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Isomer Specific Solvent Effect on Photoisomerization of Photoresponsive Polyphenylene Dendrimers with a Stilbene Core

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The efficiency of *cis*-to-*trans* isomerization of stilbene-cored polyphenylene dendrimer with alkyl chain at the pheriphery was one order of magnitude lower in hexane than in benzene, whereas that of *trans*-to-*cis* isomerization was slightly higher in hexane than in benzene.

The photochemical properties of stilbene and its analogous have been the subject of intense research.[1–10] As a part of our study on the photochemistry of stilbenes, we have reported that higher generation stilbene-cored dendrimers undergo photoisomerization with moderate efficiency in solution.[11–13] Furthermore, even a cross-linked 1,3,5-tristyrylbenzene dendrimer, where the outside of the dendrons are cross-linked to inhibit isomerization, has a photoisomerization quantum yield ($\Phi_{E\to Z}$) of 0.063, which is similar to that for a model compound ($\Phi_{E\to Z} = 0.080$).[14] We have also reported that stilbene-cored polyphenylene dendrimers (**SPD**)[15] undergo *cis*–*trans* photoisomerization on photoirradiation in a benzene solution. These compounds do not dissolve in an aliphatic nonpolar solvent, such as hexane. Here, we report the synthesis and solvent dependence of the photoisomerization behaviour of stilbene-cored polyphenylene dendrimers **1** having a long alkyl chain. Dendrimer **1** is soluble in an aliphatic nonpolar solvent, such as hexane. In addition, we found that the efficiency of *cis*-to-*trans* isomerization of **1** was strongly solvent-dependent and one order of magnitude higher in benzene than in hexane. The origin of this pronounced solvent effect on photoisomerization should be the introduction of long alkyl group at the periphery, which makes the compounds soluble even in hexane. Hexane may interact with this alkyl chain to induce molecular aggregation among the less interactive polyphenylene groups and may suppress the efficiency of *cis*-to-*trans* isomerization.

Results and Discussion

Diels–Alder reaction of alkyne-substituted stilbene **3**[15] with four molar amounts of tetraphenylcyclopentadienone **4**[16] resulted in the corresponding stilbene-cored polyphenylene dendrimer ***trans*-1** in 18% isolated yield. The structure was identified by ^{1}H and ^{13}C NMR and MALDI-TOF-MS spectrometry. After photolysis of ***trans*-1** in hexane (Scheme 1), pure ***cis*-1** was separated from ***trans*-1** by column chromatography.

***trans*-** and ***cis*-1** were soluble not only to benzene, chloroform, and THF, but also in hexane, due to the presence of tetradodecyl groups. UV absorption spectra of ***trans*-** and ***cis*-1** were measured both in hexane and in benzene. The spectra for *trans*-isomer were characterized by broad absorption bands tailing to 360 nm, whereas those of *cis*-isomer around 300–360 nm were less intense due to its loss of planarity at the core (Fig. 1a). Figure 1b shows the fluorescence and fluorescence excitation spectra of ***trans*-1** in hexane and benzene. Fluorescence emission from pure ***cis*-1** was not observed. The UV absorption, fluorescence, and fluorescence excitation spectra of ***trans*-1** are similar to those of previously reported ***trans*-SPD**, indicating that the peripheral alkyl groups in ***trans*-1** do not affect the absorption and fluorescence properties of the both dendrons and stilbene parts in the dendrimers. The fluorescence quantum yield (Φ_f) for ***trans*-1** was determined to be 0.69 in hexane and 0.70 in benzene, respectively (Table 1), which is also similar to that of ***trans*-SPD** ($\Phi_f = 0.69$).[15]

Stilbene-cored polyphenylene dendrimer ***trans*-1** exhibited different photoisomerization behaviors depending on solvents. Irradiation of ***trans*-1** both in benzene and hexane resulted in mutual *trans*–*cis* photoisomerization, as evidenced in Figs. 2a and 2b by a decrease in the absorbance between 300–360 nm, ascribed to the stilbene part. An isosbestic point in the absorption spectra during photoisomerization was clearly seen at 288 nm in benzene and at 271 nm in hexane in Figs. 2a and 2b, respectively. Inset in Figure 2 shows the time dependence of the ratio of the *trans*-isomer during photoisomerization. Under the experimental conditions used, a photostationary state (PSS) was reached within 1–2 h of irradiation. The amount of *trans*-isomer at the PSS was calculated in relation to the absorbance of an unirradiated solution of pure *trans*- and *cis*-isomers and those of the irradiated benzene solution at 345 nm and the hexane solution at 325 nm. Thus, the values of the *trans*- and *cis*-isomer ratio at the photostationary state ($([t]/[c])_{pss}$) were determined to be 12:88 in benzene and 3:97 in hexane. The ratio of the quantum yield for *trans*-to-*cis* and *cis*-to-*trans* photoisomerization ($\Phi_{t\to c}/\Phi_{c\to t}$) were calculated by following equation:

$$([c]/[t])_{pss} = (\varepsilon_t/\varepsilon_c)(\Phi_{t\to c}/\Phi_{c\to t}) \quad (1)$$

where ε_t and ε_c are molar extinction coefficient of the *trans*- and the *cis*-isomer, respectively, at the irradiated wavelength. The values for $\varepsilon_t/\varepsilon_c$ were 22 in benzene and 10 in hexane. The quantum yield for *trans*-to-*cis* photoisomerization of ***trans*-1** ($\Phi_{t\to c}$) in benzene was assumed to be the same as that of ***trans*-SPD** ($\Phi_{t\to c} = 0.14$ in benzene).[15] The initial changes in the absorbance at 345 nm of ***trans*-1** upon photoirradiation at 325 nm in benzene and in hexane were compared to give the

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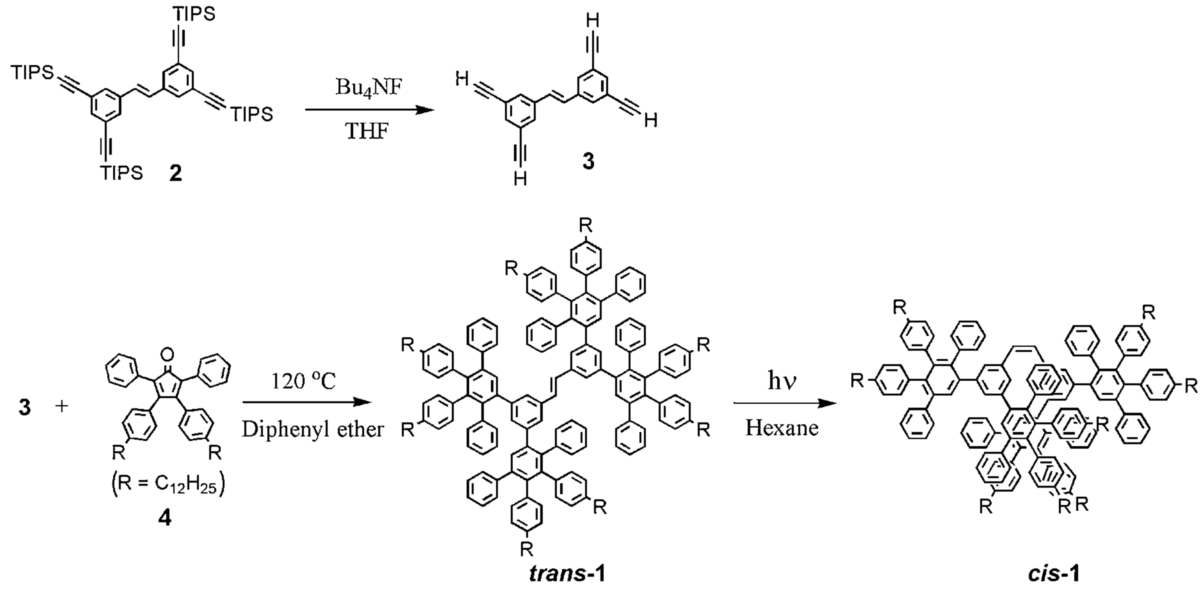

Scheme 1.

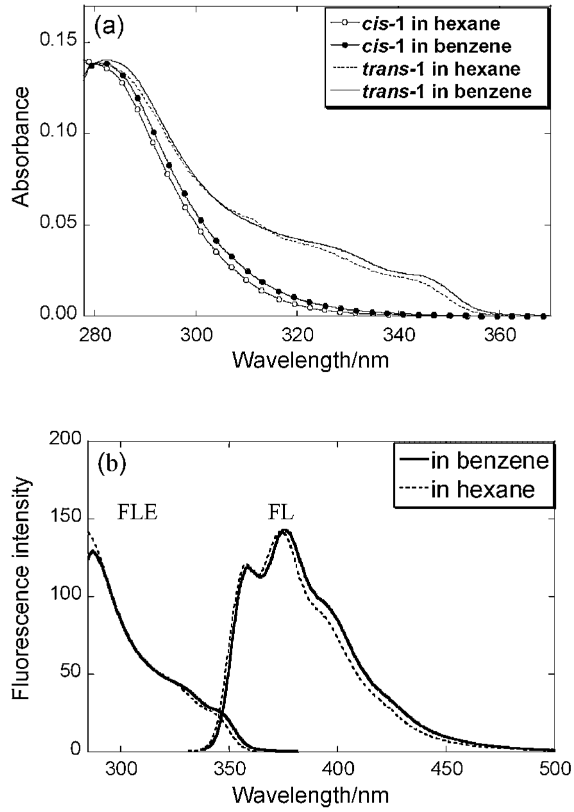

Fig. 1. (a) UV-absorption spectra of ***trans*-1** in hexane (dotted line) and in benzene (solid line) and ***cis*-1** in hexane (open circle) and in benzene (closed circle). (b) Fluorescence and fluorescence excitation spectra of ***trans*-1** in benzene (solid line) and in hexane (dotted line).

value of $\Phi_{t\rightarrow c}$ in hexane. Thus, the $\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$ values were estimated for ***trans*-1** in benzene and in hexane (Table 1). Interestingly, the value of $\Phi_{c\rightarrow t}$ in hexane (0.055) was much lower than that in benzene (0.42), whereas the values of $\Phi_{t\rightarrow c}$ in benzene (0.14) and in hexane (0.18) were similar.

Table 1. Quantum Yields of Fluorescence (Φ_f) and Photoisomerization ($\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$) for Dendrimer **1**

Solvents	$\Phi_{f\ (trans)}$	$\Phi_{t\rightarrow c}$	$\Phi_{c\rightarrow t}$
Benzene	0.70	0.14	0.42
Hexane	0.69	0.18	0.055

The results indicate that the activation energy for *cis*-to-*trans* photoisomerization of ***cis*-1** in hexane is higher than that in benzene. Since the dendron moiety in ***cis*-1** should be structurally packed, as depicted in Scheme 1, π–π stacking interaction may play a role in increasing the activation energy for *cis*-to-*trans* isomerization and/or in accelerating the deactivation to the ground state, which should be more prominent in hexane compared to that in benzene.

In summary, stilbene-cored polyphenylene dendrimers ***trans*-1** and ***cis*-1**, having alkyl chain at the periphery, were prepared. Dendrimers ***trans*-1** and ***cis*-1** were soluble even in hexane. The calculated quantum yield for *cis*-to-*trans* photoisomerization of ***cis*-1** in hexane was much lower than in benzene, whereas the other photochemical properties, such as the quantum yield for *trans*-to-*cis* photoisomerization and fluorescence quantum yield, UV-absorption and fluorescence spectra, were similar in benzene and in hexane.

Experimental

Synthesis of *trans*-1. Tetrabutylammonium fluoride trihydrate (630 mg, 2.0 mmol) was added to a solution of compound **2**[15] (217 mg, 0.241 mmol) in THF (10 mL) and the solution was stirred at room temperature for 5 min under nitrogen. The reaction mixture was quenched by addition of water (5 mL) and was extracted with dichloromethane. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. The brown residue, including compound **3**, was washed with methanol (2 mL) and was used for next reaction without further purification.

The residue including compound **3** (59.4 mg) and dendron **4**[16] (614 mg, 0.852 mmol) were dissolved in diphenyl ether (20 mL). The solution was stirred at 120 °C for 26 h. After the reaction

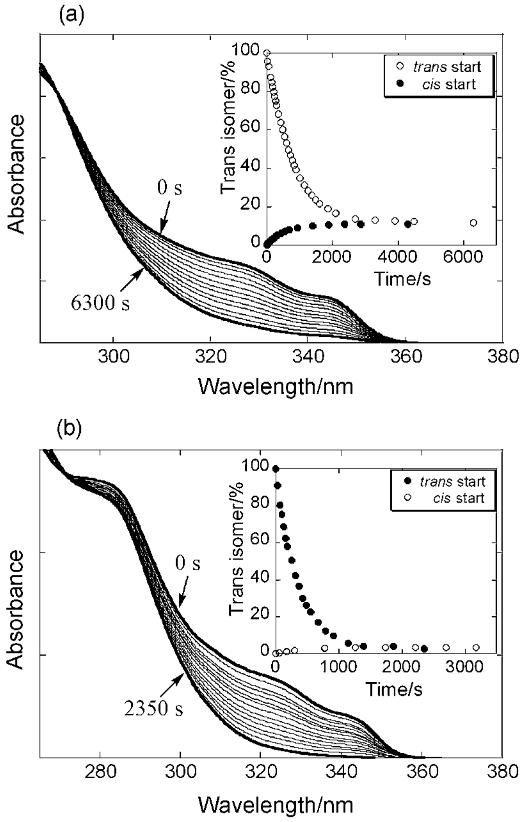

Fig. 2. (a) Change in the UV-absorption spectra of ***trans*-1** upon the irradiation with 325 nm light in benzene. Inset shows the time dependence of the ratio of *trans* isomer (%) during the photoirradiation, monitored at 325 nm in benzene. (b) Change in the UV-absorption spectra of ***trans*-1** upon the irradiation with 345 nm light in hexane. Inset shows the time dependence of the ratio of *trans* isomer (%) during the photoirradiation, monitored at 345 nm in hexane.

was finished, the solution was poured into water, extracted with dichloromethane, dried with $MgSO_4$ and filtered, and the solvent was evaporated. A crude mixture was purified by silica-gel column chromatography (hexane/chloroform = 3/1), followed by HPLC on a size-exclusion column (chloroform as a solvent) to give ***trans*-1** (128 mg, 18% yield). MALDI-TOF-MS: calcd for $C_{230}H_{234}$ $[M + Na]^+$: m/z 3069.2. Found: 3067.5. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.90 (24H, t, $J = 6.6$ Hz, CH_3), 1.15–1.20 (16H, m, CH_2), 1.20–1.38 (128H, m, CH_2), 1.38–1.46 (16H, m, CH_2), 2.36 (8H, t, $J = 6.6$ Hz, CH_2), 2.40 (8H, t, $J = 6.6$ Hz, CH_2), 6.28 (2H, s, olefin-H), 6.60–6.64 (16H, m, ArH), 6.68–6.72 (16H, m, ArH), 6.76–6.77 (8H, m, ArH), 6.80–6.83 (4H, m, ArH), 6.86–6.87 (12H, m, ArH), 6.94 (2H, s, ArH), 7.12–7.18 (20H, m, ArH), 7.24–7.26 (4H, m, ArH). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 28.8, 28.9, 29.4, 29.5, 29.7, 31.1, 31.2, 31.9, 35.3, 35.4, 125.6, 126.0, 126.1, 126.6, 126.8, 126.9, 127.3, 128.3, 130.0, 131.0, 131.1, 131.2, 131.3, 131.6, 135.9, 137.2, 137.5, 139.1, 139.3, 139.4, 139.7, 140.0, 140.1, 140.6, 141.4, 141.7, 141.8.

Synthesis of *cis*-1. Irradiation of a solution of ***trans*-1** at 365 nm in hexane for 24 h gave a mixture of *trans*- and *cis*-isomers of **1**. After evaporation, the reaction mixture was purified by silica-gel column chromatography (hexane/chloroform = 4/1), to give ***cis*-1**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (24H, t, $J = 8.0$ Hz, CH_3), 1.00–1.50 (160H, m, CH_2), 2.30–2.40 (16H, m, CH_2), 6.12 (2H, s, orefin-H), 6.32–6.35 (2H, m, ArH), 6.42–6.46 (4H, m, ArH), 6.51–6.74 (60H, m, ArH), 6.92–7.04 (16H, m, ArH).

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