier Science Ltd. All rights reserved.

Dendrimers have novel potential to mimic macromolecular functions such as enzymatic reactions and various studies have been reported.[1–5] Among them, polyphenylene dendrimers have been prepared and their molecular structures and energy transfer processes have been studied.[6–8] However, photodynamic processes of dendrimers such as isomerization in the excited state have scarcely been studied. Only dendrimers containing an azobenzene unit have been reported, where azobenzene has been incorporated in the interior, exterior, or throughout.[9–11] Azobenzene itself does not emit fluorescence and, therefore, dendrimers containing an azobenzene unit could not give any fluorescence and the excited state behavior could not be followed.

The photochemical and photophysical properties of stilbene and its related compounds have been extensively studied and covered in review articles.[12–14] They are quite important, because they are the prototype of the basic photochemical *cis–trans* isomerization and have potential for application to photochromic materials, non-linear optics, and so on.

We have been interested in the photochemical processes in largely congested systems. We have prepared stilbene dendrimers with the dendron of a benzyl ether type system, and their photochemical behavior was studied.[15] In these benzyl ether type stilbene dendrimers the surrounding dendron group is not conjugated with the core stilbene, but may function as a considerably large substituent to reduce the isomerization rate.

We have been interested in another type of dendrimer molecule where conjugation is not localized in the core but can be spread throughout the molecule. Thus, stilbene dendrimers having a peripheral polyphenylene dendron group have been prepared for the first time and the dynamic behaviors have been studied. The polyphenylene dendron group must be rather rigid compared to the benzyl ether type dendron. Therefore, the *trans–cis* isomerization should be accompanied with a considerably large conformational change compared to the dendrimers with flexible, benzyl ether type dendrons. In addition, weak conjugation may be present and the excitation could be delocalized throughout the molecules.

We wish to report here the synthesis of the polyphenylene-substituted stilbene dendrimers, *trans*-**1** and *trans*-**2**, and their photochemical behaviors. Polyphenylene-substituted stilbene dendrimers *trans*-**1** and *trans*-**2** were prepared by Diels–Alder reaction between **3** and **4** or **5** as summarized in Scheme 1. Their structures have been identified by ^{1}H NMR and MALDI-TOF mass spectrometry.[16]

Fig. 1 shows the absorption spectra of dendrimers *trans*-**1** and *trans*-**2**, in addition to those of *trans*-tetraphenylstilbene (*trans*-**6**) and *trans*-stilbene in chloroform, together with their fluorescence and fluorescence excitation spectra. The absorption edges of *trans*-**1** (360 nm) and *trans*-**2** (360 nm) are almost the same but are

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Keywords: polyphenylene; stilbene; dendrimer; excited state; fluorescence; isomerization.

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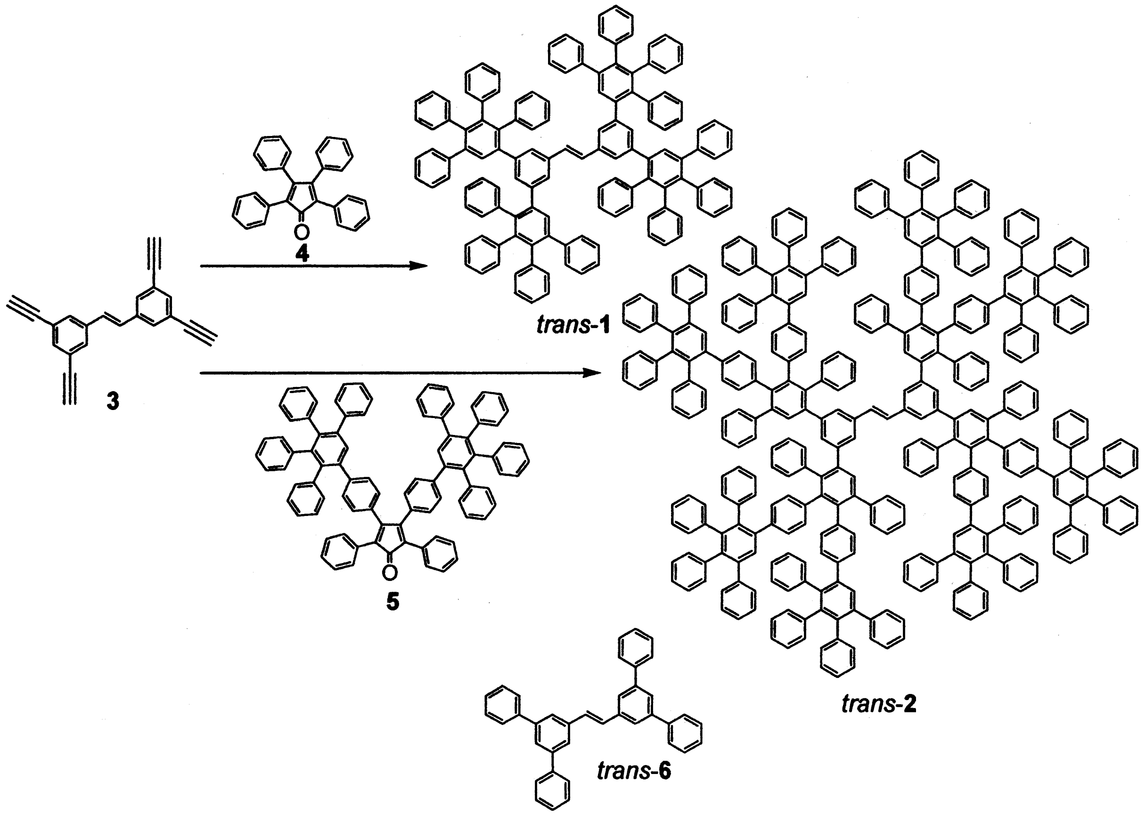

Scheme 1.

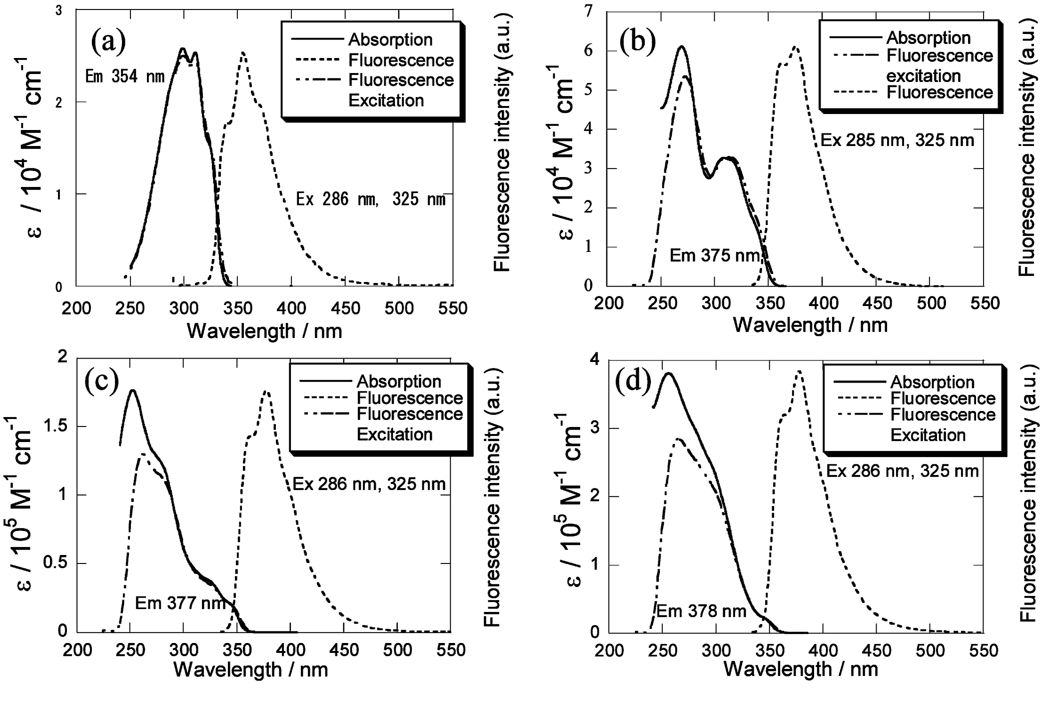

Figure 1. Absorption, fluorescence and fluorescence excitation spectra of *trans*-stilbene (a), *trans*-**6** (b), *trans*-**1** (c), and *trans*-**2** (d), in chloroform at room temperature.

slightly shifted to the longer wavelength than that of *trans*-**6** (355 nm) and *trans*-stilbene (340 nm). The absorption at longer wavelength region is assigned to that of the core stilbene. The absorbance at 250–320 nm increased with increasing of the generation of dendrimer due to the peripheral polyphenylene dendron. *trans*-**1** and *trans*-**2** exhibited fluorescence emission with the maximum wavelength at 377 and 378 nm, respectively, which is again shifted to a longer wavelength than that of *trans*-**6** (375 nm) and *trans*-stilbene. The

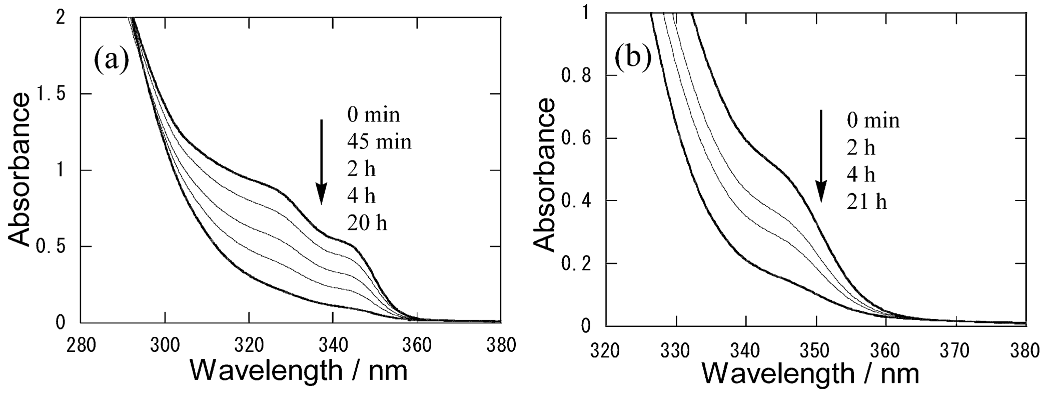

Figure 2. Decrease of absorbance of *trans*-**1** (a) and *trans*-**2** (b) on irradiation with 345 nm light in benzene at room temperature.

quantum yield of fluorescence emission (Φ_f) is considerably high and is 0.69 and 0.64 for *trans*-**1** and *trans*-**2**, respectively. These values are more than 10 times higher than that of *trans*-stilbene ($\Phi_f = 0.04$),[13,14] but are almost the same with the value of *trans*-**6** ($\Phi_f = 0.67$). Thus, the introduction of the phenyl substituent at the *meta*-position of the phenyl ring of the stilbene brought about the increase of fluorescence efficiency, which may be related to the '*meta* effect' reported for the fluorescence properties of the trans isomer of *meta*-aminostilbene.[17] The fluorescence excitation spectra are almost superimposed with the absorption spectra of the corresponding isomers. These results indicate that energy transfer from the peripheral dendron group to the core stilbene takes place quite efficiently. When we compare the fluorescence intensity of the chloroform solution of *trans*-stilbene, *trans*-**1** and *trans*-**2** at the concentration of 10^{-7} M with excitation at 285 nm, the fluorescence intensity increased 50 times more for *trans*-**1** and 100 times more for *trans*-**2** than that of the parent *trans*-stilbene. Therefore, the polyphenylenene group can act as a light-harvesting antenna for the ultraviolet light.

The singlet excitation energy was estimated from the absorption spectra and fluorescence spectra to be 81 kcal mol^{-1}, for both *trans*-**1** and *trans*-**2**. In *trans*-**1** and *trans*-**2**, the polyphenylene group is introduced on the meta position of the phenyl ring of stilbene. The singlet excitation energies of *trans*-**1** and **2** (81 kcal mol^{-1}) are slightly lower than that of *trans*-stilbene ($E_s = 85.7$ kcal mol^{-1})[11] and *trans*-**6** ($E_s = 82$ kcal mol^{-1}) indicating a slight increase of the conjugation due to the presence of the polyphenylene group.

On photoirradiation with 345 nm from the Xe lamp *trans*-**1** and *trans*-**2** underwent isomerization around the C=C double bond to give their *cis*-isomers as revealed by the decrease of the absorbance as shown in Fig. 2. The quantum yield of *trans*→*cis* isomerization was estimated to be 0.14 for both *trans*-**1** and *trans*-**2** from the initial decrease of the absorbance at 345 nm. Therefore, the efficiency of *trans*→*cis* isomerization is almost the same for both generation stilbene dendrimers, but is less than half of the value for stilbene (0.35). One can also estimate the photostationary state from the constant value of the absorbance by prolonged irradiation. Thus, *trans*-**1** gave the absorbance at 345 nm of 0.093 starting with 0.495, which is almost half of the value for *trans*-**2** of 0.155 starting with the same value 0.495. Thus, the *trans*-to-*cis* isomer ratio at the photostationary state ($([t]/[c])_{pss}$) was determined to be 8:92 and 25:75, respectively, for **1** and **2** on 345 nm light irradiation.

The molecular structure of *trans*-**1** and *trans*-**2** can be estimated from the calculation from the molecular dynamics. The steric effect of the 1,2-substitution of the phenyl ring should bring about the rotation around the single bond connecting the phenyl ring to give a windmill-like structure.

In summary, stilbene dendrimers **1** and **2** with a polyphenylene group as a large substituent capable of effecting conjugation throughout the molecule have been successfully synthesized and their photochemical properties are investigated. *trans*-**1** and *trans*-**2** exhibited fluorescence emission with considerably high quantum efficiency and *trans*–*cis* isomerization. To the best of our knowledge, this is the first clear example of the *trans*–*cis* isomerization of C=C double bond in the excited state with a highly rigid substituent.

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References

1. Bosman, A. W.; Jansenn, H. M.; Meier, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688.
2. Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300.

3. Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681–1712.
4. Tomisaka, K.; Ishida, Y.; Konishi, K.; Aida, T. *Chem. Commun.* **2001**, 133–134.
5. Choi, M.-S.; Aida, T.; Yamazaki, T.; Yamazaki, I. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3194–3198.
6. Wiesler, U.-M.; Müllen, K. *Chem. Commun.* **1999**, 2293–2294.
7. Hofkens, J.; Maus, M.; Gensch, T.; Vosch, T.; Cotlet, M.; Kohn, F.; Herrmann, A.; Mullen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2000**, *122*, 9278–9288.
8. Wiesler, U. M.; Berresheim, A. J.; Morgenroth, F.; Lieser, G.; Müllen, K. *Macromolecules* **2001**, *34*, 187–199.
9. Jiang, D.-L.; Aida, T. *Nature* **1997**, 454–456.
10. Junge, D. M.; McGrath, D. V. *Chem. Commun.* **1997**, 857–858.
11. Li, S.; McGrath, D. V. *J. Am. Chem. Soc.* **2000**, *122*, 6795–6796.
12. Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399–1420.
13. Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415–436.
14. Saltiel, J.; Sun, Y.-P. In *Photochromism, Molecules and Systems*; Dürr, H.; Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp. 64–164.
15. Mizutani, T.; Ikegami, M.; Nagahata, R.; Arai, T. *Chem. Lett.* **2001**, 1014–1015.
16. *trans*-**1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K); 6.26 (s, 2H, Olefin-H); 6.70–6.96 (Br, 66H); 7.09–7.17 (br, 20H); $\delta = 7.24$ (s, 4H): MALDI-TOFMS, found: m/z 1725.0 calcd for $C_{134}H_{92}$+Na 1725.2
trans-**2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) $\delta = 6.22$(s, 2H, Olefin-H); 6.43 (d, $J = 8$ Hz, 8H); 6.51 (d, $J = 8$ Hz, 8H); 6.60–6.93 (br, 158H); 7.01–7.05 (br, 8H); 7.10–7.17 (br, 56H), 7.18 (s, 4H); 7.43 (s, 4H); 7.47 (s, 4H): MALDI-TOFMS, found: m/z 4769.7 calcd for $C_{374}H_{252}$+Na 4769.1
17. Lewis, F. D.; Kalgutkar, R. S.; Yang, J.-S. *J. Am. Chem. Soc.* **1999**, *121*, 12045–12053.