doi:10.1246/cl.2011.1124

Remote Controlled Intramolecular Exciplex Formation and Enhanced Photoisomerization in Stilbene-cored Poly(benzyl ether) Dendrimers with Alkoxycarbonyl Surface Functional Groups

Tsutomu Takizawa and Tatsuo Arai*
Graduate School of Pure and Applied Sciences, University of Tsukuba, Ibaraki 305-8571

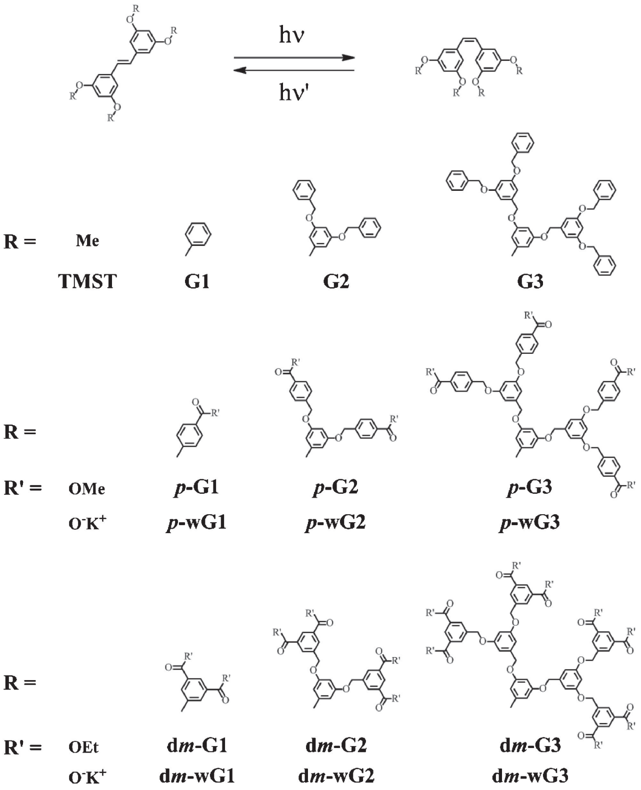
(Received July 25, 2011; CL-110620; E-mail: arai@chem.tsukuba.ac.jp)

Exciplex-induced isomerization played a key role in highly efficient photoisomerization of stilbene-cored poly(benzyl ether) dendrimers tethering two alkoxycarbonyl surface functional groups at the meta position of each terminating phenyl group. This is the first report on the control of photochemical behavior of dendrimers using intramolecular exciplex formation.

We have been studying photochemical isomerization of various types of stilbene dendrimers which are soluble in organic solvents as well as in water. Our first stilbene dendrimers having benzyl ether dendrons at the meta position of the phenyl ring of the core stilbene (**G1**–**G3** in Scheme 1) soluble in organic solvents underwent mutual *trans*–*cis* isomerization on photoirradiation.[1,2] On the other hand, introduction of hydrophilic carboxylate anion groups at the periphery of the above-mentioned dendrimers (***p*-wG1**–***p*-wG3** in Scheme 1) drastically changed the photochemical behavior to exhibit almost one-way *trans*-to-*cis* isomerization.[3,4] Thus, the substituents at the periphery of the dendrimers may alter the photochemical as well as photophysical properties of stilbene dendrimers, especially the introduction of carboxylate anions. In this respect, we have decided to prepare similar stilbene dendrimers which have two carboxylate anion groups at the meta position of each terminating phenyl group of the dendrons (**d*m*-wG1**–**d*m*-wG3** in Scheme 1) compared to one carboxylate anion group at the para position. In order to prepare these dendrimers we should prepare the ester-terminated stilbene dendrimers (**d*m*-G1**–**d*m*-G3** in Scheme 1) followed by hydrolysis to give water-soluble dendrimers. In the course of these studies, we have found that the ester-terminated dendrimer **d*m*-G1** exhibits quenching of the fluorescence emission of the core stilbene, exciplex emission in highly polar solvent DMF, and exciplex-induced *trans*–*cis* isomerization. We wish to report here the preparation and the photochemical processes of **d*m*-G1** and **d*m*-G2** induced by peripheral electron-accepting groups at the remote position.

The dendrimers were synthesized by coupling of 3,3′,5,5′-tetrahydroxystilbene with the respective dendrons. The products were characterized by ^{1}H NMR, ^{13}C NMR, MS (MALDI-TOF), and elemental analysis.[12]

Absorption spectra of dendrimers **G*n***, ***p*-G*n***, and **d*m*-G*n*** in deaerated THF solution have maxima around 310 nm resembling that of 3,3′,5,5′-tetramethoxystilbene (**TMST**) and absorption around 285 nm which are assigned to the dendrons. Fluorescence spectra of ***p*-G1** and **d*m*-G1** in deaerated THF solution have maxima around 375 nm and shoulders around 390 nm while those of **TMST** and the rest of the dendrimers have single maxima around 390 nm (Figure 1). These spectral profiles indicate that electronic interactions between the core stilbene and dendrons are negligible in the ground state in higher generation dendrimers, but the surrounding dendron groups may give some environmental effects to slightly affect the fluorescence profiles. In fact, the fluorescence intensities of ***p*-G*n*** and **d*m*-G*n*** decreased compared to those of **TMST** and **G*n*** indicating the occurrence of charge-transfer quenching of the excited state stilbene core by the surrounding ester-terminated peripheries of the dendrons.



Scheme 1. Structure and photochemical *trans*–*cis* isomerization of **TMST** and stilbene dendrimers.

To better understand the nature of this fluorescence quenching, fluorescence properties of **d*m*-G1** and **d*m*-G2** were investigated in deaerated solvents of different polarity in comparison with **TMST** (Table 1). Benzene was chosen as the nonpolar solvent, DMF as polar solvent, and THF as intermediate. As was the case in **TMST**, absorption maxima showed little solvent effect while fluorescence maxima showed a red shift in polar solvent. Interestingly, a weak broad fluorescence band around 490 nm and a very weak shoulder around 470 nm were observed for **d*m*-G1** and **d*m*-G2** respectively in DMF

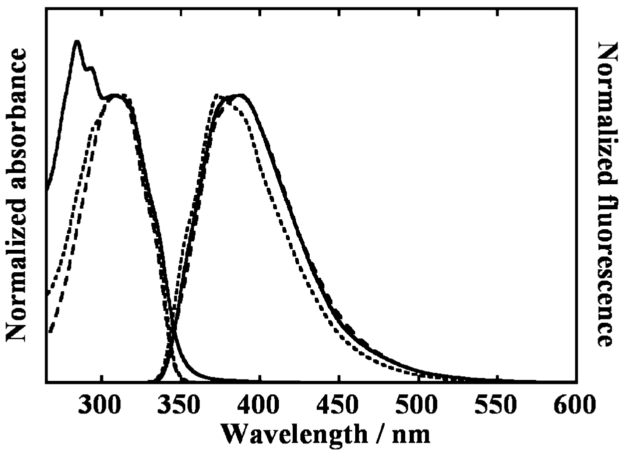


Figure 1. Absorption and fluorescence spectra (Ex. 310 nm) of **TMST** (dashed line), **d*m*-G1** (dotted line), and **d*m*-G2** (solid line) in deaerated THF solution.

Table 1. Experimental values of **TMST**, **d*m*-G1**, and **d*m*-G2** in deaerated solvents

Compound	Solvent	λ_{abs} /nm	λ_{em} /nm	$\Delta\nu_{ss}$ /cm^{-1}	Φ_f	τ_s /ns
TMST[a]	Benzene	310	373	5600	0.24	4.1
	THF	309	390	6700	0.27	10.0
	DMF	313	392	6500	0.38	16.6
d*m*-G1	Benzene	311	374	5400	0.23	1.8
	THF	313	373	5100	0.14	2.6
	DMF	316	393	6200	0.02	0.5/5.7
d*m*-G2	Benzene	313	376	5400	0.20	5.0
	THF	308	387	6600	0.21	7.4
	DMF	308	397	7300	0.11	5.2/23.8

[a]Ref. 5.

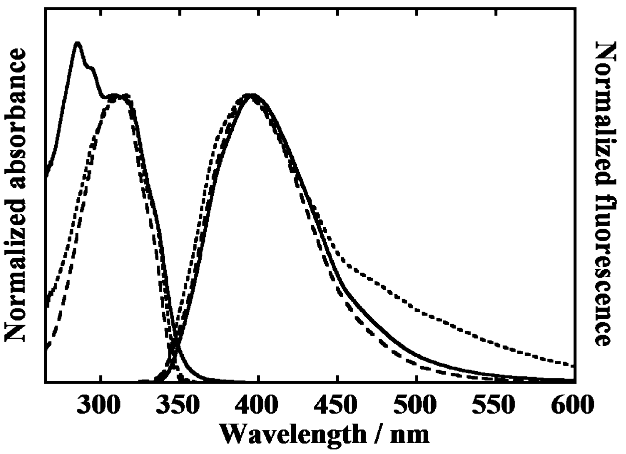


Figure 2. Absorption and fluorescence spectra (Ex. 310 nm) of **TMST** (dashed line), **d*m*-G1** (dotted line), and **d*m*-G2** (solid line) in deaerated DMF solution.

Table 2. Experimental values of **TMST** and stilbene dendrimers in deaerated THF solution

Compound	Φ_f	$\Phi_{t\to c}$	τ_s/ns	$k_f/10^7\,s^{-1}$
TMST[a]	0.27	0.38	10.0	2.7
G1[b]	0.43	0.32	9.7	4.4
***p*-G1**[c]	0.27	0.27	4.6	5.9
d*m*-G1	0.14	0.30	2.6	5.4
G2[b]	0.43	0.32	9.3	4.6
***p*-G2**[c]	0.39	0.26	6.8	5.7
d*m*-G2	0.21	0.50	7.4	2.8

[a]Ref. 5. [b]Ref. 2. [c]Ref. 4.

solution (Figure 2). These fluorescence bands are assigned to emission of stilbene–dendron exciplex formed through intramolecular charge transfer. The fluorescence decays in DMF were biexponential. The shorter component in DMF solution may be assigned to quenched monomer fluorescence while the longer component is assigned to the exciplex emission. Singlet lifetimes and quantum yields of fluorescence of all the dendrimers decreased compared to those of **TMST** in THF and DMF, indicating the occurrence of singlet quenching. The degree of quenching was higher in more polar solvents and lower generation dendrimers as was calculated from the lifetimes as follows: 74% in THF and >97% in DMF for **d*m*-G1**, and 26% in THF and 69% in DMF for **d*m*-G2**.

The above fluorescence quenching can be followed by lifetime measurements of fluorescence of the core stilbene. When compared within each generation, the singlet lifetimes decrease, except in **d*m*-G2** and especially apparent in the first generation dendrimers, with increasing number of alkoxycarbonyl surface functional groups indicating that the stilbene core is quenched by the surrounding dendrons (Table 2). One can suppose the effects of substituents on the phenyl ring of the peripheral dendrons as the degree of intramolecular exciplex formation. The through-space-charge-transfer interaction between the core stilbene as electron donor and peripheral phenyl group with alkoxycarbonyl groups as electron acceptor results in exciplex formation. In this case, the photoexcitation of the core stilbene induces the charge-transfer interaction to produce the exciplex to decrease the singlet lifetime of stilbene core. The acceptor strength is largest in isophthalate, intermediate in *p*-toluate, and smallest in benzene peripheral moiety of **d*m*-G*n***, ***p*-G*n***, and **G*n*** respectively. Exciplex gains better stabilization with larger acceptor strength of the acceptor, and therefore, excited singlet stilbene is more efficiently quenched.

A rough estimation of free energy change of electron transfer between the core and dendrons can be made from Weller's equation using the following numbers:

$$\Delta G_{ET} = E_{ox}(D) - E_{red}(A) - E_{00} + C \qquad (1)$$

$E_{ox}(D) = 1.11$ eV (**TMST**), $E_{red}(A) = -2.54$ eV (diethyl 5-methylisophthalate), -2.92 eV (methyl *p*-toluate) vs. Ag/AgCl in THF solution (peak top of oxidation wave was taken for **TMST** because of irreversible oxidation); $E_{00} = 3.59$ eV (first generation), 3.55 eV (second generation); $C = 0.04$ eV (THF), -0.06 eV (DMF). $\Delta G_{ET} = 0.10$, 0.14, 0.48, and 0.52 eV in THF for **d*m*-G1**, **d*m*-G2**, ***p*-G1**, and ***p*-G2**, and 0.00 and 0.04 eV in DMF for **d*m*-G1** and **d*m*-G2**. Reasonable exciplex formation, but not charge separation, is expected from these estimations.[6]

All of the dendrimers undergo *trans–cis* photoisomerization as can be seen from the decrease in absorbance of the absorption maximum and fluorescence intensity on irradiation with UV light in deaerated THF solution (Figure 3). Isomerization quantum yields did not decrease in spite of the shorter singlet lifetimes. One possibility is that isomerization from the excited singlet

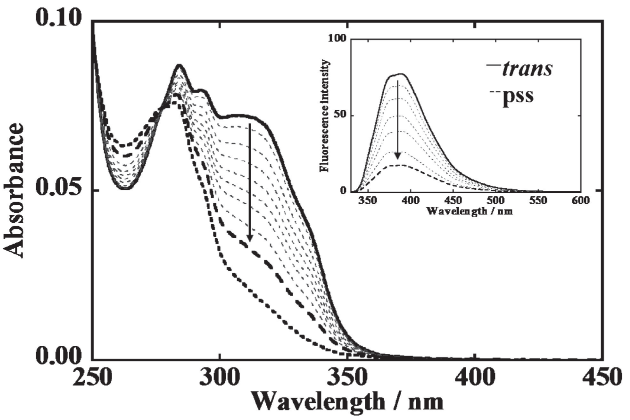


Figure 3. Change of absorption spectra of **d*m*-G2** in deaerated THF solution on irradiation at 310 nm. Spectra of *trans*-isomer (solid line), photostationary state (dashed line), and calculated *cis*-isomer (dotted line) are shown. Inset shows simultaneous change of fluorescence specta.

state is accelerated. However, this seems unlikely because the activation barrier of torsion around the double bond in the singlet excited state was found to be 5.5 kcal mol^{-1} from the temperature dependence of singlet lifetime of **d*m*-G1** in THF compared to 4.2 kcal mol^{-1} of **TMST** in acetonitrile.[5] Hence, it is most probable that efficient isomerization proceeds via triplet excited state of stilbene formed by intersystem crossing of the singlet exciplex. Apparently, the deactivation behavior of the singlet exciplex differs with generation. Intersystem crossing may be more efficient and/or the nonradiative decay may be slower in **d*m*-G2** compared to **d*m*-G1** leading to isomerization quantum yields of highly enhanced 0.50 and nearly equal 0.30 respectively. Many stilbene exciplexes in which stilbene is the acceptor are known, but there are few in which stilbene acts as the donor. Lewis reported that when intermolecular stilbene exciplex is formed with fumaronitrile, the triplet stilbene efficiently formed via intersystem crossing undergoes *trans–cis* isomerization.[7] Aloisi et al. reported that quantum yield of exciplex-induced isomerization was higher than the intrinsic value.[8]

Similar yet different correlation in the second generation could be the result of complex conformations of the dendrons which affect the distance to and the degree of crowding around the stilbene core. Actually, the less efficient quenching of the excited singlet state can be interpreted as the result of less effective charge-transfer interaction due to the longer distance between donor and acceptor.

The rate constants for singlet quenching were estimated by taking the difference of the rate constants for excited singlet state deactivation between the dendrimers and **TMST** as follows: $2.8 \times 10^8\,\mathrm{s}^{-1}$ in THF and $>1.9 \times 10^9\,\mathrm{s}^{-1}$ in DMF for **d*m*-G1**, $4.0 \times 10^7\,\mathrm{s}^{-1}$ in THF and $1.3 \times 10^8\,\mathrm{s}^{-1}$ in DMF for **d*m*-G2**, $1.2 \times 10^8\,\mathrm{s}^{-1}$ in THF for ***p*-G1**, and $5.0 \times 10^7\,\mathrm{s}^{-1}$ in THF for ***p*-G2**.[12]

The fact that exciplex emission was observed in both **d*m*-G1** and **d*m*-G2** indicates that the peripheral phenyl groups in these spherical dendrimers are able to approach the core stilbene spatially to interact because direct overlap of molecular orbitals of donor and acceptor is necessary for exciplex formation. The fact that the rate of singlet quenching is more than 10 times larger for **d*m*-G1** compared to **d*m*-G2** means that the peripheral phenyl group in **d*m*-G2** is more than 10 times less likely to quench the core because it is more sterically crowded around the core in **d*m*-G2**. It is obvious that the steric effect governing the ability of the peripheral phenyl group to get into the quenching radius of the core is active in THF as well because the rate of singlet quenching is higher for ***p*-G2** compared to **d*m*-G2** in spite of the lower acceptor strength. Stilbene surrounded with acceptor moieties in dendrimers may create a large-charge-transfer complex or exciplex in a whole molecular level compared to a localized charge-transfer excited state of **TMST**.

As to the study on intramolecular-exciplex formation, Vogtle et al. reported exciplex formation and emission in cyclam–naphthalene dendrimer like structures.[9] Li et al. reported the occurrence of intramolecular electron transfer and exciplex formation between aniline and pyrene moiety, and naphthalene and dimethoxybenzene moiety in fan-shaped aryl ether dendrimers.[10,11] However, these reports only concern the exciplex formation in dendrimer-like structures. Our studies have two different important points. First we have prepared conventional dendrimer molecules having donor at the central core and acceptor at the whole periphery of the dendrimers. Second, our compounds exhibit not only the exciplex formation by fluorescence quenching of the core stilbene but also highly efficient isomeization of the double bond induced by the exciplex formation. To the best of our knowledge, this paper reports the first experimental findings of exciplex formation followed by the acceleration of the whole structural change of spherical dendrimer molecules.

In conclusion, it was found that in stilbene-cored dendrimers **d*m*-G1** and **d*m*-G2**, the peripheral phenyl groups quench the excited singlet state of the core stilbene by exciplex formation via charge-transfer interactions. Moreover, exciplex-induced isomerization via excited triplet-state stilbene formation by intersystem crossing of singlet exciplex was found to be the significant mechanism in highly efficient photoisomerization.

This work was supported by a Grant-in-Aid for Scientific Research in a Priority Area “New Frontiers in Photochromism” (No. 471) and a Grant-in-Aid for Scientific Research (B) (No. 23350075) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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