Synthesis and Photoisomerization of Enediyne-Type Dendrimers with Benzyl Ether Dendrons

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Dendrimers with enediynes at the core and a benzyl ether-type dendron at the surrounding periphery were prepared as pure *cis*- and *trans*-isomers. Intramolecular energy-transfer efficiency and emission properties as well as photoisomerization around the C=C double bond were studied.

Lots of studies have been reported on the photoisomerization and photophysical properties of simple olefins, such as stilbenes and polyenes.[1–3] Besides the extensive studies on olefinic compounds, relatively few have involved the photochemistry of enediyne-type compounds.[4–6] Enediyne compounds may undergo a thermal cyclization reaction to give the di-radicals as reactive intermediates.[7–11] Photochemical cyclization reaction of some of the enediyne molecules have also been reported.[12–16] Because of the lack of basic research on the photochemical properties of enediyne compounds, we have studied and reported the photochemical behaviors of enediynes having phenyl substituents with and without donor–acceptor substituents on the both end of the triple bonds.[5,6]

We have been interested in the effect of large substituent on the photochemical conformational change of the nanosecond timescale by synthesizing dendrimers with the substituents having different generation dendrons of hydrophobic or hydrophilic properties. Among them, stilbene-cored dendrimers with hydrophobic benzyl ether-type dendron undergo *trans–cis* isomerization quite efficiently even for the higher generation dendrimers.[17] Thus, the dendron group as a large substituent scarcely suppresses the photoisomerization efficiency of stilbene. By introducing a hydrophilic substituent, such as carboxylate group at the periphery, the surrounding dendron caused a change in the photochemical behavior of the core stilbene to induce almost one-way *trans–cis* isomerization.[18,19]

We have already found and reported that both *cis* and *trans* isomers of enediyne compounds with phenyl group at the both end of carbon–carbon triple bond exhibit fluorescence emission and undergo intersystem crossing to the triplet state to give the triplet lifetime of ca. 300 ns. In addition, photochemical *cis–trans* isomerization was observed. In this study, we are focused on the effect of benzyl ether-type dendron on the photochemical processes both in the excited singlet state and triplet state. We report here the fluorescence, isomerization and the triplet state behaviors of dendrimer structure of enediyne compounds.

Result and Discussion

Synthesis. The dendrimers ***cis*-** and ***trans*-G1–G4** were prepared as illustrated in Scheme 1, and their structures were identified by MALDI-TOF-Mass and NMR spectroscopes.

Optical Properties. Figure 1 shows the absorption, fluorescence, and fluorescence excitation spectra of **G1–G4** in THF at room temperature. The absorption band around 300–350 nm was mainly due to the π–π^* band of the enediyne unit, and the band at shorter wavelength region around 280 nm was ascribed to the benzyl ether-type dendrons. The values of the extinction coefficient (ε) at 331 nm were 2.1×10^4 and $3.9 \times 10^4\,\text{cm}^{-1}\,\text{M}^{-1}$ for ***cis*-** and ***trans*-G1**, respectively. Although the absorption spectra of **G2–G4** were almost the same at longer wavelength region, the absorbance at 280 nm increased with increasing generation due to the absorption spectra of benzyl ether-type dendron group. The fluorescence quantum yield of ***trans*-G1–G4** and ***cis*-G1–G4** on excitation at 320 nm was determined to be 0.59–0.66 and 0.34–0.38 (Table 1), respectively, at room temperature. These results indicate that the excited singlet states of ***cis*-** and ***trans*-G1–G4** exist as the energy well to be able to emit fluorescence. The fluorescence excitation spectra in Fig. 1 showed a peak at 280 nm, indicating that the energy transfer from the surrounding dendron group to the core enediyne took place efficiently. The efficiency of this energy-transfer process was estimated from the comparison of the absorption spectra and fluorescence excitation spectra to be 86 and 73% for ***cis*-** and ***trans*-G3**, 58 and 78% for ***cis*-** and ***trans*-G4**, respectively. Interestingly, even the higher generation dendrimer **G4** showed energy transfer efficiency of more than 50%. Fluorescence lifetime was measured to be 1 ns for the *trans* isomers. The fluorescence lifetime of *cis* isomer was shorter than the detection limit of our instrument to be <0.5 ns. Thus, the generation scarcely affected the fluorescence lifetime.

Figure 2 shows the change in the absorption spectra on excitation at 332 nm in THF. The absorbance changed to give the photostationary state of *trans*-to-*cis* isomer ratios of 52/48, 51/49, 53/47, and 45/55 for **G1**, **G2**, **G3**, and **G4**,

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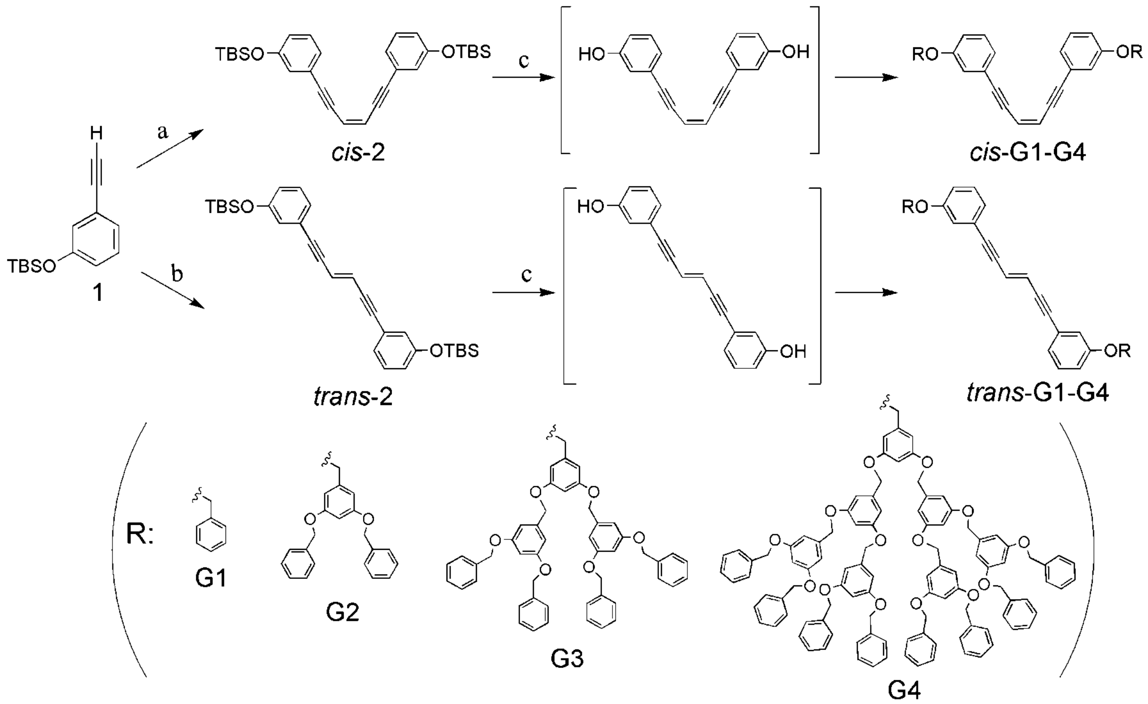

Scheme 1. a) *cis*-1,2-Dichloroethene, butylamine, Pd(PPh)$_2$Cl$_2$, CuI, benzene. b) *trans*-1,2-Dichloroethene, butylamine, Pd(PPh)$_2$Cl$_2$, CuI, benzene. c) Benzyl bromide for ***cis***- and ***trans*-G1**, 3,5-bis(benzyloxy)benzyl bromide for ***cis***- and ***trans*-G2**, 3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyl bromide for ***cis***- and ***trans*-G3**, and 3,5-bis[3,5-bis[3,5-bis(benzyloxy)benzyloxy]benzyloxy]benzyl bromide for ***cis***- and ***trans*-G4**, respectively, K$_2$CO$_3$, THF–DMF (3:1).

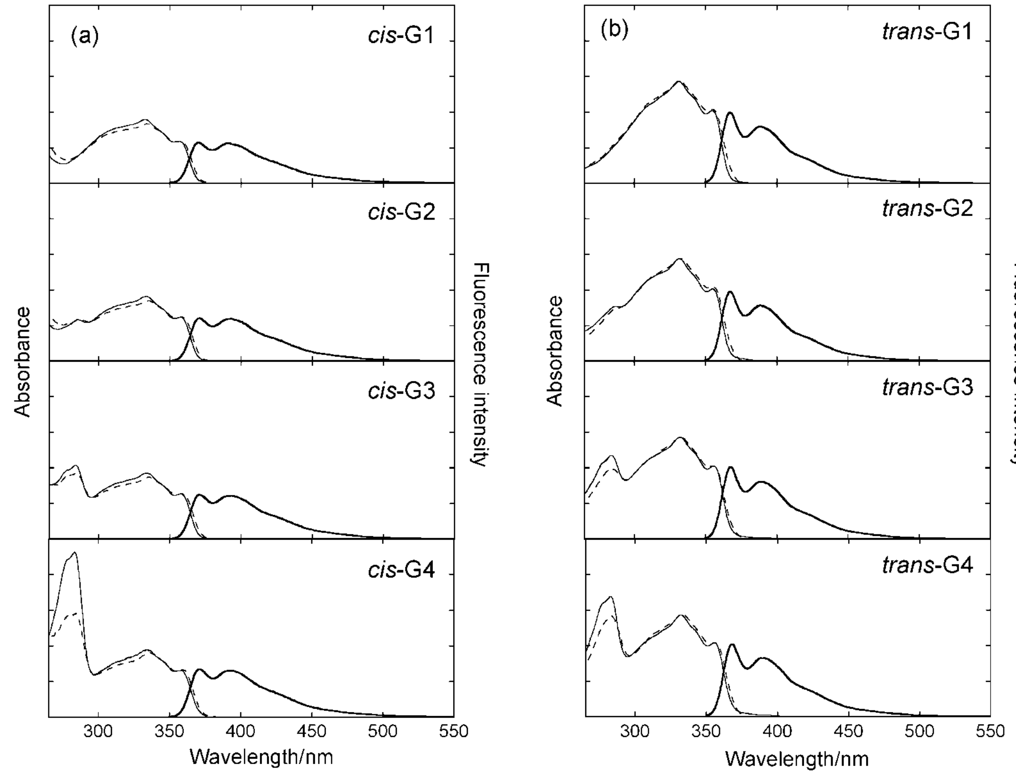

Fig. 1. Absorption (thin line), fluorescence (solid line), and fluorescence excitation spectra (dash line) of ***cis*-G1–G4** (a) and ***trans*-G1–G4** (b) in THF.

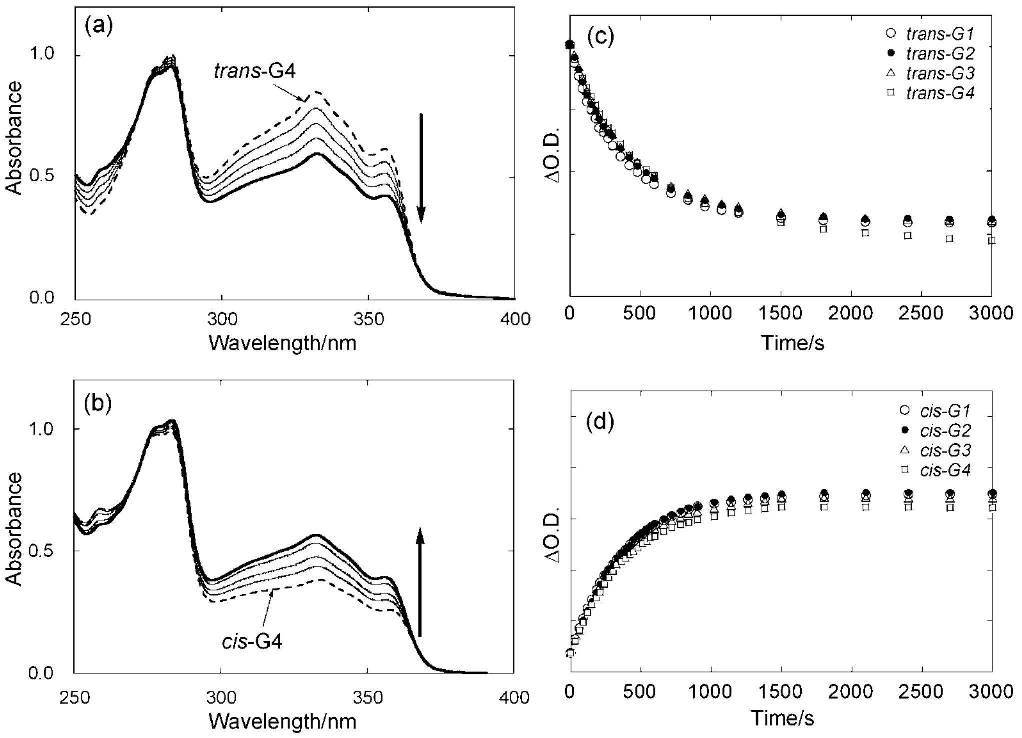

Fig. 2. Change in the absorption spectra of ***trans*-G4** (a) and ***cis*-G4** (b) upon irradiation at 332 nm in THF under Argon. Comparison of the absorbance change during the irradiation, monitored at 332 nm for ***trans*-G1–G4** (c) and ***cis*-G1–G4** (d).

Table 1. Quantum Yields of Fluorescence and Photoisomerization for ***cis*-G1–G4** and ***trans*-G1–G4**

	cis-Isomer		*trans*-Isomer	
	Φ_f	$\Phi_{c\rightarrow t}$	Φ_f	$\Phi_{t\rightarrow c}$
G1	0.38	0.30	0.63	0.18
G2	0.37	0.32	0.59	0.19
G3	0.37	0.32	0.59	0.18
G4	0.34	0.26	0.66	0.19

respectively. The values of the quantum yield of *cis*-to-*trans* and *trans*-to-*cis* photoisomerization ($\Phi_{c\rightarrow t}$ and $\Phi_{t\rightarrow c}$) were not affected by the generation (Table 1) indicating that the large dendron group scarcely affected the isomerization in the excited state. The *cis*–*trans* isomerization needs the twisting of the double bond to give the perpendicular conformation in the excited state, followed by deactivation to the ground-state perpendicular conformation and further twisting to give the isomer or reacting back to the starting conformation. The lack of the effect of dendrimers on the photoisomerization indicates that the large dendron substituent does not affect the twisting around the double bond to give the twisted excited state.

The fluorescence intensities of **G1** and **G4** were reduced by the presence of oxygen. In this quenching process, oxygen accelerates intersystem crossing to the triplet state, in which the isomerization takes place. For example, the efficiency of *cis*-to-*trans* photoisomerization of ***cis*-G1** under oxygen was 0.36, which was ca. 20% higher than that under argon atmosphere ($\Phi_{c\rightarrow t} = 0.30$, Table 1). Thus, oxygen accelerates the *cis*-to-*trans* isomerization by the following processes. Intersystem crossing from the singlet excited state of *cis*-isomer to the triplet excited state is promoted by oxygen, and in the excited triplet state, the *cis*-isomer undergoes isomerization with high efficiency, producing the *trans* isomer in the ground state.

Usually, the singlet excited state of aromatic compounds is quenched by molecular oxygen with a rate constant of $2 \times 10^{10}\,M^{-1}\,s^{-1}$ (k_q) in organic solvents,[20] and the excited singlet state of ***cis*-** and ***trans*-G1** is expected to be quenched by oxygen with $k_q[O_2] = 3 \times 10^8\,s^{-1}$. The deactivation rate constant of the excited singlet state of ***cis*-G1** is the inverse of the singlet lifetime and must be faster than $2 \times 10^9\,s^{-1}$ ($=1/\tau_s$) and is one order of magnitude faster than that of $k_q[O_2] = 3 \times 10^8\,s^{-1}$. Thus, about 10% of the excited singlet state of ***cis*-G1** may be quenched by oxygen under oxygen atmosphere. Oxygen induced the intersystem crossing from the singlet excited state to the triplet excited state, in which the isomerization took place to give the 50% *trans* isomer from the resulted *cis* triplet excited state. The quantum yield of *cis*-to-*trans* isomerization of ***cis*-G1** was 0.30 in the absence of oxygen under argon atmosphere. If 10% of the excited singlet state of ***cis*-G1** is quenched by oxygen to give the triplet excited state, in which deactivation occurs to yield the *trans* isomer with a quantum yield of $0.1 \times 0.5 = 0.05$, this value is ca. 20%, and therefore, the increase in the quantum yield of *cis*-to-*trans* isomerization can be explained by the acceleration of the intersystem crossing by oxygen.

GPC Analysis. Although the *cis* and *trans* isomers of azobenzene-type dendrimers have been reported to be separatable by GPC, ultrafast non-radiative deactivation as well as the lack of fluorescence emission disturbs the study of fundamental photochemical properties of azobenzene dendrimers.

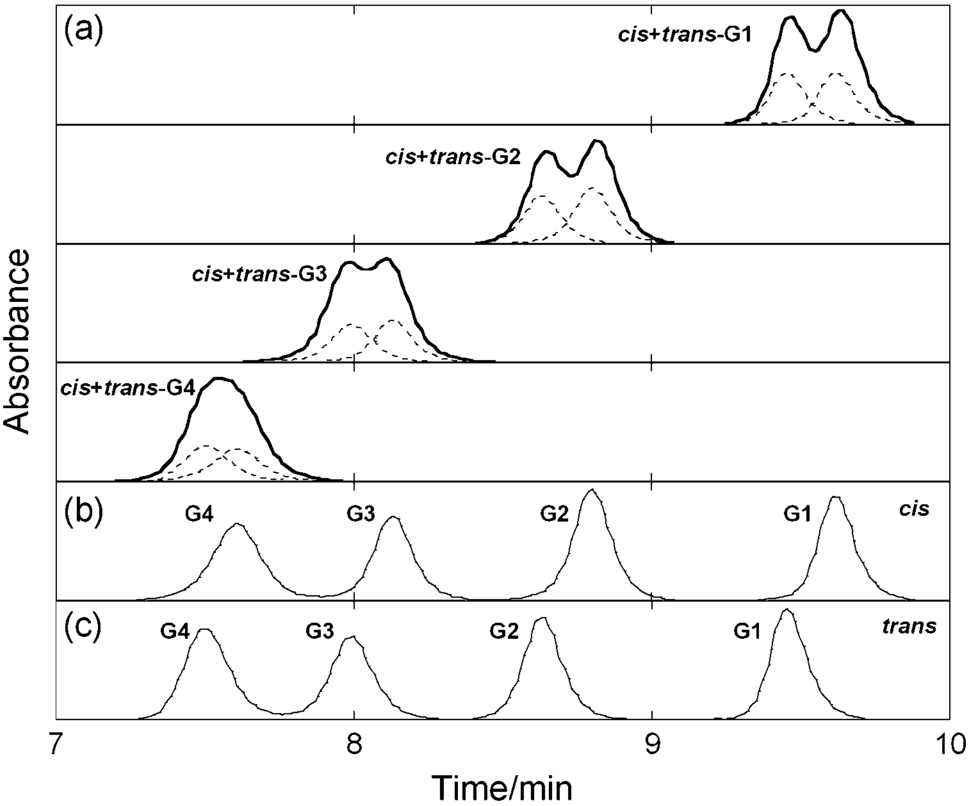

Fig. 3. (a) GPC chromatograms of the *cis* and *trans* mixtures of **G1**–**G4** dendrimers (solid line). Overlay of GPC chromatograms of *cis*- and *trans*-isomer (dashed line). (b) GPC chromatograms of the ***cis*-G1**–**G4** mixtures and (c) ***trans*-G1**–**G4** mixtures.

The present endiyne-type compounds exhibited fluorescence emission with considerably high quantum yield. If separation can be achieved by GPC, the photochemical isomerization processes can more easily be followed. In this respect, we have investigated the GPC profile of the dendrimers.

Figure 3 shows the HPLC data with GPC column. In the lower generation dendrimer, *cis* and *trans* isomer could be separated to give two peaks with retention times of 9.61 and 9.45 min for ***cis***- and ***trans*-G1**, respectively. With an increase in the generation, the retention time became shorter, and the separation became less clear. However, the retention time of the *cis* and *trans* isomers was still different even in **G4** (7.60 and 7.50 min for ***cis***- and ***trans*-G4**, respectively), and the *cis* isomer came later indicating that the *cis* isomers in **G1**–**G4** dendrimers have more compact structure than *trans* isomers. The surrounding dendron groups are flexible, but the conformation of the core enediyne group seems to control the molecular size, of which the *cis* isomer seems to be smaller than *trans* isomer.

Conclusion

In summary, the enediyne-type dendrimer compounds were successfully prepared for the first time as pure *cis* and *trans* isomers. They underwent efficient photochemical isomerization even with large dendron substituents. Furthermore, fluorescence lifetime and the triplet lifetime were scarcely affected by dendron substitution. However, the molecular structure of the *cis* and *trans* isomers of higher generations of **G4** were a little different as revealed by GPC experiments. Thus, the change in the size and the molecular structure of the dendritic compounds may be used to prepare and to construct molecules with new emissive and/or reactive properties.

Experimental

Solvents and commercially available compounds were purchased from standard suppliers and purified by standard methods. ^{1}H NMR spectra were measured with a Bruker ARX-400 (400 MHz for ^{1}H 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.

***cis*-2.** A mixture of *cis*-1,2-dichloroethene (164 mg, 1.69 mmol), copper(I) iodide (28 mg, 0.15 mmol), bis(triphenylphosphine)palladium dichloride (56 mg, 0.08 mmol), and butylamine (349 mg, 4.7 mmol) and compound **1**[21] (832 mg, 3.59 mmol) in benzene (20 mL) were stirred at room temperature for 11 h. The reaction mixture was quenched with water, and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (50 mL), and the combined organic layer was dried over $MgSO_4$, filtered, and concentrated to dryness. The residue was purified by silica-gel column chromatography (hexane/CH_2Cl_2 1:1) to give ***cis*-2** (580 mg 1.19 mmol) in 70% yield. ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.22–7.13 (4H, m, ArH), 6.97 (2H, dd, $J = 1.5$ Hz, $J = 4.0$ Hz, ArH), 6.80 (2H, ddd, $J = 1.5$ Hz, $J = 4.0$ Hz, $J = 8.0$ Hz, ArH), 6.08 (2H, s, CH=CH), 0.97 (18H, s, C–CH_3), 0.18 (12H, s, Si–CH_3).

***trans*-2.** A mixture of *trans*-1,2-dichloroethene (149 mg, 1.54 mmol), copper(I) iodide (27 mg, 0.15 mmol), bis(triphenylphosphine)palladium dichloride (52 mg, 0.08 mmol), and butylamine (312 mg, 4.23 mmol) and compound **1** (792 mg, 3.41 mmol) in benzene (20 mL) were stirred at room temperature for 15 h. The reaction mixture was quenched with water, and the organic layer was separated. The aqueous phase was further extracted with CH_2Cl_2 (50 mL), and the combined organic layer was dried over $MgSO_4$, and filtered, and the solvent was evaporated. The residue was purified by silica-gel column chromatography (hexane/CH_2Cl_2 20:1) to give ***trans*-2** (192 mg, 0.39 mmol) in 25% yield. ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.16 (2H, t, $J = 8.0$ Hz, ArH), 7.05 (2H, ddd, $J = 1.5$ Hz, $J = 4.0$ Hz, $J = 8.0$ Hz, ArH), 6.92 (2H, dd, $J = 1.5$ Hz, $J = 4.0$ Hz, ArH), 6.80 (2H, ddd, $J = 1.5$ Hz, $J = 4.0$ Hz, $J = 8.0$ Hz, ArH), 6.25 (2H, s, CH=CH), 0.97 (18H, s, $C(CH_3)_3$), 0.19 (12H, s, $Si(CH_3)_2$).

***cis*-G1 (Typical Procedure).** A mixture of ***cis*-2** (204 mg, 0.42 mmol), K_2CO_3 (201 mg, 1.45 mmol), 18-crown-6 ether (38 mg, 0.15 mmol), and benzyl bromide (158 mg, 0.92 mmol) in dry acetone (30 mL) were refluxed under nitrogen for 2 h. After evaporation to dryness, the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The mixture was purified by silica-gel column chromatography (hexane/ethyl acetate 5:1) to give ***cis*-G1** as a white solid (112 mg, 0.25 mmol, 60% yield): ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.41–7.30 (10H, m, ArH), 7.24 (2H, t, $J = 8.2$ Hz, ArH), 7.16–7.13 (4H, m, ArH), 6.96 (2H, ddd, $J = 1.2$ Hz, $J = 2.4$ Hz, $J = 8.2$ Hz, ArH), 6.10 (2H, s, CH=CH), 5.01 (4H, s, CH_2OAr); Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49; N, 0.00%. Found: C, 87.08; H, 5.67; N, 0.00%.

***cis*-G2.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.41–7.29 (20H, m, ArH), 7.21 (2H, t, $J = 8.2$ Hz, ArH), 7.14–7.10 (4H, m, ArH), 6.91–6.88 (2H, m, ArH), 6.62 (4H, d, $J = 2.0$ Hz, ArH), 6.55 (2H, t, $J = 2.0$ Hz, ArH), 6.10 (2H, s, CH=CH), 4.99 (8H, s, CH_2OAr), 4.91 (4H, s, CH_2OAr); MALDI-TOF-MS Calcd for $C_{60}H_{48}O_6$ $[M + Na]^+ = 887.4$; Found 887.3.

***cis*-G3.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.43–7.22 (40H, m, ArH), 7.18 (2H, t, $J = 8.2$ Hz, ArH), 7.13–7.09 (4H, m, ArH), 6.91–6.86 (2H, m, ArH), 6.64 (8H, d, $J = 2.1$ Hz, ArH), 6.58 (4H, d, $J = 2.1$ Hz, ArH), 6.54 (4H, t, $J = 2.1$ Hz, ArH), 6.50 (2H, t, $J = 2.1$ Hz, ArH), 6.07 (2H, s, CH=CH), 4.98 (16H, s, CH_2OAr), 4.88 (8H, s, CH_2OAr); MALDI-TOF-MS Calcd for $C_{116}H_{96}O_{14}$ $[M + Na]^+ = 1735.7$; Found 1736.2.

***cis*-G4.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.40–7.27 (80H, m, ArH), 7.22–7.15 (2H, m, ArH), 7.04–7.01 (4H, m, ArH), 6.92–6.88 (2H, m, ArH), 6.66–6.63 (28H, m, ArH), 6.55–6.51 (14H, m, ArH), 6.02 (2H, s, CH=CH), 5.00 (32H, s, CH_2OAr), 4.95 (16H, s, CH_2OAr); MALDI-TOF-MS Calcd for $C_{228}H_{192}O_{30}$ $[M + Na]^+ = 3432.4$; Found 3431.4.

***trans*-G1 (Typical Procedure).** A mixture of ***trans*-2** (85 mg, 0.18 mmol), K_2CO_3 (100 mg, 0.72 mmol), 18-crown-6 ether (23 mg 0.09 mmol), and benzyl bromide (90 mg, 0.62 mmol) in dry acetone (30 mL) were refluxed under nitrogen for 17 h. After evaporation to dryness, the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The mixture was purified by silica-gel column chromatography (hexane/CH_2Cl_2 4:1) to give ***trans*-G1** as a white solid (62 mg, 0.14 mmol, 78%): ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.47–7.32 (10H, m, ArH), 7.25 (2H, t, $J = 8.2$ Hz, ArH), 7.11–7.06 (4H, m, ArH), 6.99–6.95 (2H, m, ArH), 6.28 (2H, s, CH=CH), 5.08 (4H, s, CH_2OAr). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49; N, 0.00%. Found: C, 87.11; H, 5.63; N, 0.00%.

***trans*-G2.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.44–7.29 (20H, m, ArH), 7.23 (2H, t, $J = 8.2$ Hz, ArH), 7.09–7.03 (4H, m, ArH), 6.96–6.91 (2H, m, ArH), 6.67 (4H, d, $J = 2.0$ Hz, ArH), 6.58 (2H, t, $J = 2.0$ Hz, ArH), 6.28 (2H, s, CH=CH), 5.04 (8H, s, CH_2OAr), 5.00 (4H, s, CH_2OAr); MALDI-TOF-MS Calcd for $C_{60}H_{48}O_6$ $[M + Na]^+ = 887.4$; Found 886.5.

***trans*-G3.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.43–7.28 (40H, m, ArH), 7.21 (2H, t, $J = 8.0$ Hz, ArH), 7.07–7.04 (4H, m, ArH), 6.95–6.91 (2H, m, ArH), 6.69–6.64 (12H, m, ArH), 6.58–6.53 (6H, m, ArH), 6.25 (2H, s, CH=CH), 5.03 (16H, s, CH_2OAr), 4.97 (8H, s, CH_2OAr); MALDI-TOF-MS Calcd for $C_{116}H_{96}O_{14}$ $[M + Na]^+ = 1735.7$; Found 1736.2.

***trans*-G4.** ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ 7.40–7.25 (80H, m, ArH), 7.23–7.16 (2H, m, ArH), 7.05–7.01 (4H, m, ArH), 6.92–6.87 (2H, m, ArH), 6.67–6.63 (28H, m, ArH), 6.56–6.52 (14H, m, ArH), 6.22 (2H, s, CH=CH), 4.99 (32H, s, CH_2OAr), 4.94 (16H, s, CH_2OAr). MALDI-TOF-MS Calcd for $C_{228}H_{192}O_{30}$ $[M + K]^+ =$; 3449.4; Found 3452.8.

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References

1 J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrightonand, O. C. Safiriou, in *Organic Photochemistry*, ed. by O. L. Chapman, Marcel Dekker, New York, **1973**, Vol. 3, p. 1.

2 J. Saltiel, J. L. Charlton, in *Rearrangements in Ground and Excited States*, ed. by P. Mayo, Academic Press, New York, **1980**, Vol. 3, p. 25.

3 T. Arai, K. Tokumaru, *Chem. Rev.* **1993**, *93*, 23.

4 N. P. Bowling, R. J. McMahon, *J. Org. Chem.* **2006**, *71*, 5841.

5 H. Sakakibara, M. Ikagami, K. Isagawa, S. Tojo, T. Majima, T. Arai, *Chem. Lett.* **2001**, 1050.

6 Y. Miki, A. Momotake, T. Arai, *Org. Biomol. Chem.* **2003**, *1*, 2655.

7 A. Basak, S. Mandal, S. Bag, *Chem. Rev.* **2003**, *103*, 4077.

8 Y. Sugiura, Y. Uesawa, Y. Takahashi, J. Kuwahara, J. Golik, T. W. Doyle, *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 7672.

9 N. Zein, M. Poncin, R. Nilakantan, G. A. Ellestad, *Science* **1989**, *244*, 697.

10 Y. Sugiura, T. Arakawa, M. Uesugi, T. Shiraki, H. Ohkuma, M. Konishi, *Biochemistry* **1991**, *30*, 2989.

11 M. Hirama, T. Gomibuchi, K. Fujiwara, Y. Sugiura, M. Uesugi, *J. Am. Chem. Soc.* **1991**, *113*, 9851.

12 A. Evenzahav, N. J. Turro, *J. Am. Chem. Soc.* **1998**, *120*, 1835.

13 J. M. O'Connor, S. J. Friese, B. L. Rodgers, *J. Am. Chem. Soc.* **2005**, *127*, 16342.

14 P. J. Benites, R. C. Holmberg, D. S. Rawat, B. J. Kraft, *J. Am. Chem. Soc.* **2003**, *125*, 6434.

15 I. V. Alabugin, M. Manoharan, *J. Am. Chem. Soc.* **2003**, *125*, 4495.

16 A. E. Clark, E. R. Davidson, J. M. Zaleski, *J. Am. Chem. Soc.* **2001**, *123*, 2650.

17 M. Uda, T. Mizutani, J. Hayakawa, A. Momotoke, M. Ikegami, R. Nagahata, T. Arai, *Photochem. Photobiol.* **2002**, *76*, 596.

18 J. Hayakawa, A. Momotake, T. Arai, *Chem. Commun.* **2003**, 94.

19 A. Momotake, J. Hayakawa, R. Nagahata, T. Arai, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1195.

20 J. Saltiel, B. W. Atwater, in *Advanced in Photochemistry*, ed. by D. H. Volman, G. S. Hammond, K. Gollnick, Wiley-Interscience Publication, **1988**, Vol. 14, pp. 1–90.

21 D. Bonafoux, S. Bonar, L. Christine, M. Clare, A. Donnelly, J. Guzova, N. Kishore, P. Lennon, A. Libby, S. Mathialagan, W. McGhee, S. Rouw, C. Sommers, M. Tollefson, C. Tripp, R. Weier, S. Wolfson, Y. Min, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2870.