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ARTICLES

Solvent Effect on the Photochemical Properties of Symmetrically Substituted *trans*-3,3′,5,5′-Tetramethoxystilbene

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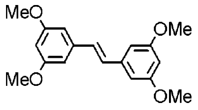
Photochemical properties of *trans*-3,3′,5,5′-tetramethoxystilbene (TMST) have been studied in various polar solvents. The Stokes shift of *trans*-TMST was found to be increased with increasing solvent polarity. The fluorescence lifetime of *trans*-TMST experienced a large solvent effect changing from 2.3 ns in cyclohexane to 16.6 ns in acetonitrile. These results indicate that the excited singlet state of *trans*-TMST has a charge-transfer (CT) character. On the basis of the obtained results, the interior polar environment of a water-soluble TMST dendrimer is discussed.

Photochemical properties of stilbene and its related compounds have been studied extensively.[1−3] The isomerization and fluorescence emission properties of stilbenes are strongly dependent on the structure; introduction of different aromatic ring or substituent groups in the phenyl ring of stilbene induces considerable modification of the electronic environment around the stilbene ring leading to significant changes in its physical and photochemical properties. For example, one-way cis−trans photoisomerization of stilbene both in the excited singlet and triplet states was found to take place although one of the phenyl rings was replaced by the anthracene ring providing a potential energy surface different from that of the parent stilbene.[4] In addition, the results of excited-state behaviors of electron-donating and electron-withdrawing substituted stilbenes[5−9] and their analogues[10,11] indicated the important role of the intramolecular charge-transfer (ICT) state or twisted intramolecular charge-transfer (TICT) state on deactivation.

We and Lewis et al. previously reported that the photochemical behavior of several mono-substituted hydroxystilbenes is highly dependent upon the position of the hydroxyl substituent.[12,13] The photoinduced addition of water was found to be more efficient in *meta*-hydroxystilbene than in *ortho*- and *para*-hydroxystilbene in acetonitrile/water binary solvent mixtures.[12] Furthermore, we have studied stilbenoid dendrimers where the stilbene works as a core of the dendrimer to investigate the effect of bulky dendron subunits on the excited-state properties.[14−16] We have already reported the photochemical behavior of water-soluble stilbene dendrimers (WSDs) having potassium carboxylate at the surrounding benzyl ether-type dendron attached at each of the meta positions of the phenyl ring of stilbene.[17−19] In the higher generation of WSDs, the fluorescence maximum shifted to a shorter wavelength region and the efficiency of intramolecular energy transfer from the peripheral dendron to the stilbene core increased with increasing concentration of a salt, KCl.[19] These results suggest that the water-soluble dendrimers having stilbene as a photoresponsive core may be assumed to be a model compound for a photoresponsive biomolecule and/or a photoreversible unimolecular micelle, and the observed blue-shifting in the fluorescence spectrum of stilbene is ascribed to the lessening of the interaction with water, since the stilbene core is shielded gradually in a three-dimensional fashion by the increasing generation of peripheral dendrons. Therefore, in such a dendritic structure, the interaction of the stilbene core with surrounding solvents, that is, the polar environment surrounding the stilbene core, can be well tuned by the generation of peripheral dendrons.



***trans*-TMST**

Figure 1. Structure of the trans isomer of 3,3′,5,5′-tetramethoxystilbene (TMST).

To survey the interior protic landscape of WSDs, it is of fundamental importance to study the photochemical properties of the core moiety, that is, 3,3′,5,5′-tetramethoxystilbene (TMST)[20,21] (Figure 1), separately in solvents of various polarities. Previously, we reported only the qualitative behavior of cis−trans photoisomerization and photocyclization to produce dihydrophenanthrene-type compounds.[21] In the present study, we have estimated the quantum yields of isomerization and fluorescence and the fluorescence lifetime in solvents having various polarities for *trans*-TMST. The conformation and local environment of the stilbene core in WSDs is discussed on the basis of the drastic solvent effect on the fluorescence behavior of *trans*-TMST.

Experimental Section

Material and Solvents. Synthesis and characterization of *trans*-TMST have already been reported in the previous paper.[21]

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TABLE 1: Spectroscopic Parameters for *trans*-TMST and Water-Soluble Stilbene Dendrimers

	solvent	λ_{abs} (nm)	$\epsilon \times 10^4$ (M^{-1} cm^{-1})	λ_{cm} (nm)	$\Delta\nu_{0,0}$ (nm)	$\Delta\nu_{st} \times 10^3$ (cm^{-1})	$\Delta\nu_{1/2} \times 10^3$ (cm^{-1})
	hexane	304	2.80	366	337	5.6	3.9
	cyclohexane	304	2.98	366	333	5.6	4.0
	benzene	310	3.11	373	343	5.6	4.2
	chloroform	309	2.81	388	344	6.6	4.5
	ethyl acetate	306	3.14	380	340	6.4	4.5
	tetrahydrofuran	309	3.19	390	342	6.7	4.5
	dichloromethane	308	2.90	390	344	6.8	4.5
	2-propanol	305	2.84	388	341	7.0	4.7
	methanol	306	2.95	395	342	7.4	4.7
	dimethylformamide	313	3.15	392	344	6.5	4.6
	acetonitrile	307	2.97	395	343	7.2	4.7
G1	2 mM KOH aq.	307	1.85	424	368	9.1	5.0
G2	2 mM KOH aq.	311	1.81	411	360	7.6	5.2
G3	2 mM KOH aq.	313	1.81	389	354	5.9	4.6

All the solvents for preparing solutions were of UV and fluorescence spectroscopic grade and were used without further purification.

Methods. Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 spectrophotometer and on a Hitachi F-4500 fluorimeter, respectively. Fluorescence lifetimes were determined with a Horiba NAES-1100 time-resolved spectrofluorimeter. Quantum yields of fluorescence emission were determined by using naphthalene ($\Phi_f = 0.23$) as a standard.[22] A correction of the difference in the 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 0.08, and the integration of the fluorescence spectra over wavenumber was plotted against absorbance at excitation wavelength. The slope of these plots gives the relative value of the fluorescence quantum yield. The quantum yield of trans−cis isomerization of *trans*-TMST in tetrahydrofuran was determined on irradiation at 313 nm from a 150-W xenon lamp through a monochromator. The sample solution was deaerated by bubbling argon and irradiated for 15 min to keep the conversion within 8%. Light intensity was determined by tris(oxalato)ferrate(III) actinometry.[23] The concentrations of each isomer in tetrahydrofuran were determined by high-performance liquid chromatography through a column (Kanto RP-18) eluting with methanol/water = 80:20. The quantum yields in various solvents were determined by comparison of the rate of initial absorbance change in the optically matched solution at 308 nm with that of the trans isomer in tetrahydrofuran under the same irradiation conditions ($\lambda_{ex} = 308$ nm).

Results and Discussion

Absorption and Fluorescence Spectra. A compilation of the photochemical properties, absorption maxima, fluorescence maxima (λ_{abs} and λ_{em}, respectively), Stokes shifts ($\Delta\nu_{st}$), and molar extinction coefficient (ϵ) of λ_{abs}, of *trans*-TMST in various solvents are summarized in Table 1. The 0,0 transitions ($\lambda_{0,0}$) were estimated from the intersection of normalized absorption and fluorescence spectra. *trans*-TMST exhibited absorption at the wavelength region of 300−360 nm with λ_{max} at around 303−313 nm in all solvents. Apparently, absorption spectra exhibited only a slight red-shift (≤4 nm) with varying solvent polarity, indicating that the solvent−solute interaction is indeed small in the ground state of *trans*-TMST. The molar extinction coefficient at the absorption maximum of *trans*-TMST has almost the same values in all solvents investigated ($\epsilon = (2.8-3.0) \times 10^4$ M^{-1} cm^{-1}) (Figure 2).

Figure 3 shows the normalized fluorescence spectra of *trans*-TMST measured in various solvents. The fluorescence maxima of *trans*-TMST are reported in Table 1 and found to be independent of excitation wavelength in all solvents. In contrast to the absorption spectrum, the fluorescence spectrum showed vibrational structure in nonpolar solvents such as hexane; however, as the polarity of the solvent increased in order, the vibrational feature diminished gradually and the spectrum became structureless accompanied by a significant broadening. Noticeably, both the extent of broadening and losing the vibrational feature increased with increasing solvent polarity, that is, an increase of the half-width of the fluorescence band with increasing solvent polarity was found for *trans*-TMST. The maxima of the fluorescence spectra (λ_{em}) showed a considerable red-shift on going from hexane (366 nm) to acetonitrile (395 nm). The Stokes shift of *trans*-TMST increased with increasing solvent polarity from 5600 cm^{-1} in hexane to 7200 cm^{-1} in acetonitrile.

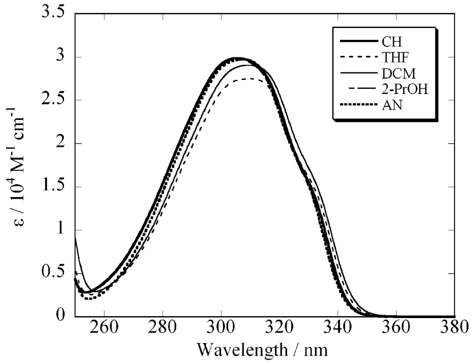


Figure 2. Absorption spectra of *trans*-TMST in cyclohexane (CH), tetrahydrofuran (THF), dichloromethane (DCM), 2-propanol (2-PrOH), and acetonitrile (AN).

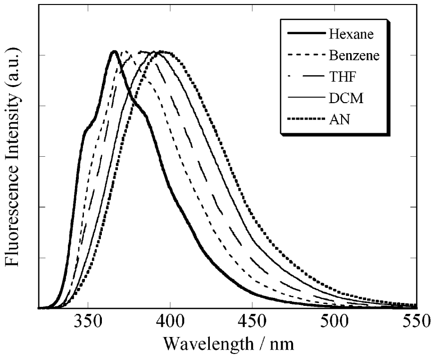


Figure 3. Fluorescence spectra of *trans*-TMST in hexane, benzene, tetrahydrofuran (THF), dichloromethane (DCM), and acetonitrile (AN).

TABLE 2: Quantum Yields of Fluorescence (Φ_f) and Photoisomerization ($\Phi_{t\rightarrow c}$), Fluorescence Lifetime (τ_s), Rate Constants for Fluorescence (k_f), and Photoisomerization (k_{iso}) for *trans*-TMST and Water-Soluble Stilbene Dendrimers

	solvent	$\Phi_f{}^a$	τ_s (ns)	$\Phi_{t\rightarrow c}$	$k_f{}^d \times 10^7$ (s^{-1})	$k_{iso}{}^e \times 10^8$ (s^{-1})
	hexane	0.21	2.6	0.38^c	8.1	2.9
	cyclohexane	0.19	2.3	0.39^c	8.3	3.4
	benzene	0.24	4.1	0.31^c	5.9	1.5
	chloroform	0.16	5.3	0.35^c	3.0	1.3
	ethyl acetate	0.27	10.0	0.36^c	2.7	0.72
	tetrahydrofuran	0.27	10.0	0.38^b	2.7	0.76
	dichloromet hane	0.23	8.9	0.39^c	2.6	0.87
	2-propanol	0.31	10.8	0.23^c	2.9	0.43
	methanol	0.28	14.8	0.33^c	1.9	0.44
	dimethylformamide	0.38	14.3	0.31^c	2.7	0.43
	acetonitrile	0.29	16.6	0.32^c	1.8	0.39
G1	2 mM KOH aq.	0.21^f	15.0^f	0.17^f	1.4^f	0.22^f
G2	2 mM KOH aq.	0.05^f	$11.1/2.1^f$	0.47^f		
G3	2 mM KOH aq.	0.17^f	$12.1/3.7^f$	0.15^f		

[a] Determined by comparison with the fluorescence of naphthalene in cyclohexane as a standard ($\Phi_f = 0.23$). [b] Determined by the observation of each isomer by HPLC, and the light intensity was estimated by tris(oxalato)ferrate(III) actinometry. [c] Comparison of the absorbance change with that in THF as a standard under the same irradiation condition. [d] $k_f = \Phi_f/\tau_s$. [e] $k_{iso} = 2 \times \Phi_{t\rightarrow c}/\tau_s$. [f] Ref 17.

Quantum Yields for Fluorescence and Photoisomerization and Singlet Lifetimes. The fluorescence quantum yields (Φ_f) of *trans*-TMST determined at room temperature in several polar solvents are reported in Table 2. The magnitude of Φ_f was slightly increased (0.2−0.3) with increasing solvent polarity, the values of which are more than 1 order of magnitude larger than the value of $\Phi_f = 0.016$ as reported[24] for parent *trans*-stilbene.

Upon irradiation with 308-nm light under argon, the trans isomers of TMST underwent isomerization around the C═C double bond to give the corresponding cis isomer in various solvents. Quantum yields for photoisomerization ($\Phi_{t\rightarrow c}$) of *trans*-TMST in solvents of different polarities are compiled in Table 2. The values of $\Phi_{t\rightarrow c}$ for the *trans*-TMST were found to be almost constant over solvent polarities, but were smaller than the value of $\Phi_{t\rightarrow c} = \sim 0.5$ reported for the parent *trans*-stilbene.[24] Assuming that the decay of the perpendicular p* state yields a 1:1 ratio of trans/cis isomers,[2] the sum of the fluorescence and isomerization quantum yields ($\Phi_f + 2 \times \Phi_{t\rightarrow c}$) for *trans*-TMST in all solvents is within the experimental error of 1.0. This finding suggests that other channels of nonradiative decay are absent.

The fluorescence lifetimes (τ_s) of the *trans*-TMST determined by the single-photon counting method under an argon atmosphere at room temperature in different solvents are summarized in Table 2. All decays could be fitted well by single-exponential decay. The fluorescence lifetime of *trans*-TMST is 2.6 and 2.3 ns in nonpolar solvents such as hexane and in cyclohexane, respectively. The lifetime increased with increasing solvent polarity to give 4.1, 5.3, and 10 ns in benzene, chloroform, and ethyl acetate, respectively. In tetrahydrofuran, dichloromethane, and 2-propanol, these lifetimes were almost constant and gave the same values as those obtained in ethyl acetate. The fluorescence lifetime showed a significant increase in more polar solvents, giving values of 14.8, 14.3, and 16.6 ns in methanol, *N*,*N*-dimethylformamide, and acetonitrile, respectively. Therefore, the fluorescence lifetime of *trans*-TMST displays large variation with solvent polarity, the value of which is 7-fold longer in acetonitrile than in cyclohexane. Unlike the Φ_f values, the τ_s values of *trans*-TMST are considerably longer in acetonitrile than in cyclohexane. These results indicate that the stability of the lowest excited singlet state of *trans*-TMST is sensitive to solvent polarity.

On the basis of the results mentioned above, the value of the rate constants for fluorescence ($k_f = \Phi_f \tau_s{}^{-1}$) of *trans*-TMST can be evaluated from the fluorescence lifetime and its quantum yields (Table 2). Since the fluorescence lifetime of *trans*-TMST shows the 7-fold increment on going from nonpolar to polar solvent and the yield of fluorescence remains almost constant over the solvent polarity, it is expected from the above relation that the value of the fluorescence rate constant will decrease with increasing the solvent polarity. On the other hand, the rate constant for fluorescence can also be evaluated from the relation of the molar extinction coefficient. Since the difference of the molar extinction coefficient for *trans*-TMST was found to be small among the solvents employed as mentioned above, there should be a small difference in the estimated fluorescence rate constants. However, the observed longer fluorescence lifetimes, that is, the smaller magnitude of estimated rate constants, in the solvents of high polarities indicate that the lowest excited singlet state of the *trans*-TMST was affected largely by solvent polarity to give a stable fluorescent excited state different from the locally excited state (LE) in polar solvent. *trans*-TMST may exhibit fluorescence from the LE state and the excited charge-transfer state (CT) in nonpolar solvent and in polar solvent, respectively (Figure 4). Furthermore, rate constants for isomerization ($k_{iso} = 2\Phi_{t\rightarrow c}\tau_s{}^{-1}$) (Table 2) of *trans*-TMST can be evaluated from the fluorescence lifetime and the isomerization quantum yield ($\Phi_{t\rightarrow c}$). Since the isomerization quantum yield ($\Phi_{t\rightarrow c}$) was almost constant over all the solvents, the rate constant of isomerization was modulated only by the fluorescence lifetime and showed a decreasing trend upon going from the solvent of lower polarity to higher; this indicates that isomerization from the CT state is suppressed due to the extreme stability.

Solvatochromic Measurement and Dipole Moments. The solvent-dependent shifts in fluorescence spectra can be used to determine the dipole moment of the emissive excited states using the Lippert−Mataga equation (eq 1).[25−27]

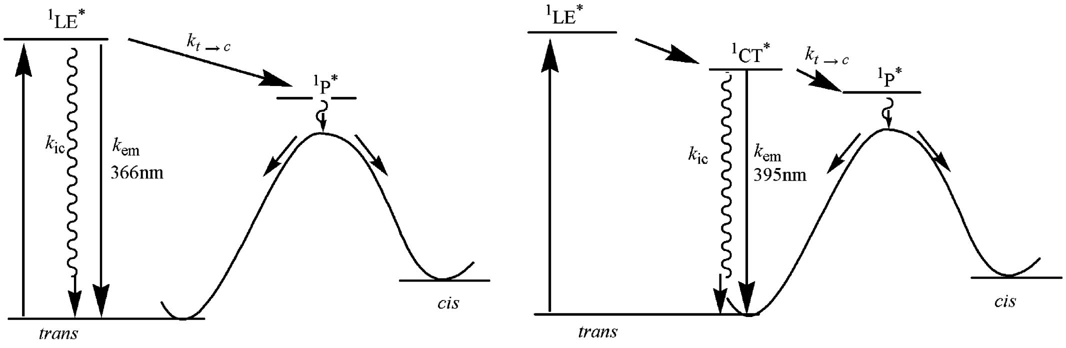
$$\Delta\nu_{st} = \nu_{abs} - \nu_{fl} = [2\mu_e(\mu_e - \mu_g)/hca^3]\,\Delta f \qquad (1)$$

where

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$$

Furthermore, ν_{abs} and ν_{fl} are the absorption and fluorescence maxima, μ_g and μ_e are the ground and the excited-state dipole moments, a is the solvent cavity radius in Å, ϵ is the solvent dielectric constant, and n is the solvent refractive index. Figure 5 shows the plot of the solvatochromic shifts of the fluorescence maxima ($\Delta\nu_{st}$) of *trans*-TMST as a function of the solvent polarity (Δf), which in turn results in a straight line. The dipole moment of the excited state of *trans*-TMST was determined from the slope of the straight line (5415 cm^{-1}) to be μ_e 9.5D based on $\mu_g = 2.5$D using the MOPAC/AM1 method. Therefore, the dipole moment in the excited state of *trans*-TMST has a large value. These results suggest that *trans*-TMST has a charge-transfer character in the excited singlet state.

Solvent Effect of the *meta*-Methoxy Group on the Stilbene on Photochemical Behaviors. In this section, we focus on the effect of solvent polarity on the photochemical behaviors of stilbene derivatives having electron-donating groups at the meta position of the phenyl ring. Recently, Lewis and Pincock et al. have reported that the meta substituents prolong the fluorescence



(a) in nonpolar solvents (b) in polar solvents

Figure 4. Simplified scheme for the formation and decay of the fluorescent ^{1}CT* state and ^{1}LE state and isomerization of the *trans*-TMST (a) in nonpolar solvents and (b) in polar solvents.

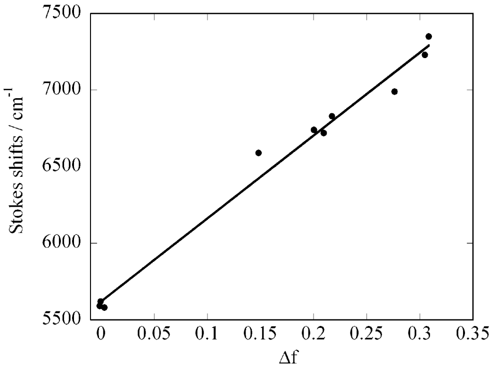


Figure 5. Lippert−Mataga plot for *trans*-TMST. The Δf parameter is calculated according to eq 1 for cyclohexane, hexane, benzene, chloroform, ethyl acetate, tetrahydrofuran, dichloromethane, 2-propanol, methanol, *N*,*N*-dimethylformamide, and acetonitrile in order of increasing polarity.

lifetime of the stilbene chromophore and lead to the high fluorescence quantum yields in comparison with para-substituted stilbene derivatives, and they attributed this phenomenon to the so-called “meta-effect of stilbene”.[9,28,29] Besides, in some meta-substituted stilbene derivatives, the fluorescence spectra were found to be shifted to the longer wavelength region with increasing solvent polarity providing the evidence for the charge-transfer (CT) character of the fluorescent singlet state.[30] Therefore, we have discussed the solvent polarity effect on the excited-state properties among *trans*-TMST and these meta-substituted stilbenes.

trans-TMST displays extensive variation of the florescence lifetime in various polarity solvents; those of *trans*-TMST were 2.3 ns in cyclohexane and 16 ns in acetonitrile, while those of 3-aminostilbene changed slightly from 7.5 ns in cyclohexane to 11.7 ns in acetonitrile.[28a] Furthermore, the Stokes shifts of *trans*-TMST were also found to be larger than those of 3-aminostilbene ($\Delta\nu_{st}$: 2720 cm^{-1} and 3900 cm^{-1} for hexane and acetonitrile, respectively) in nonpolar and polar solvents (Table 1), respectively. These results indicate that the fluorescence behaviors of *trans*-TMST are more sensitive to solvent polarity than those of 3-aminostilbene. Increasing polarity results in an increase in quantum yield of photoisomerization for 3-aminostilbene ($\Phi_{t \to c}$: 0.09 in cyclohexane and 0.23 in acetonitrile), while the quantum yields of fluorescence decrease substantially with increasing solvent polarity (Φ_f: 0.78 in cyclohexane and 0.40 in acetonitrile). However, the quantum yields of fluorescence and photoisomerization of *trans*-TMST are almost the same value in all solvents investigated ($\Phi_f = 0.2-0.3$ and $\Phi_{t \to c} = 0.3-0.4$). The activation energy (E_a) for the trans−cis isomerization of the *trans*-TMST in the ground state was calculated by the Arrhenius equation by examining the temperature dependence in cyclohexane and acetonitrile solution. The E_a and the frequency factor (A) for the trans−cis isomerization were calculated to be 4.5 kcal mol^{-1} and 7.6 $\times 10^{10}$ s^{-1}, respectively, in cyclohexane and 4.2 kcal mol^{-1} and 4.7 $\times 10^{11}$ s^{-1}, respectively, in acetonitrile. In addition, the activation energy barrier for twisting of the excited singlet state of *trans*-TMST is much lower than that of 3-aminostilbene in hexane ($E_a \geq 7$ kcal mol^{-1}). Besides, in polar solvent, the deactivation from the excited state of 3-aminostilbene takes place in the excited triplet state after undergoing intersystem crossing from the excited singlet state.[28a] In contrast, *trans*-TMST gave no detectable T-T absorption spectra indicating that the trans−cis isomerization process in the triplet state has only a small contribution, if any. The above results indicate that the solvent effect on the excited-state properties of *trans*-TMST is different from that of 3-aminostilbene.

Then, the effect of solvent polarity on the photochemical properties of *trans*-TMST was also compared with several *meta*-methoxy-substituted stilbene derivatives. The effects of solvent polarity on the fluorescence maximum and the fluorescence lifetime of mono-substituted stilbene such as 3-methoxystilbene are practically solvent-independent ($\lambda_{em} = 358$ nm and $\tau_s = 0.7$ ns in cyclohexane and $\lambda_{em} = 359$ nm and $\tau_s = 0.9$ ns in acetonitrile), while those of disubstituted stilbene such as 3,5-dimethoxystilbene exhibited fluorescence at much longer wavelengths with longer fluorescence lifetimes in the more polar solvent ($\lambda_{em} = 364$ nm and $\tau_s = 3.6$ ns in cyclohexane and $\lambda_{em} = 390$ nm and $\tau_s = 16.9$ ns in acetonitrile).[29] These effects on the fluorescence behavior of *trans*-TMST (Table 2) are comparable to those of 3,5-dimethoxystilbene. These results suggest that introduction of at least two methoxy substituents at the meta position of the phenyl ring for stilbene leads to a significantly longer singlet lifetime and a solvatochromic effect on the fluorescence behaviors of the stilbene which possesses charge-transfer character in the excited state.[29b]

It is reported that a 3,5-dimethoxy group enhances the reactivity of benzyl carbon.[31] In this case, different electron density between the ground and excited states causes a relatively long fluorescence lifetime and unusual photoreactivity. In addition, the increase of dipole moment in the excited state results in the remarkable solvent−polarity dependence. The intramolecular CT state seems to be stable in acetonitrile due to the high polarity and may be the origin of prolonged emission lifetime in comparison with that of the nonpolar solvent.

A 3,5-dimethoxy group is known to induce high photoreactivity at the carbon part of the olefin in comparison with a 3-methoxy group. Since this may affect the dipole moment of

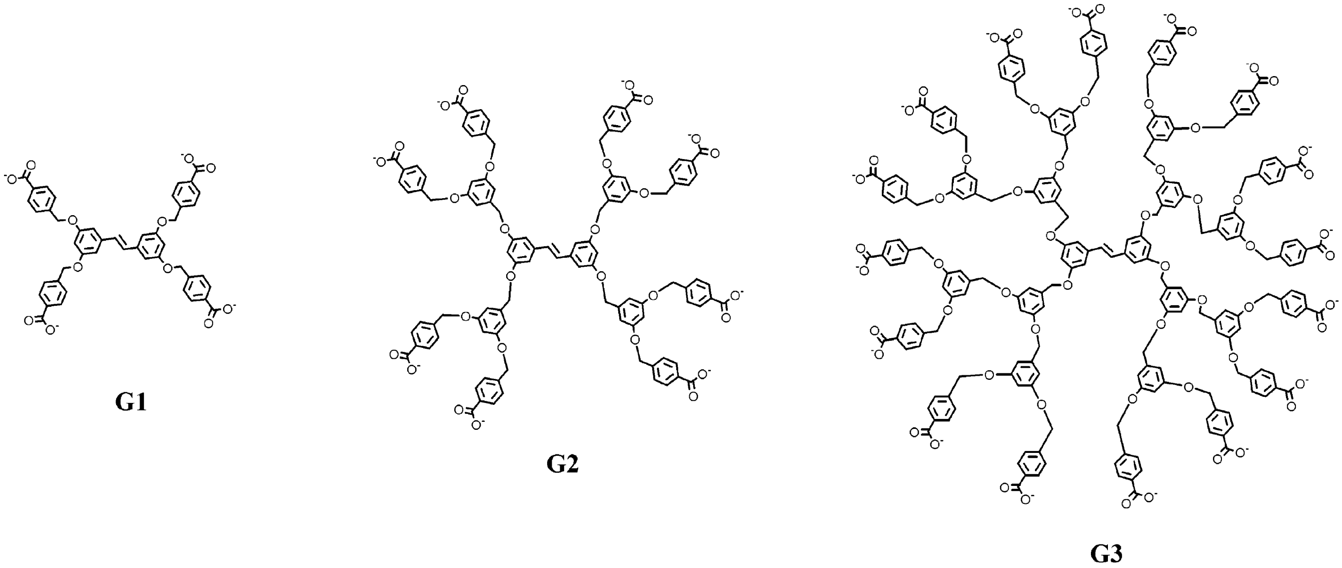


Figure 6. Structure of the trans isomer of water-soluble stilbene dendrimers (WSDs).

excited stilbene, properties of the excited state such as fluorescence spectra and lifetime in 3,5-dimethoxystilbene seem to remarkably depend on solvent polarity in relation to 3-methoxystilbene. Considering the chemical reactivity in the excited stilbene derivative, the long lifetime observed in acetonitrile has an advantage in efficient photochemical reaction.

Comparison with Water-Soluble Stilbene Dendrimers (WSDs). The basic photochemical properties of *trans*-TMST were compared with stilbenoid dendrimers having a poly(benzyl ether) dendron with a carboxylate anion at the periphery (WSDs)[17−19] (Figure 6). Note that the *trans*-TMST corresponds to the 0th generation of WSDs. The following two points are noteworthy about WSDs.

(1) The absorption maximum of the stilbene core in the dendrimer shifted to a longer wavelength at higher generations to give λ_{abs} of 307, 310, and 315 nm, respectively, for G1, G2, and G3 and a shoulder at a longer wavelength region around 340−360 nm for G2WSD and G3WSD.[17] The solubility of WSDs in water was found to increase with increasing the generation because of an increase of the number of the carboxylate group and benzyl ether dendron group with the generation. Therefore, the observed red-shifting on the absorption spectrum with increasing generation may be caused by decreasing interaction of water and *trans*-TMST core. However, the absorption spectrum of *trans*-TMST was found to be almost unaffected by the solvent polarity, thus the observed red-shifting in the absorption maximum of WSDs may arise from the other possible reasons rather from the interaction of water and stilbene core. In addition, one can compare the molar extinction coefficient of the $\pi-\pi^*$ absorption band at 300−315 nm of the stilbene moiety of WSDs and *trans*-TMST. The value of WSDs ($\epsilon = <2 \times 10^4$ M^{-1} cm^{-1}) is smaller than that of the *trans*-TMST in various organic solvents ($\epsilon = \sim 3 \times 10^4$ M^{-1} cm^{-1}). The smaller ϵ of WSDs suggests that there are some extents of electronic and conformational interactions between the stilbene core and benzyl ether dendron in water. The stilbene core in G1 is considered to be twisted around the single bond between the ethylenic carbon and the aromatic ring by the carboxylate group at the periphery, which may take an orientation to cover the ethylene core three-dimensionally. In such a circumstance, the surrounding dendron group may have a congested environment for the core stilbene, and the degree of such congestion increases with increasing generation of dendron. As a result, we inferred that the absorption maximum for the stilbene core of WSDs red-shifted with increasing generation due to hydrophobic interaction between benzyl ether dendrons.

(2) The fluorescence maximum of WSDs showed a blue-shift (λ_{em} 424, 411, and 389 nm for G1, G2, and G3, respectively) with increasing generation, although that of *trans*-TMST showed a red-shift with increasing solvent polarity as described above. The blue-shifting of the fluorescence maximum of WSDs with increasing generation indicates the decrease of interaction between water and excited state of stilbene at the inner environment of higher generations.[18] The fluorescence lifetime of G1 has been determined to be 15 ns with single-exponential decay. As mentioned above, the fluorescence lifetime of *trans*-TMST is very sensitive to solvent polarity, which changed from 2.6 ns in nonpolar solvents such as hexane to 16.6 ns in polar solvents such as acetonitrile. Therefore, the observed long fluorescence lifetime indicates that the excited state of G1 is in the vicinity of a considerable polar environment, the polarity of which is comparable to that of acetonitrile. On the other hand, the fluorescence decay curves of G2 and G3 were fitted to a bi-exponential function to give a longer lifetime (11 ns) and a shorter lifetime (2−3 ns), where the longer lifetime of the 11-ns component indicates the region of intermediate polarity comparable to that of ethyl acetate, while the shorter one of 2−3 ns indicates the region of minimum polarity such as hexane. The ratio of longer lifetime and shorter lifetime of WSDs was 26/74 and 20/80 for G2 and G3, respectively. These results clearly imply that the increasing generation of WSDs decreases the interaction between the excited singlet state of stilbene and water due to the increase of the hydrophobic dendron subunits.

Conclusion

We have revealed that the meta-effect on the fluorescence behavior of stilbene is observed in a symmetrically substituted compound with a methoxy group. *trans*-TMST displays large solvent-induced fluorescence shifts in various polar solvents. In addition, the effect is considerably larger and the fluorescence lifetime in a polar solvent is 7-fold longer than in a nonpolar solvent. To the best of our knowledge, the lifetime observed as 16.6 ns for *trans*-TMST in acetonitrile should be the longest lifetime of a stilbene compound symmetrically substituted on the phenyl rings. It should be mentioned at the last stage of the discussion that the symmetrically substituted *trans*-TMST suffered a strong effect of solvent polarity on the excited singlet state properties.

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