

Control of Photoisomerization in Water-soluble Stilbene Dendrimers by Conformation of Dendrons: How Water-soluble Dendrimer Molecules Are Dissolved in Water

Tsutomu Takizawa and Tatsuo Arai*

Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8571

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Photoisomerization behaviors of carboxylate anion-terminated water-soluble stilbene dendrimers were controlled by difference in conformation of dendrons brought about by difference in number of surface functional groups. This is the first report to discuss in detail how solvent molecules surround dendrimer molecules to dissolve them and to reveal the crucial role that conformation of dendrons plays in determining photochemical properties of water-soluble dendrimers through optical spectroscopy.

Since the synthesis of poly(benzyl ether) stilbene dendrimers (**Gn**; $n = 1, 2,$ and 3), our first stilbene-cored dendrimers with benzyl ether type dendrons which underwent mutual *trans-cis* photoisomerization in organic solvent, we have been studying fluorescence and photochemical properties of various types of stilbene-cored dendrimers and the core itself (TMST), especially photoisomerization.^{1–5} We have found that substituents at the periphery of the dendrimers, or surface functional groups, may alter their photophysical and photochemical behavior. Particularly interesting are poly(benzyl ether) stilbene dendrimers with hydrophilic carboxylate anion surface functional groups (**p-wGn**; $n = 1, 2,$ and 3) which exhibit almost one-way *trans-to-cis* photoisomerization in water.^{5–8} Although it was suggested that certain properties of the dendrons were responsible for the unusual photochemical behavior, exactly how the stilbene core was affected was far from being well understood.⁸ In this respect, we have synthesized water-soluble stilbene dendrimers with twice the number of carboxylate anion surface functional groups compared to **p-wGn** (**dm-wGn**; $n = 1, 2,$ and 3) (Figure 1). It was expected that these dendrimers would be surrounded by solvent water molecules in a different way to display different state of dissolution and conformation of the dendrons compared to **p-wGn** due to increase in surface charge. From analysis of photophysical and photochemical behavior of these dendrimers, we explored how solvent water molecules surround the dendrimer molecules to dissolve them and how the state of dissolution determines the conformation of the dendrons in an effort to reveal the mechanism of the unusual photoisomerization of water-soluble stilbene dendrimers. We wish to report here the preparation and photochemical behavior of **dm-wGn** as well as how conformation of dendrons may be used to control photoisomerization.

The carboxylate anion-terminated stilbene dendrimers **dm-wGn** were synthesized by hydrolysis of ester-terminated stilbene dendrimers.⁵ The products were characterized by ¹HNMR and mass spectrometry (MALDI-TOF).¹³

Absorption spectra of **dm-wGn** in deaerated 2×10^{-3} M aqueous KOH solution have absorption around 300–350 nm whose molar extinction coefficients are independent of generation and absorption around 280 nm whose molar extinction

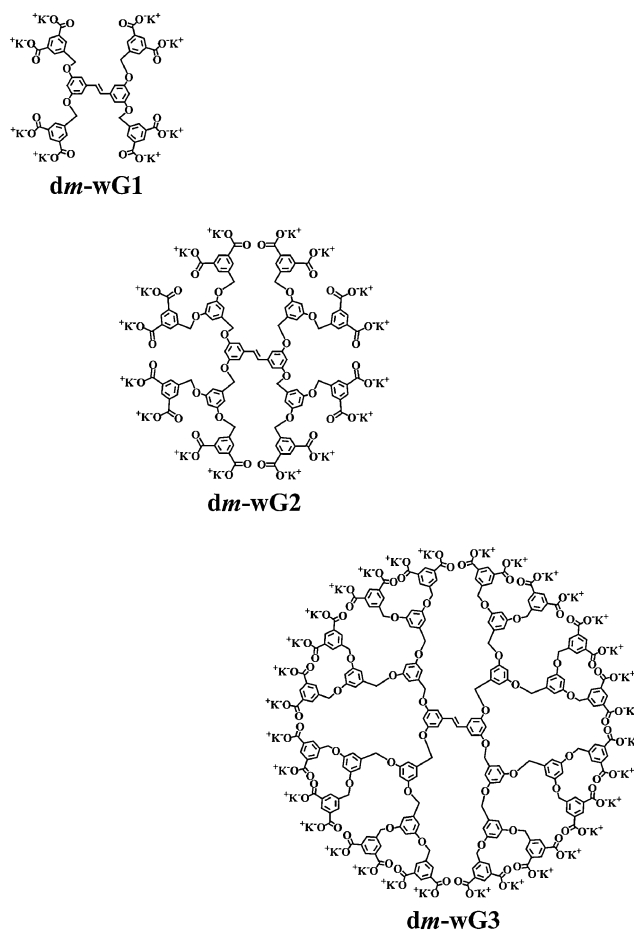


Figure 1. Structures of carboxylate anion-terminated stilbene dendrimers (**dm-wGn**; $n = 1, 2,$ and 3).

coefficients increase with increasing generation, which are assigned to absorption of the stilbene core and absorption of the dendrons, respectively (Figure 2). A slight red shift of absorption spectrum of *trans-dm-wG3* and slightly smaller molar extinction coefficients of **dm-wGn** compared to **dm-Gn** can be attributed to hydrophobic interactions between the stilbene core and the dendrons which induce molecular structures different from those in organic solvents.⁸ Fluorescence spectra of *trans-dm-wGn* in deaerated 2×10^{-3} M KOH aqueous solution were almost completely the same between *trans-dm-wG1* and *trans-dm-wG2*, and blue shifted in *trans-dm-wG3* indicating that stabilization of the excited singlet state of the stilbene core by solvent water molecules is nearly the same between the first and second generations, and decreases in the third (Figure 3). In other words, interactions of solvent water

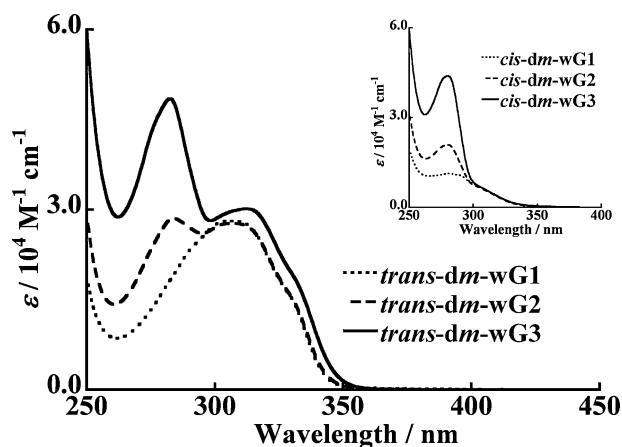


Figure 2. Absorption spectra of *trans-dm-wGn* and *cis-dm-wGn* (inset) in deaerated 2×10^{-3} M aqueous KOH solution.

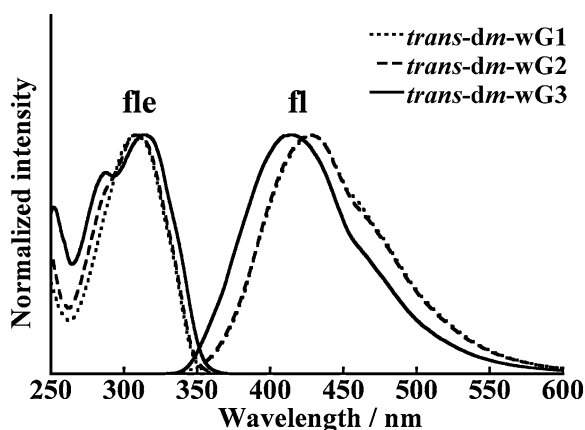


Figure 3. Fluorescence (fl) and fluorescence excitation spectra (fle) of *trans-dm-wGn* in deaerated 2×10^{-3} M aqueous KOH solution.

molecules with and polarity of environment around the stilbene core are similar between *trans-dm-wG1* and *trans-dm-wG2* while they decrease in *trans-dm-wG3*.^{4,6} Fluorescence decay curves of *trans-dm-wGn* in deaerated 2×10^{-3} M aqueous KOH solution fit biexponential functions suggesting that the environment around the stilbene core may not be uniform.⁸ Rate constants of fluorescence quenching by oxygen obtained from Stern–Volmer plots using average lifetimes decreased with increasing generation indicating that the stilbene core is less exposed to the surrounding environment in higher generation dendrimers (Table 1).¹³ The fluorescence properties of *trans-dm-wGn* show that hydrophobic interactions between the stilbene core and the dendrons make it more and more difficult for solvent water molecules to approach the stilbene core as the dendrons become bulkier with increasing generation.

These results are qualitatively similar to those obtained from *p-wGn* in 2×10^{-3} M aqueous KOH solution, but are decisively different quantitatively (Table 1). The molar extinction coefficients of *trans-p-wGn* at the absorption maxima of the stilbene core were smaller than $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ while those of *trans-dm-wGn* were around $3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The blue shift of

Table 1. Fluorescence properties of *trans-dm-wGn* in deaerated 2×10^{-3} M aqueous KOH solution

	λ_{fl} /nm	$\Delta\nu_{ss}$ / 10^3 cm^{-1}	Φ_f	Φ_{ET}	τ_{ave} /ns	k_q / $10^9 \text{ M}^{-1} \text{ s}^{-1}$
<i>trans-dm-wG1</i>	429	9.37	0.21	—	16.3	7.0
<i>trans-dm-wG2</i>	428	9.32	0.18	0.42	12.2	6.3
<i>trans-dm-wG3</i>	414	7.90	0.18	0.31	13.9	4.9

fluorescence maximum from the first to third generation of *trans-p-wGn* was 35 nm while that of *trans-dm-wGn* was 15 nm. In fact, the wavelength of fluorescence maximum of *trans-p-wG3*, which was 389 nm, corresponds to that of *trans-TMST* in THF solution whereas that of *trans-dm-wG3*, which was 414 nm, has no equivalent to any fluorescence of *trans-TMST* in organic solvents meaning that polarity of environment around the stilbene core is close to THF in *trans-p-wG3* and higher than acetonitrile in *trans-dm-wG3*.^{4,6} The efficiencies of energy transfer from the dendrons to the stilbene core estimated by comparison of absorption and fluorescence excitation spectra of the two constitutional units of *trans-p-wG2* and *trans-p-wG3* were 49 and 31%, respectively, while those of *trans-dm-wG2* and *trans-dm-wG3* were 42 and 31%, respectively.^{6,8}

The fact that molar extinction coefficients were larger, blue shift of fluorescence maximum with increasing generation was smaller, and efficiencies of energy transfer from the dendrons to the stilbene core were smaller for *dm-wGn* than *p-wGn* can be understood by considering how water-soluble stilbene dendrimers are dissolved in water. Hydrophobic interactions between the stilbene core and the dendrons act in *p-wGn* to create a congested environment around the core in which the dendrons take a shrunken conformation. Because the dendrons are gathered around the stilbene core, solvent water molecules cannot interact with the core so easily. In *dm-wGn*, the increase in surface charge increases electrostatic repulsion among the carboxylate anion surface functional groups which keeps the dendrons from taking a shrunken conformation and makes them take a stretched out conformation. With much more free space inside the dendrimer molecule, solvent water molecules are able to more easily go into the dendrimer decreasing the hydrophobic interactions and increasing the polarity of environment around the stilbene core. The less congested environment leads to more planar conformation of the stilbene core and higher molar extinction coefficients. It also leads to elongation of average dendron-to-core distance and smaller energy transfer efficiencies. Moreover, water molecules being much more accessible to the stilbene core leads to smaller blue shift of fluorescence maximum. From the above results and considerations, it can be said that *dm-wGn* takes a stretched out conformation with larger free space around the stilbene core than *p-wGn* which takes a shrunken conformation with little free space. These differences in conformation of the dendrons in water-soluble stilbene dendrimers resulted from changes in interactions between dendrimer and solvent water molecules brought about by the differences in number of carboxylate anion surface functional groups. Furthermore, these results confirmed the idea that fluorescence properties of the core chromophore may be used as an indicator of polarity and interactions with solvent molecules inside the dendrimer molecules.

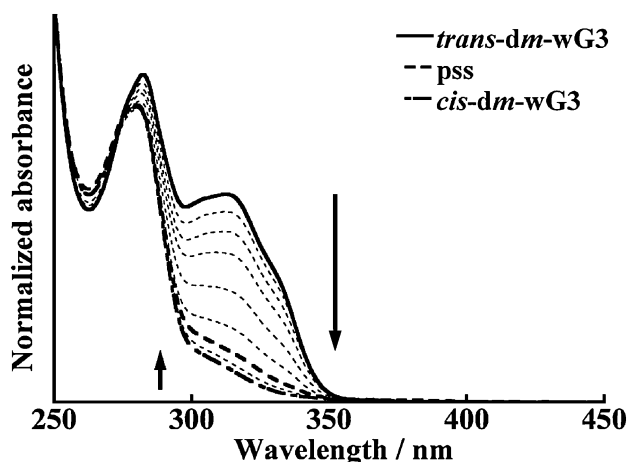


Figure 4. Change of absorption spectra of **dm-wG3** in deaerated 2×10^{-3} M aqueous KOH solution on irradiation at 330 nm normalized at isosbestic point.

In order to investigate how the difference in conformation of the dendrons affects photochemical behavior of water-soluble stilbene dendrimers, photoirradiation experiments were undertaken. On irradiation at 330 nm in deaerated 2×10^{-3} M aqueous KOH solution, both *trans*- and *cis*-isomers of **dm-wGn** underwent mutual *trans-cis* photoisomerization as can be seen from the change in absorption spectra (Figure 4). Isomerization quantum yields ($\Phi_{\rightarrow c}$) of *trans-dm-wG1*, *trans-dm-wG2*, and *trans-dm-wG3* were 0.45, 0.40, and 0.48, respectively. The two-way *trans-cis* photoisomerization of **dm-wG3** is distinctively different from the one-way *trans-to-cis* photoisomerization of **p-wG3** as can be seen from the isomer ratios at photostationary state ($([t]/[c])_{\text{pss}}$) which were determined to be 8/92, 14/86, and 10/90 for **dm-wG1**, **dm-wG2**, and **dm-wG3**, and 6/94, 1/99, and 0/100 for **p-wG1**, **p-wG2**, and **p-wG3**, respectively. A slight increase of absorbance around 250–275 nm was also observed upon irradiation of *cis-dm-wGn* indicating the occurrence of photocyclization of the stilbene core.³ This was also something that was not observed for **p-wGn**.

These results suggest that the difference in free space around the stilbene core arising from the difference in conformation of the dendrons alters the photochemical properties of water-soluble stilbene dendrimers. More specifically, *cis-to-trans* photoisomerization and photocyclization of the *cis*-isomers are inhibited for **p-wG3** because of the lack of free space for the rotation of the double bond in photoisomerization and conrotatory ring-closing in photocyclization whereas both reactions occur for the *cis*-isomers of **dm-wG3** which has enough free space around the stilbene core. The one-way *trans-to-cis* photoisomerization of **p-wG3** occurs because the volume of the stilbene core decreases upon *trans-to-cis* isomerization and the shrunken conformation of the dendrons inhibits *cis-to-trans* isomerization which requires an increase in volume of the core.⁸ Another way to interpret these results is to say that the degree of contraction of water-soluble dendrimers can be controlled by the number of hydrophilic surface functional groups which in turn determines the photochemical behavior of the core chromophore.

Most of the research on dendrimers is focused on specific phenomena unseen in compounds with low molecular weights,

and information on how exactly dendrimer molecules exist in solution including their conformation and how solvent molecules interact with them has been limited. What little is known was most often obtained from theoretical and computational methods.^{9–12} This report is unique in that experimental findings particularly photophysical and photochemical observations are the basis of discussing states of dissolution and conformation of dendrons of water-soluble dendrimers. Moreover, it was found that conformation of dendrons may be utilized to control photoisomerization of the core chromophore. It was also shown here that fluorescence of core chromophores can be used as an indicator of penetration of solvent molecules within a dendrimer molecule. To the best of our knowledge, this is the first report to reveal the important relationship between photochemical behavior of the core chromophore and conformation of the dendrons in water-soluble dendrimers through optical spectroscopy.

In conclusion, it was found that conformation of the dendrons in water-soluble stilbene dendrimers can be altered by the number of carboxylate surface functional groups, and that it determines the size of free space and the polarity of environment around the stilbene core. Furthermore, the difference in free space around the stilbene core between **p-wG3** and **dm-wG3** brought about the difference in photochemical behavior between them which underwent one-way and two-way photoisomerization respectively.

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