

Synthesis and Photochemical Characteristics of Amphiphilic Eneidyne Dendrimers

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Amphiphilic eneidyne-cored dendrimers were prepared as pure *cis* and *trans* isomers. All dendrimers were fluorescent to give fluorescence quantum yield of 0.10–0.64, and they underwent efficient photochemical isomerization with quantum yields of 0.22–0.50 in THF. In water, other photochemical reactions took place. Fluorescence or triplet lifetimes were also strongly affected by dendrimer generation and solvent polarity. The structure–photochemical property relationship of new photoresponsive dendrimers is discussed.

The photochemical behavior of arylethenes and related compounds has been the subject of intense research.^{1–3} Among those, we have focused our attention on the effect of aromatic groups on the photoisomerization of C=C double bonds between one-way and two-way isomerization.^{2,4–6} These studies are quite important in view of the photoisomerization mechanism of chromoproteins such as rhodopsin and phytochrome,^{7–10} or development of photoresponsive materials having photoisomerizable cores such as C=C (or N=N) double bonds. In the latter case, an approach using dendrimers is interesting because when large dendrons are directly or indirectly connected to a photoresponsive dye, a small structural change at C=C double bonds by photoirradiation could be amplified to a whole structure change. In this respect, several dendrimers with stilbene core have been prepared and the effect of the large dendron group has been explored.^{11–13} Thus, stilbene dendrimers with benzyl ether dendra at the periphery effectively underwent mutual photoisomerization in organic solvent such as THF.¹¹ Figure 1 shows dendrimers with hydrophobic benzyl ether dendra (a) and also shows a dendrimer with a hydrophilic group at the terminus of a phenyl ring (b). The hydrophilic stilbene dendrimers underwent specific photoisomerization from the *trans* isomer to the *cis* isomer. Furthermore, a fast process on a 10 ns time scale and a slow process on a time scale of μ s to ms was observed.¹⁴

As to the photoisomerization of eneidyne compounds, we have reported the mutual isomerization of bis-phenylethynylethene where both *cis* and *trans* isomers gave fluorescence emission and intersystem crossing to the triplet state: the isomerization took place both in the excited singlet state and triplet state.¹⁵ The potential energy surface of the triplet state was estimated by quenching experiments with azulene and oxygen: the triplet state is equilibrated among the *trans* (³t*), *cis* (³c*), and twisted conformation (³p*). The observation of

the fluorescence emission not only in *trans* isomer but also in *cis* isomer and the contribution of ³c* in the equilibration in the excited triplet state with ³t* and ³p* support the almost planar structure due to the absence of steric effects even in the *cis* isomer.

We have been interested in the effect of large substituents of the dendritic structure in eneidyne compounds. The photochemical and photophysical properties of dendritic eneidyne in organic solvent have been studied.¹⁶ Studies on photochemistry and GPC analysis of dendrimers in organic solvent have been reported. We wish to report here the photochemistry of eneidyne type dendrimers in aqueous solution at physiological pH.

Results and Discussion

Synthesis. Amphiphilic eneidyne-cored dendrimers, *cis*- and *trans*-G n ($n = 1, 3$, and 4 for *cis* form, $n = 1$ and 3 for *trans* form) were newly synthesized as illustrated in Scheme 1. Their structures were identified by MALDI-TOF MS and NMR spectroscopy.

Optical Properties. Figures 2a and 2b show the absorption spectra of *cis*- and *trans*-G1 and *cis*- and *trans*-G3 in THF, MeOH, and water at room temperature under Ar. For all dendrimers, the absorption band around 300–400 nm which is almost the same between these two dendrimers is mainly due to the π – π^* band of the eneidyne unit, and that around 280 nm is higher in absorbance for G3 than for G1 and is assigned mainly due to the dendron units. In water, G1 showed red-shift of the absorption maximum and smaller extinction coefficient at 300–400 nm compared to those in THF and MeOH. However, G3 gave similar absorption spectra in MeOH and water, but showed different absorption spectrum in THF. These results indicate that surrounding dendron units of G3 provided a greatly different environment of the core unit compared to those of G1.

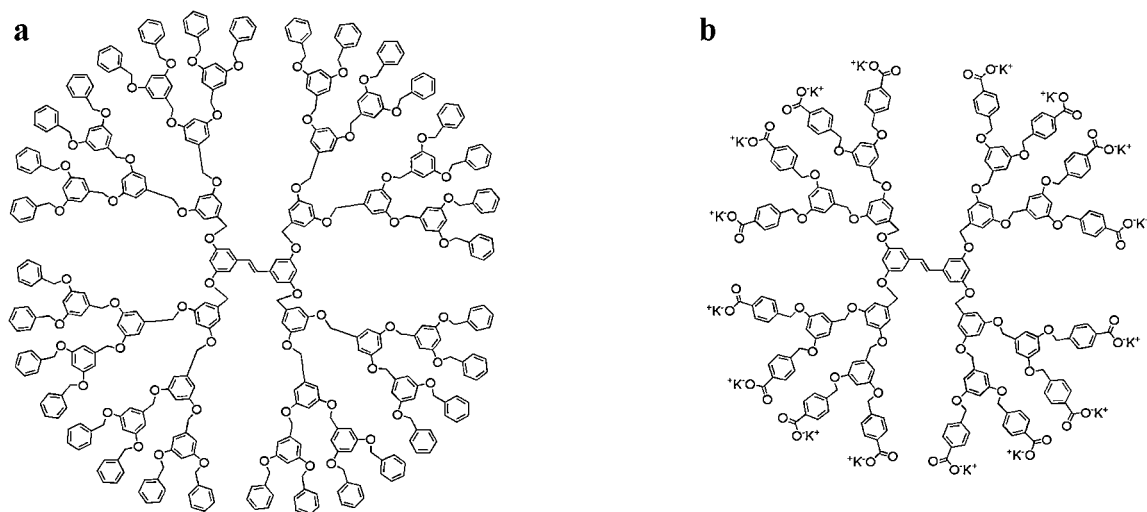
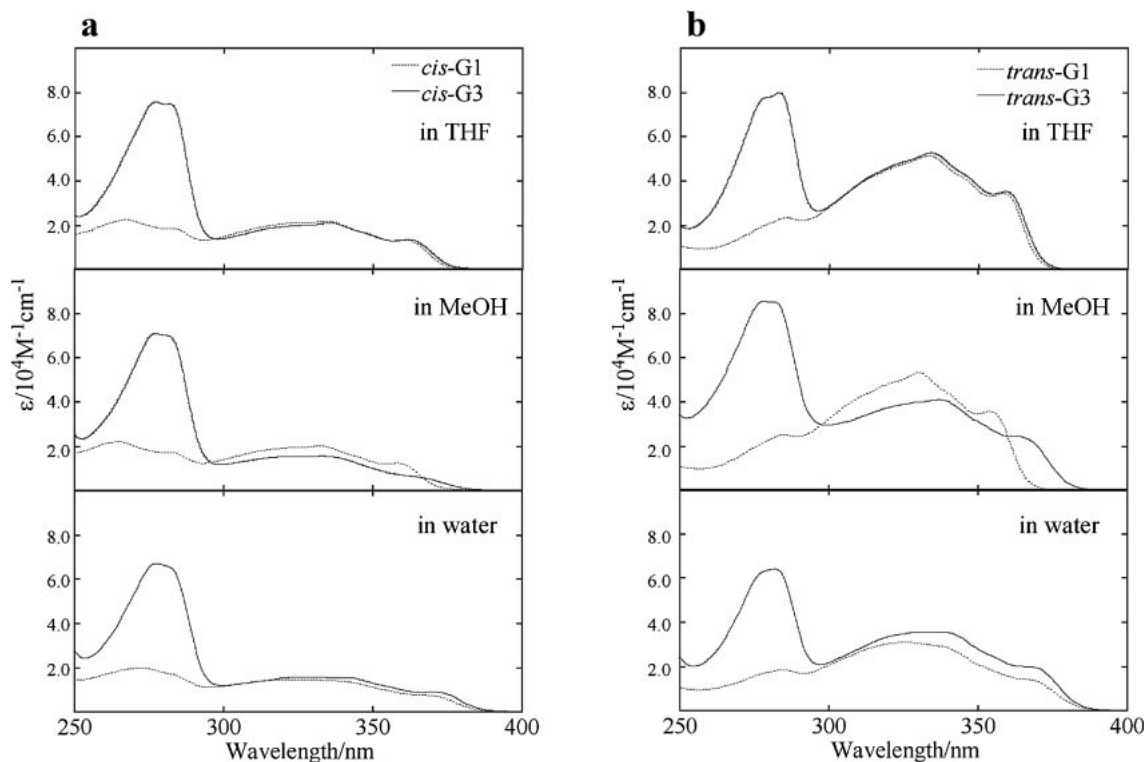


Figure 1.

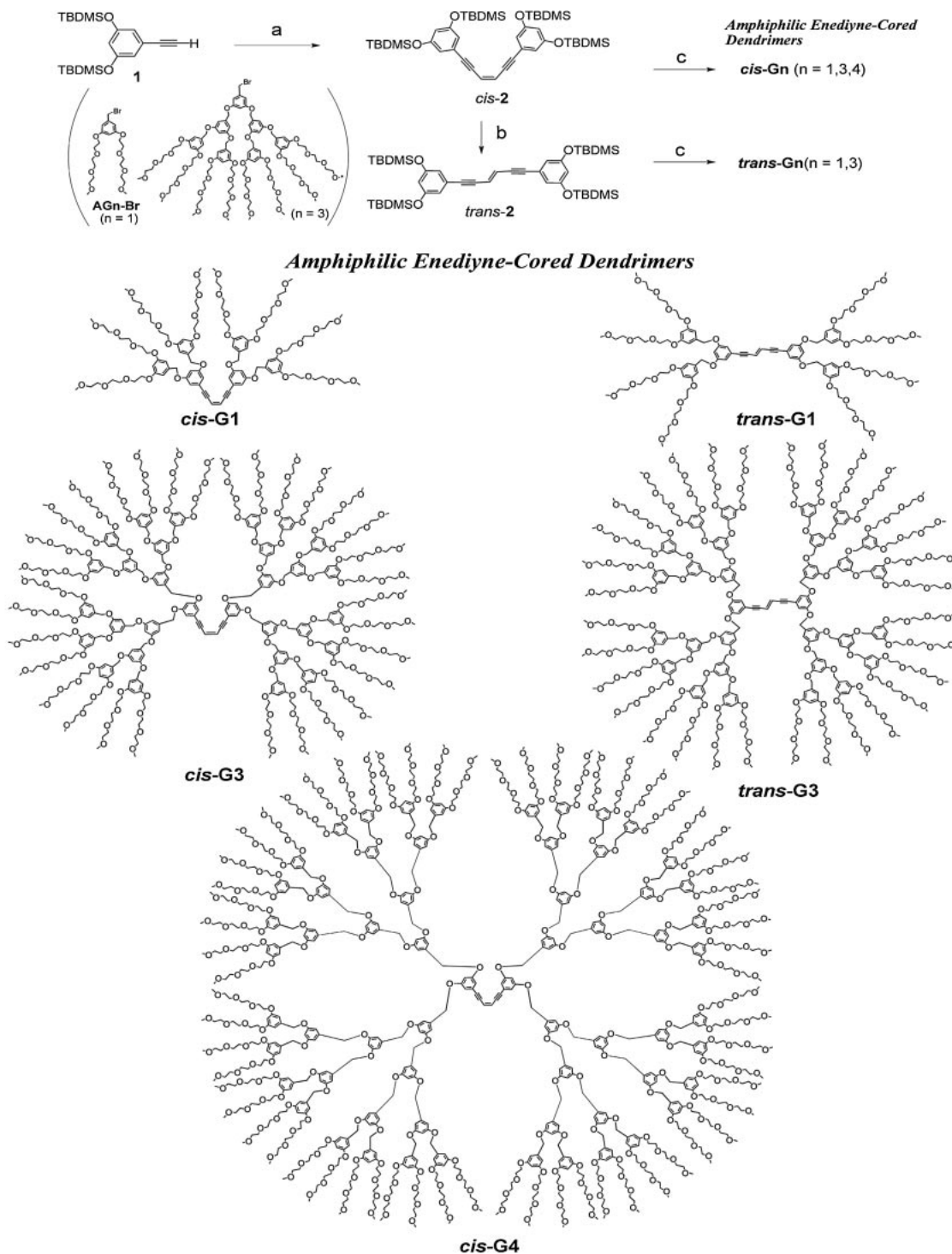
Figure 2. Absorption spectra of *cis*-G1 and *cis*-G3 (a) and *trans*-G1 and *trans*-G3 (b) in THF, MeOH, and water.

Fluorescence and fluorescence excitation spectra of *cis*-G1 and *cis*-G3 are shown in Figure 3. The fluorescence values of *trans* isomers are shown in Table 1. The fluorescence spectrum derived from the enediyne unit of *cis*-G1 in water ($\lambda_{\text{max}}(\text{FL}) = 408 \text{ nm}$) showed large red-shift (34 nm) compared to THF ($\lambda_{\text{max}}(\text{FL}) = 374 \text{ nm}$) (Figure 3a). On the other hand, those of *cis*-G3 showed similar shape and small spectral shift between THF ($\lambda_{\text{max}}(\text{FL}) = 374 \text{ nm}$) and water ($\lambda_{\text{max}}(\text{FL}) = 385 \text{ nm}$) (Figure 3b).

The fluorescence quantum yield was determined to be 0.34 and 0.38 in THF and 0.11 and 0.23 in water for *cis*-G1 and *cis*-G3, respectively (Table 1). 32 triethylene glycol units at the termini of peripheral dendron groups in *cis*-G3 forced the

spherical structure of the dendrimer surrounding the core enediyne unit at the center. Therefore, one can expect that G3 exists as a globular structure in water solution and this structure may inhibit self aggregation between enediyne unit for G3.

Figure 4 shows the change of the absorption spectra of *cis*-G3 on excitation at maximum wavelength in THF (a) and water (b). In THF *cis*-G3 underwent *cis*-*trans* isomerization to give the *trans*/*cis* isomer ratio at the photostationary state, $([t]/[c])_{\text{pss}} = 42/58$. However, in water, the absorbance decreased due to the *cis*-*trans* isomerization accompanied by other photochemical reactions as revealed by the appearance of a new band at longer wavelength than the absorption band derived from *cis*-*trans* isomerization of the enediyne unit. The



Scheme 1. a) *cis*-1,2-Dichloroethylene, Pd(PPh₃)₂Cl₂, CuI, *n*-BuNH₂, benzene, b) irradiation (308 nm) in benzene, and c) AGn-Br (*n* = 1, 3, or 4), K₂CO₃, 18-crown-6-ether, *cis*- or *trans*-2, THF.

photochemical reaction other than the *cis*–*trans* isomerization can be followed by GPC analysis (Figure 5), where the retention time of the product is shorter than the starting compound *cis*-G3 indicating that the molecular weight of the product is higher than *cis*-G3.

cis-G1 underwent *cis*–*trans* photoisomerization in THF to give the photostationary state isomer composition of ([*t*]/[*c*])_{pss} to be 48/52 as shown in the change of the absorption spectra

upon photoirradiation. In water *cis*-G1 underwent *cis*–*trans* photoisomerization and also other photochemical reactions as revealed by the slow rise of the absorbance at a longer wavelength region at 380 nm. Actually, one can determine the molecular weight of the main product as high as 3913.5 which is almost double of that of *cis*-G1 by MALDI-TOF MS. The photoinduced reaction other than photoisomerization of *cis*-G3 and *cis*-G1 observed in water may not necessarily be

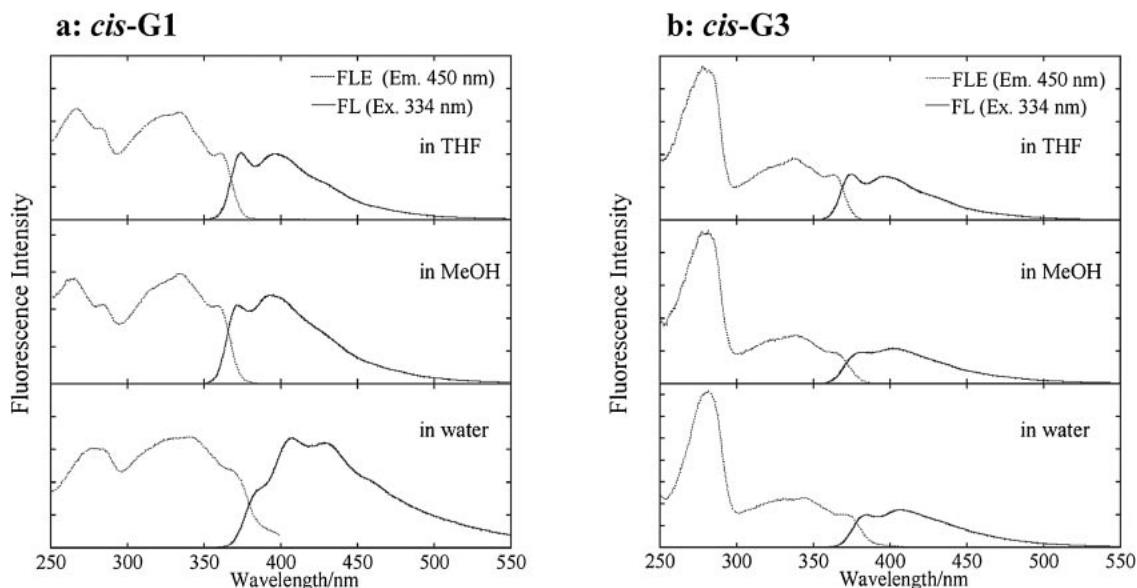


Figure 3. Fluorescence and fluorescence excitation spectra of *cis*-G1 and *cis*-G3 in THF, MeOH, and water under argon at room temperature.

Table 1. Absorption Maximum ($\lambda_{\max}(\text{abs})$), Extinction Coefficient (ϵ), Fluorescence Maximum ($\lambda_{\max}(\text{FL})$), Fluorescence Quantum Yield (Φ_f), Quantum Yield for Photoisomerization (Φ_{iso}), Quantum Yield for Intersystem Crossing (Φ_{isc}), Lifetime for Excited Singlet State (τ_s), and Lifetime for Excited Triplet State (τ_T) for Amphiphilic Eneidyne-Cored Dendrimers

Substrate	Solvent	$\lambda_{\max}(\text{abs})/\text{nm}$	$\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$	$\lambda_{\max}(\text{FL})/\text{nm}$	Φ_f	Φ_{iso}	Φ_{isc}	$\tau_s/\text{ns}^{\text{a}}$	$\tau_T/\mu\text{s}$
<i>cis</i> -G1	THF	267, 334, 361	22500, 21700, 13300	374, 396	0.34	0.50	0.37	1.07	0.57
	MeOH	264, 332, 358	22000, 20200, 12300	371, 393	0.14	0.27	0.25	0.81	0.98
	Water	272, 324	19800, 14800	408, 428	0.11	—	0.05	1.17	—
<i>cis</i> -G3	THF	277, 336, 362	75800, 20800, 13300	374, 396	0.38	0.42	0.43	1.43	0.72
	MeOH	277, 334	71000, 15500	382, 402	0.21	0.18	0.24	1.56	2.1, 11
	Water	278, 327, 371	67200, 15700, 9100	385, 407	0.23	—	0.16	1.44	8.2, 54
<i>trans</i> -G1	THF	286, 333, 358	23400, 51400, 34500	371, 392	0.64	0.22	0.16	0.90	0.60
	MeOH	284, 330, 354	25000, 53000, 35800	368, 391	0.19	0.22	0.09	0.47	1.0
	Water	284, 324	18600, 30900	409, 432	0.10	—	0.03	1.24	—
<i>trans</i> -G3	THF	283, 334, 359	80000, 52700, 35200	372, 394	0.64	0.25	0.20	0.94	0.75
	MeOH	282, 338, 364	85200, 40900, 24500	378, 403	0.26	—	0.11	0.93	1.4, 14
	Water	282, 338, 367	64100, 35600, 20000	383, 406	0.20	—	0.11	1.01	8.5, 53
<i>cis</i> -G4	THF	277, 335, 361	140000, 22600, 14200	374, 396	0.39	—	—	—	—
	MeOH	278, 335, 369	132000, 15900, 8700	379, 401	0.18	—	—	—	—
	Water	278, 339	123000, 15600	382, 405	0.25	—	—	—	—

a) Average fluorescence lifetime.

intermolecular dimerization between two enediyne units, because the reaction rate of *cis*-G3 was not very much slower than that of *cis*-G1 (Figures 4d and 4e), despite the large dendron groups in *cis*-G3. Thus, this photochemical reaction is at the moment not totally elucidated, but one could at least mention that it should be a photochemical oligomerization such as dimerization.

Figure 6 shows the transient spectra and decay profiles of the transient species of *cis*- and *trans*-G3 and *cis*- and *trans*-G1 observed on 308 nm laser excitation in THF, MeOH, and water. In THF, the observed transient from *cis*- and *trans*-G3 with 720 and 750 ns, respectively, was quenched by oxygen and assigned to the triplet state of enediyne unit (Figures 6a–6c). The transient spectra and decay profile of *cis*- and *trans*-G1 (Figures 6d–6f) is almost the same to those of G3, but the

decay time constant is slightly shorter in G1 than in G3: the triplet lifetime of *cis*- and *trans*-G1 is 570 and 600 ns and these values should be the same within the experimental uncertainty. The increase of the triplet lifetime in THF with increasing generation indicates that the surrounding dendron group may affect the molecular motion of the deactivation. One can expect the potential energy surface of isomerization of these enediynes to be similar to that of the parent compound bisphenylethyne (BEE).¹⁵ Thus, $^3t^*$, $^3p^*$, and $^3c^*$ should be populated in the excited triplet state and be equilibrated. The equilibrium constant among $^3c^*$, $^3p^*$, and $^3t^*$ in BEE is estimated to be 35:11:54.¹⁵ The triplet lifetime of G1 is longer than that of BEE indicating that the alkoxy substituent increases the triplet state lifetime probably increasing the population of the planar $^3c^*$ and $^3t^*$. Further increase in the triplet lifetime in G3 compared

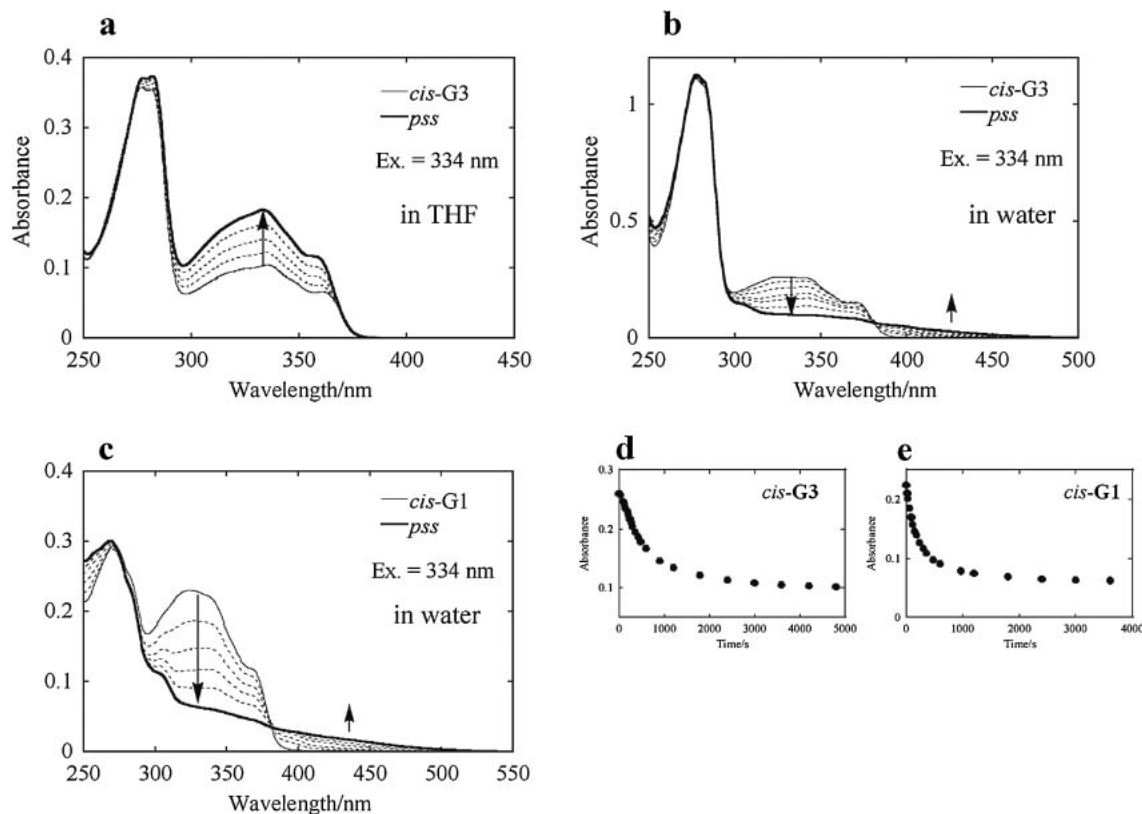


Figure 4. Change in the absorption spectra upon 334 nm irradiation for *cis*-G3 in THF (a), for *cis*-G3 in water (b), and for *cis*-G1 in water (c). The time-dependence of the absorbance during 334 nm light irradiation for *cis*-G3 (d) and for *cis*-G1 (e) in water.

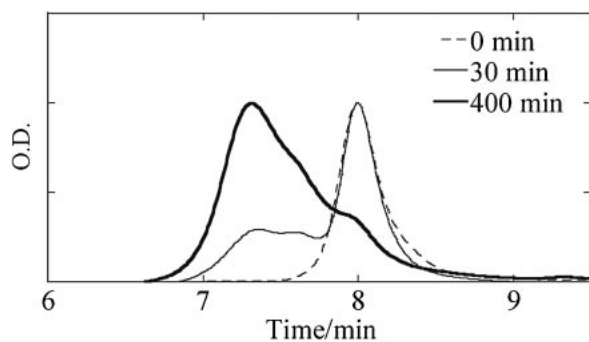


Figure 5. Overlay of GPC chromatograms of *cis*-G3 before irradiation (dash line), irradiated (334 nm) for 30 min (thin line), and for 400 min (solid line) in water.

to G1 indicates the further increase of the population of the planar $^3c^*$ and $^3t^*$ by introduction of the large dendron group or the suppression of the deactivation from the excited triplet state to the ground state or the suppression of the rate constant of the twisting around the double bond from the planar $^3c^*$ and $^3t^*$ to twisted $^3p^*$.

The triplet lifetime of G3 (1.7 μ s) (Figure 6g) in MeOH is also longer than that of G1 (1 μ s) (Figure 6h). The decay curve in G3 fits two exponential functions with 1.7 μ s due to the triplet state and ca. 10 μ s due to the ground state.

The observed transient of G3 in water showed double exponential function to be 8.2 and 54 μ s (Figure 6i). While the shorter lived transient was quenched by oxygen and assigned to the triplet state of the enediyne unit, the longer lived transient

was not quenched by oxygen. The observed transient with 54 μ s lifetime could be assigned to the radical species of the enediyne unit and subsequent reactions such as hydrogen abstraction to give dimerization product. Such photoinduced intermolecular reaction of enediyne in water has not been reported, but the GPC analysis to observe the photochemical product of higher molecular weight may support the above discussion.

As to the triplet lifetime, both *cis* and *trans* isomers of the same generation gave quite similar values within experimental uncertainty. However, the triplet lifetime increased with increasing generation from 580 ± 20 ns of G1 to 730 ± 20 ns of G3 in THF and 1 to 1.7 μ s in MeOH. Because of the lower solubility of G1 in water, we could not successfully observe the transient spectra in water. If we compare the triplet lifetime in different solvent, the lifetime increased from 580 ns to 1 μ s in G1 from THF to MeOH. But the triplet lifetime increased from 730 ns to 1.7 μ s in G3 from THF to MeOH and further increases to 8.5 μ s in water.

The solvent effect to increase the triplet lifetime should be caused by the hydrogen-bonding interaction with protic solvent at the periphery to induce hydrophobic interaction of the molecule.

Conclusion

Amphiphilic enediyne-cored dendrimers were successfully prepared as pure *cis* and *trans* isomers. All dendrimers were fluorescent in each solvent to give fluorescence quantum yield of 0.10–0.64. The fluorescence spectrum of *cis*-G1 was red-

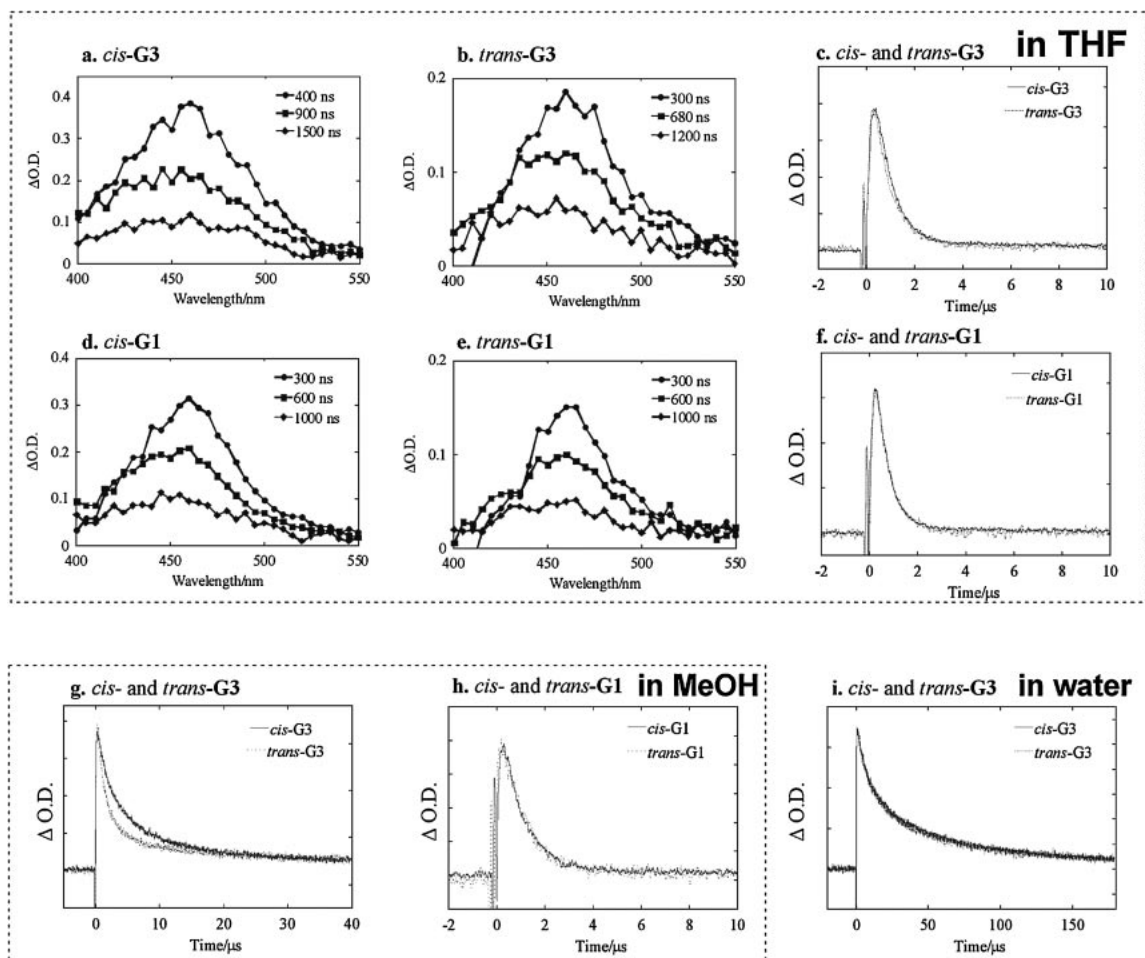


Figure 6. Transient spectra for *cis*-G3 (a) and *trans*-G3 (b) and decay profiles of *cis*- and *trans*-G3 (c) in THF. Transient spectra for *cis*-G1 (d) and *trans*-G1 (e) and decay profiles of *cis*- and *trans*-G1 (f) in THF. Decay profiles of *cis*- and *trans*-G3 (g) and *cis*- and *trans*-G1 (h) in MeOH. Decay profiles of *cis*- and *trans*-G3 (i) in water.

shifted by 34 nm in water, compared to those in organic solvents. On the other hand, spectral shift in *cis*-G3 was small between organic solvent and water. In THF all dendrimers underwent efficient photochemical isomerization even with large dendron substituents. The quantum yields of photochemical isomerization in THF were 0.22–0.50. In water, other photochemical reactions took place, as revealed by the appearance of a new band at longer wavelength than the absorption band of *cis* and *trans* isomers. The triplet lifetime in THF increased in higher generation indicating that the surrounding dendron group may affect the molecular motion of the deactivation. The observed transient of G3 in water showed double exponential function. The shorter lived transient was assigned to the triplet state of the enediyne unit, the longer lived transient was probably due to formation of ground state intermediates such as radical species.

Experimental

Solvents and commercially available compounds were purchased from standard suppliers and purified by standard methods. ^1H NMR spectra were measured with a Bruker ARX-400 (400 MHz for ^1H NMR) spectrometer in solution of CDCl_3 with tetramethylsilane as an internal standard. UV absorption and

fluorescence spectra were recorded on a Shimadzu UV-1600 UV–visible spectrophotometer and on a Hitachi F-4500 fluorescence spectrometer, respectively. MALDI-TOF MS measurements were taken on using 2-(4-hydroxyphenylazo)benzoic acid (HABA) as a matrix without adding any salts.

Quantum yield of fluorescence emission and quantum yield of photoisomerization were determined by a procedure previously reported.¹¹ Laser flash photolysis was also performed according to a previous paper.¹¹

***cis*-1,6-Bis[3,5-di(*tert*-butyldimethylsilyl)oxy]hex-1,5-diyne-3-ene (*cis*-2).** A mixture of **1**¹⁷ (1.29 g, 3.56 mmol), *cis*-1,2-dichloroethylene (158 mg, 1.63 mol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (20 mg, 0.03 mmol), CuI (32 mg, 0.18 mmol), *n*- BuNH_2 (710 mg, 9.63 mmol) in deaerated benzene (10 mL) was stirred at rt for 3 h. The reaction was quenched by addition of water (50 mL) and the mixture was extracted with dichloromethane (50 mL $\times$ 3). The organic layer was washed with brine and was dried over MgSO_4 . After evaporation, the residue was purified by silica gel chromatography (eluent: hexane/dichloromethane = 5/1) to give *cis*-2 as colorless oil (910 mg, 75%).

^1H NMR (CDCl_3 , 400 MHz, Me_4Si): δ 6.59 (4H, d, J = 2.4 Hz, ArH), 6.32 (2H, t, J = 2.4 Hz, ArH), 6.06 (2H, s, $\text{CH}=\text{CH}$), 0.95 (36H, s, $\text{C}(\text{CH}_3)_3$), 0.16 (24H, s, $\text{Si}(\text{CH}_3)_2$); ^{13}C NMR (CDCl_3 , 100 MHz, Me_4Si): δ 156.36, 123.89, 119.20, 116.66, 113.55,

97.42, 86.38, 25.59, 18.14, -4.47; Elemental analysis. Anal. Calcd for $C_{42}H_{68}O_4Si_4$: C, 67.32; H, 9.15; N, 0.00%. Found: C, 67.20; H, 9.30; N, 0.00%.

trans-1,6-Bis[3,5-di(*tert*-butyldimethylsilyloxy)hex-1,5-diyne-3-ene (trans-2). Laser flash photolysis was performed to a solution of *cis*-2 (600 mg 0.80 mmol) in benzene (5 mL) in a quartz cell. After irradiation time reached 2.5 h, solvent was evaporated. The residue was purified by column chromatography eluting with hexane–dichloromethane 10:1 to give *trans*-2 as a white solid (230 mg, 38%).

1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.57 (4H, d, $J = 2.0$ Hz, ArH), 6.33 (2H, t, $J = 2.0$ Hz, ArH), 6.25 (2H, s, CH=CH), 0.98 (36H, s, $C(CH_3)_3$), 0.20 (24H, s, $Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ 156.43, 123.82, 120.71, 116.70, 113.57, 94.79, 87.60, 25.64, 18.19, -4.41; Elemental analysis. Anal. Calcd for $C_{42}H_{68}O_4Si_4$: C, 67.32; H, 9.15; N, 0.00%. Found: C, 67.13; H, 9.12; N, 0.00%. mp 84–86 °C.

cis-G1 (Typical Procedure). A mixture of *cis*-2 (248 mg, 0.33 mmol), amphiphilic dendron AG1-Br¹⁸ (760 mg, 1.54 mmol), K_2CO_3 (380 mg, 2.75 mmol), 18-crown-6-ether (79 mg, 0.30 mmol) in THF (30 mL) was refluxed under nitrogen for 15 h. After reaction was completed, the mixed solution was filtered and evaporated. The residue was purified by silica gel chromatography (eluent: dichloromethane/MeOH = 25/1) followed by GPC chromatography ($CHCl_3$) to give *cis*-G1 as pale yellow oil (348 mg, 54%).

1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.74 (4H, d, $J = 2.4$ Hz, core-ArH), 6.54 (2H, t, $J = 2.4$ Hz, core-ArH), 6.50 (8H, d, $J = 2.0$ Hz, den-ArH), 6.41 (4H, t, $J = 2.0$ Hz, den-ArH), 6.08 (2H, s, core-CH=CH), 4.86 (8H, s, den- CH_2 -Ar), 4.05 (16H, t, $J = 4.8$ Hz, den- CH_2), 3.80 (16H, t, $J = 4.8$ Hz, den- CH_2), 3.71–3.63 (48H, m, den- CH_2), 3.54–3.52 (16H, m, den- CH_2), 3.36 (24H, s, den-O- CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ 160.03, 159.60, 138.77, 124.40, 119.80, 110.55, 105.99, 103.76, 101.18, 97.68, 87.14, 71.91, 70.77, 70.62, 70.54, 69.94, 69.62, 67.44, 59.01; MALDI-TOF MS (m/z) [$M + Na$]⁺ calcd for $C_{102}H_{148}O_{36}Na$, 1971.96; found, 1973.42.

cis-G3. 1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.79 (4H, d, $J = 2.4$ Hz, core-ArH), 6.66–6.49 (70H, m, core + den-ArH), 6.41 (16H, t, $J = 2.4$ Hz, den-ArH), 6.07 (2H, s, core-CH=CH), 4.95–4.83 (56H, m, den- CH_2 -Ar), 4.05 (64H, t, $J = 4.8$ Hz, den- CH_2), 3.78 (64H, t, $J = 4.8$ Hz, den- CH_2), 3.72–3.56 (192H, m, den- CH_2), 3.54–3.45 (64H, m, den- CH_2), 3.34 (96H, s, den-O- CH_3); MALDI-TOF MS (m/z) [$M + Na$]⁺ calcd for $C_{438}H_{628}O_{156}Na$, 8407.14; found, 8407.64.

cis-G4. 1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.80 (4H, s, core-ArH), 6.70–6.44 (150H, m, core + den-ArH), 6.38 (32H, t, $J = 2.0$ Hz, den-ArH), 6.06 (2H, s, core-CH=CH), 4.96–4.82 (120H, m, den- CH_2 -Ar), 4.02 (128H, t, $J = 4.8$ Hz, den- CH_2), 3.75 (128H, t, $J = 4.8$ Hz, den- CH_2), 3.70–3.54 (384H, m, den- CH_2), 3.52–3.42 (128H, m, den- CH_2), 3.31 (192H, s, den-O- CH_3); MALDI-TOF MS (m/z) [$M + K$]⁺ calcd for $C_{886}H_{1268}O_{316}K$, 17003.42; found, 17003.10.

trans-G1. 1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.68 (4H, d, $J = 2.0$ Hz, core-ArH), 6.57 (10H, m, core-ArH + den-ArH), 6.45 (4H, t, $J = 2.2$ Hz, den-ArH), 6.26 (2H, s, core-CH=CH), 4.94 (8H, s, den- CH_2 -Ar), 4.11 (16H, t, $J = 4.8$ Hz, den- CH_2), 3.84

(16H, t, $J = 4.8$ Hz, den- CH_2), 3.75–3.62 (48H, m, den- CH_2), 3.57–3.53 (16H, m, den- CH_2), 3.37 (24H, s, den-O- CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, Me_4Si): δ 160.12, 159.63, 138.82, 124.17, 120.84, 110.54, 106.06, 103.75, 101.19, 94.92, 87.80, 71.93, 70.83, 70.66, 70.58, 70.05, 69.67, 67.52, 59.05; MALDI-TOF MS (m/z) [$M + Na$]⁺ calcd for $C_{102}H_{148}O_{36}Na$, 1971.96; found, 1971.53.

trans-G3. 1H NMR ($CDCl_3$, 400 MHz, Me_4Si): δ 6.76 (4H, d, $J = 2.0$ Hz, core-ArH), 6.71–6.67 (26H, m, core + den-ArH), 6.60–6.51 (44H, m, den-ArH), 6.43 (16H, t, $J = 2.2$ Hz, den-ArH), 6.27 (2H, s, core-CH=CH), 4.97–4.80 (56H, m, den- CH_2 -Ar), 4.08 (64H, t, $J = 4.8$ Hz, den- CH_2), 3.81 (64H, t, $J = 4.8$ Hz, den- CH_2), 3.73–3.56 (192H, m, den- CH_2), 3.54–3.44 (64H, m, den- CH_2), 3.34 (96H, s, den-O- CH_3); MALDI-TOF MS (m/z) [$M + Na$]⁺ calcd for $C_{438}H_{628}O_{156}Na$, 8407.14; found, 8410.60.

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References

- 1 G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, C. Dalton, *J. Am. Chem. Soc.* **1964**, *86*, 3197.
- 2 T. Arai, K. Tokumaru, *Chem. Rev.* **1993**, *93*, 23.
- 3 R. S. H. Liu, *Acc. Chem. Res.* **2001**, *34*, 555.
- 4 T. Arai, K. Tokumaru, *Adv. Photochem.* **1995**, *20*, 1.
- 5 T. Arai, T. Karatsu, H. Sakuragi, K. Tokumaru, *Tetrahedron Lett.* **1983**, *24*, 2873.
- 6 J. Saltiel, Y. Zhang, D. F. Sears, Jr., *J. Am. Chem. Soc.* **1996**, *118*, 2811.
- 7 Y. Inoue, W. Rüdiger, R. Grimm, M. Furuya, *Photochem. Photobiol.* **1990**, *52*, 1077.
- 8 T. Yoshizawa, G. Wald, *Nature* **1963**, *197*, 1279.
- 9 H. Kandori, S. Matuoka, Y. Shichida, T. Yoshizawa, *Photobiochem. Photobiol.* **1989**, *49*, 181.
- 10 R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, C. V. Shank, *Science* **1991**, *254*, 412.
- 11 M. Uda, T. Mizutani, J. Hayakawa, A. Momotake, M. Ikegami, R. Nagahata, T. Arai, *Photochem. Photobiol.* **2002**, *76*, 596.
- 12 J. Hayakawa, A. Momotake, T. Arai, *Chem. Commun.* **2003**, 94.
- 13 A. Momotake, J. Hayakawa, R. Nagahata, T. Arai, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1195.
- 14 H. Tatewaki, N. Baden, A. Momotake, T. Arai, M. Terazima, *J. Phys. Chem. B* **2004**, *108*, 12783.
- 15 H. Sakakibara, M. Ikegami, K. Isagawa, S. Tojo, T. Majima, T. Arai, *Chem. Lett.* **2001**, 1050.
- 16 N. Yoshimura, A. Momotake, Y. Shinohara, Y. Nishimura, T. Arai, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1995.
- 17 T. Gbitter, F. Hampel, J.-P. Gisselbrecht, A. Hirsch, *Chem.—Eur. J.* **2002**, *8*, 408.
- 18 M. Brewis, M. Helliwell, N. B. McKeown, *Tetrahedron* **2003**, *59*, 3863.