

## Photochemical Properties of 3,3'-Disubstituted Stilbene Dendrimers

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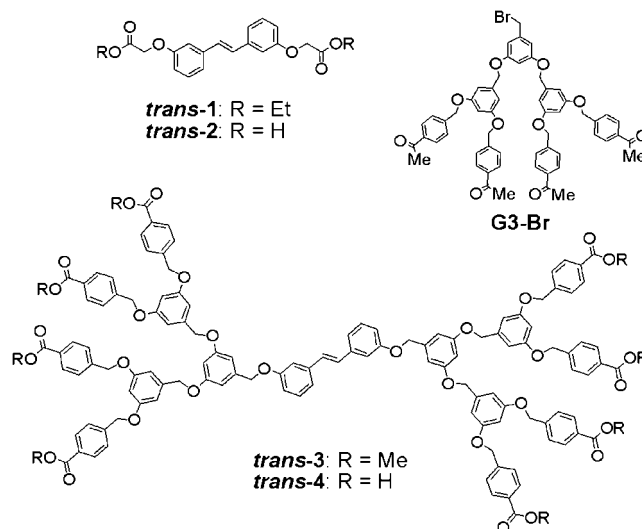
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The quantum yield of isomerization and the fluorescence lifetime of newly synthesized 3,3'-disubstituted water-soluble stilbene dendrimer *trans*-4 were significantly different from those of model compounds. The results indicate that not only properties of dendrimer surfaces but also substituent positions are important for dendrimer photochemistry.

Photochemical properties of small molecular weight chromophores in dendrimers have been studied.<sup>1–10</sup> When a small chromophore that changes structure under photoirradiation is introduced as a dendrimer core, the small structural changes of the core can be amplified to a large structural change of the whole molecule. By this strategy, we have prepared several dendrimers having a photoresponsive molecular structure.<sup>11–13</sup>

In organic solvents, stilbene dendrimers with benzyl ether dendron groups at the 3,3',5,5'-position of the core stilbene have been studied.<sup>14,15</sup> 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 aqueous solution, photochemical behaviors of water-soluble stilbene dendrimers have been studied. Interestingly, a third generation dendrimer exhibited one-way trans-to-cis isomerization upon photoirradiation.<sup>16</sup> The quantum yield of the isomerization as well as the fluorescence quantum yields and fluorescence lifetimes of these dendrimers have also been reported.<sup>17</sup>

Here, we report the photochemical properties of 3,3'-disubstituted stilbene dendrimers *trans*-3 and the corresponding potassium salts *trans*-4 and their standard compounds *trans*-1 and *trans*-2 (Figure 1). In aqueous solution, the quantum yield of isomerization ( $\Phi_{t \rightarrow c}$ ) for *trans*-4 was 0.063 and was much lower than that for standard *trans*-2 ( $\Phi_{t \rightarrow c} = 0.36$ ) (Table 1). In addition, the fluorescence lifetime of *trans*-4 in aqueous solution was calculated to be two exponential functions to give 0.70 and 4.55 ns.



**Figure 1.** Structures of stilbene dendrimers *trans*-3 and -4, their standard molecules *trans*-1 and -2, and dendritic bromide G3-Br.

**Table 1.** Fluorescence Quantum Yield, Lifetime of Excited Singlet State, Quantum Yield of Trans-to-Cis Photochemical Isomerization for *trans*-1–4

|                 | Solvents    | $\Phi_f$ | $\tau_s$ /ns               | $\Phi_{t \rightarrow c}$ |
|-----------------|-------------|----------|----------------------------|--------------------------|
| <i>trans</i> -1 | THF         | 0.21     | <0.5                       | 0.40                     |
| <i>trans</i> -2 | 1 mM KOH aq | 0.14     | <0.5                       | 0.36                     |
| <i>trans</i> -3 | THF         | 0.28     | 0.73                       | 0.35                     |
| <i>trans</i> -4 | 1 mM KOH aq | 0.14     | 0.70 (0.97)<br>4.55 (0.03) | 0.063                    |

### Results and Discussion

Figures 2a–2d show the absorption, fluorescence, and fluorescence excitation spectra of *trans*-1 and -3 in THF and the corresponding potassium salts *trans*-2 and -4 in  $1 \times 10^{-3}$  M KOH aqueous solution, respectively. In Figures 2c and 2d, the increase in the absorption maximum at 277–280 nm indicates increments of the benzyl ether group. All compounds exhibited absorption at 300–360 nm with  $\lambda_{\max}$  at 310–315 nm due to the *trans*-stilbene cores. The absorption band of the stilbene moiety appeared in almost the same region.

In THF, the fluorescence spectra were similar to each other to give  $\lambda_{\max} = 363$  and 365 nm, respectively, for *trans*-1 and -3. The fluorescence maximum of their corresponding potassium salts in aqueous solution slightly shifted to a longer wavelength to give  $\lambda_{\max} = 372$  and 373 nm, for *trans*-2 and -4, respectively. The fluorescence excitation spectra of the core stilbene at 300–360 nm appeared at almost the same region as the absorption spectra for *trans*-1 and -2, but the spectral profiles of the fluorescence excitation spectra of *trans*-3 and -4 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 in *trans*-3 in THF, whereas the excited singlet energy transfer from the dendron moiety to the core stilbene was observed in *trans*-4 in aqueous solution. One can estimate the energy-transfer efficiency by comparing the absorption spectra and the fluores-

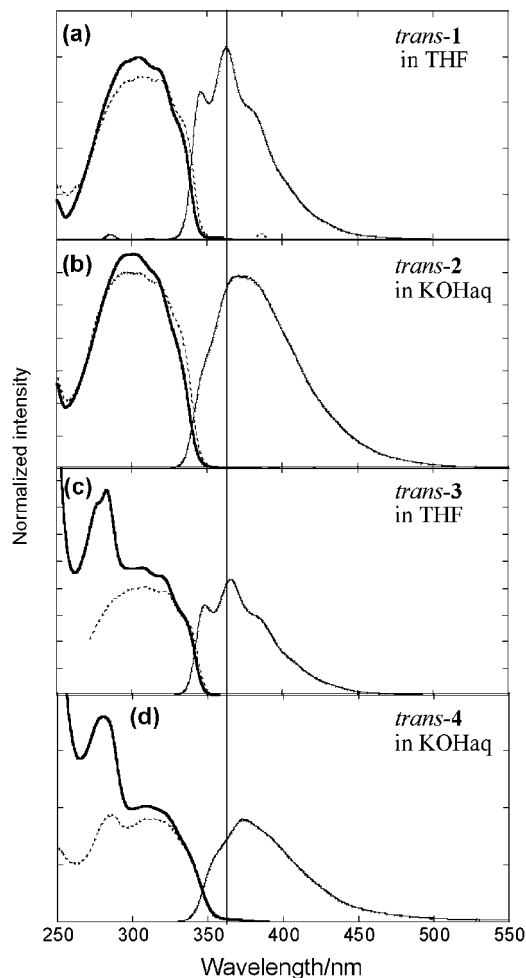
cence spectra of the dendron part and the stilbene part to be 20% for *trans*-4. In THF, the fluorescence quantum yield ( $\Phi_f$ ) of *trans*-1 (0.21) is slightly lower than that for *trans*-3 (0.28) (Table 1). In aqueous solution, those of both *trans*-2 and -4 are 0.14. *trans*-1 and -2 gave a fluorescence lifetime of <0.5 ns and that for *trans*-3 was 0.73 ns with single-exponential decay. On

the other hand, the fluorescence decay curves do not fit a single-exponential function, but rather fit two exponential functions to give 0.70 and 4.55 ns for *trans*-4. The shorter lifetime (0.70 ns) and the longer lifetime (4.55 ns) could be assigned to the monomer fluorescence and excimer or aggregated form, respectively. These results indicate that the structure and environment are not uniform in 4 in aqueous solution. Furthermore, one can increase the fluorescence lifetime of the stilbene core effectively by introducing a large dendron group at the periphery of stilbene.

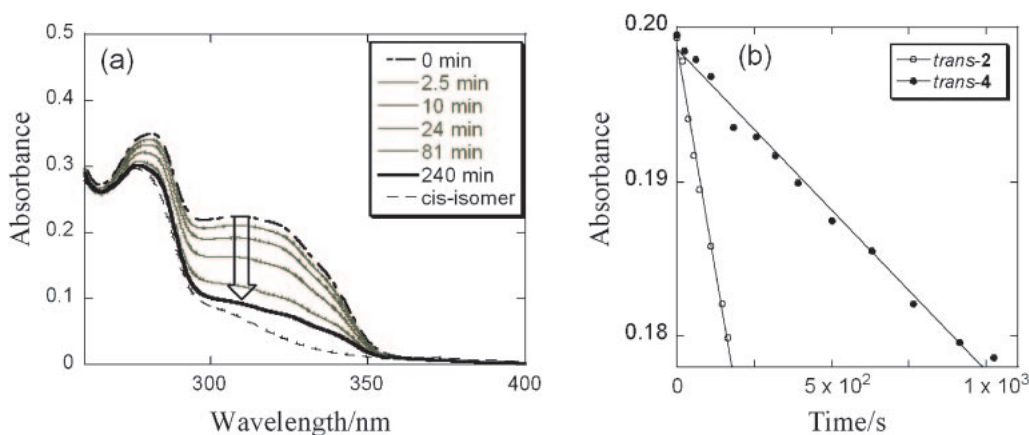
On irradiation with 320 nm light under argon, the *trans* isomers 1–4 underwent isomerization around the double bond to give the corresponding *cis* isomer (Figure 3). The quantum yields of the *trans*-to-*cis* isomerization were similar among 1–3 (0.35–0.40), while that for *trans*-4 was much lower (0.063). Figure 3b shows the time profile of the change of absorbance at 320 nm for *trans*-2 and -4.

One can compare the isomerization properties of these 3,3'-disubstituted dendrimers to another stilbene dendrimer series having four dendron groups at the 3,3',5,5'-positions on stilbene (5 and 6 in Figure 4).<sup>15–17</sup> In the series of 3,3',5,5'-tetrasubstituted dendrimers, the isomerization efficiency of higher generations were similar to those of lower generations. In those cases the time scale for rotation about the C=C double bond does not change from lower to higher generations, probably due to their volume conserving isomerization mechanism. It was found that the conformational change of the stilbene core completes within the excited-state lifetime, followed by the conformational change of the dendron part on a different time scale. These isomerization properties may be observed when the dendrimers exist as monomer in THF for 5 or unimolecular micelle in aqueous solution for 6, so that this isomerization behavior can apply to 3,3'-disubstituted stilbene *trans*-3 in THF. On the other hand, the isomerization quantum yield of *trans*-4 is much lower than the others. In addition, the fluorescence lifetime of *trans*-4 was 0.70 and 4.55 ns. These results suggest that *trans*-4 does not exist unimolecularly in aqueous solution.

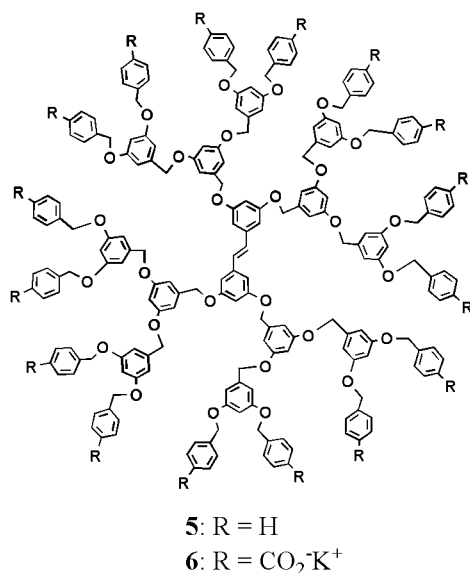
In summary the photochemical properties of 3,3'-disubstituted stilbene dendrimers *trans*-3 and the corresponding potassium salts *trans*-4 and their standard compounds *trans*-1 and -2 were studied. The fluorescence decay curves fit two



**Figure 2.** Absorption (solid line), fluorescence (dotted line), and fluorescence excitation spectra (dashed line) of *trans*-1–4.



**Figure 3.** (a) Change in the absorption spectra of *trans*-4 in KOH aq upon irradiation at 320 nm at room temperature under argon. (b) Time dependence of the absorbance (320 nm) of *trans*-2 and -4 in KOH aqueous solution upon photoirradiation.



**Figure 4.** Structures of the stilbene dendrimer **5** and water-soluble stilbene dendrimer **6**.

exponential functions to give 0.70 and 4.55 ns for *trans*-**4**, indicating that the environment of *trans*-**4** in aqueous solution is not uniform. The quantum yield of isomerization ( $\Phi_{t \rightarrow c}$ ) for dendrimer *trans*-**4** was 0.063 and was much lower than that for *trans*-**2** ( $\Phi_{t \rightarrow c} = 0.36$ ), indicating that dendritic molecules soluble in water may form a specific environment by varying aggregated systems depending on the concentration to control the efficiency of photochemical reaction and the excited state properties.

### Experimental

**Measurement.** Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4000 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with a Horiba NAES-1100 time-resolved spectrofluorometer. The quantum yields of fluorescence emissions and the quantum yield of the *trans*-to-*cis* isomerization were determined by procedures in Ref. 15.

***trans*-1.** Ethyl bromoacetate (0.417 g, 2.50 mmol) was added to a mixture of *trans*-3,3'-dihydroxystilbene (0.0750 g, 0.353 mmol), K<sub>2</sub>CO<sub>3</sub> (0.233 g, 1.69 mmol), and 18-crown-6 (50 mg) in dry acetone (50 mL) and the mixture was refluxed for 18 h. After cooling down to room temperature, the mixture was filtered and evaporated. The crude product was purified with column chromatography eluting with dichloromethane/hexane = 1/1 and then with gradually increasing proportion of dichloromethane (to dichloromethane 100%) to give product as a white solid (121 mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  7.28 (t,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 5.0$  Hz, 2H), 7.07–7.06 (m, 2H), 7.04 (s, 2H), 6.83–6.81 (m, 2H), 4.66 (s, 4H), 4.29 (q,  $J = 10$  Hz, 4H), 1.31 (t,  $J = 10$  Hz, 6H). Elemental analysis: Anal. Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>6</sub>: C, 68.74; H, 6.29; N, 0.00%. Found: C, 68.54; H, 6.39; N, 0.00%.

***trans*-2.** 1 M KOH aqueous solution (0.6 mL) was added to the mixture of *trans*-**1** (51 mg, 0.13 mmol) in ethanol/benzene (8 mL/11 mL) and the mixture was refluxed for 2 h. After the solvents were evaporated to remove benzene, water (10 mL) was added to the residue to give a red solution, which was then stirred at

80 °C for 15 h. The aqueous solution was cooled down to room temperature. 1 M HCl was slowly added dropwise to the solution to acidify to pH 3 and the obtained precipitate was filtered and washed five times with water to give **2** (35 mg, 81% yield). <sup>1</sup>H NMR (400 Hz, DMSO-*d*<sub>6</sub>):  $\delta$  7.31–7.16 (m, 8H), 6.84–6.81 (m, 2H), 4.72 (s, 4H). Elemental analysis: Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>6</sub>: C, 65.85; H, 4.91; N, 0.00%. Found: C, 65.62; H, 5.03; N, 0.00%.

***trans*-3.** *trans*-**3** was synthesized according to the above procedure using G3-Br. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si):  $\delta$  7.93 (d,  $J = 8.0$  Hz, 16H), 7.36 (d,  $J = 8.0$  Hz, 16H), 7.15 (t,  $J = 8.0$  Hz, 2H), 7.00–6.99 (m, 4H), 6.94 (s, 2H), 6.76 (d,  $J = 8.0$  Hz, 2H), 6.59–6.57 (m, 12H), 6.44–6.42 (m, 6H), 4.97 (s, 16H), 4.92 (s, 4H), 4.87 (s, 8H), 3.81 (s, 24H). MALDI-TOF MS Calcd for C<sub>128</sub>H<sub>112</sub>O<sub>30</sub>Na [M + Na]: 2151.7, found: 2151.1.

***trans*-4.** *trans*-**4** was synthesized according to the above procedure using *trans*-**3**. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.92 (d,  $J = 10$  Hz, 16H), 7.50 (d,  $J = 10$  Hz, 16H), 7.24–7.20 (m, 6H), 7.13 (d,  $J = 10$  Hz, 2H), 6.87 (d,  $J = 10$  Hz, 2H), 6.70 (s, 12H), 6.62 (s, 4H), 6.58 (s, 2H), 5.15 (s, 16H), 4.95 (s, 8H), 4.87 (s, 4H). MALDI-TOF MS Calcd for C<sub>120</sub>H<sub>96</sub>O<sub>30</sub>Na [M + Na]: Calcd for 2041.0, found: 2040.1.

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