BCSJ Award Article

Energy Transfer and *trans–cis* Isomerization in Dendrimer Aggregates

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Received November 15, 2010
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Stilbene-cored dendrimers having benzophenone peripheries with alkyl chains formed 1 µm and 4 nm aggregates in methylcyclohexane (MCH) for *trans*-**1** and *trans*-**2**, respectively. Even in the aggregates, *trans*-**1** underwent efficient *trans–cis* photoisomerization from the excited triplet state produced via intramolecular two-step energy transfer.

Dendrimers can work as unimolecular micelles and studies of inclusion of guest molecules inside dendrimers have been reported.[1] If the dendrimer core undergoes structural change after photoisomerization,[2] inclusion and release of a guest molecule may be controlled by photoirradiation. For this purpose, efficient structural change at the core moiety by photoirradiation is important. Recently, we have reported efficient and clean photochemical *trans–cis* isomerization by round-trip energy transfer in stilbene-cored dendrimers with benzophenone peripheries.[3] The *trans–cis* photoisomerization of the stilbene core via the triplet state was initiated by energy transfer from the excited singlet state stilbene core to the benzophenone periphery followed by intersystem crossing to produce benzophenone triplet and then triplet energy transfer from the benzophenone units back to the stilbene core (Figure 1). The quantum yields for the round-trip energy transfer were extremely high ($\Phi_{\mathrm{ERT}} = 0.94$–$0.99$). Accordingly, the quantum yields for photoisomerization were still high ($\Phi_{t\rightarrow c} = 0.38$–$0.47$) despite the involvement of two energy-transfer steps.

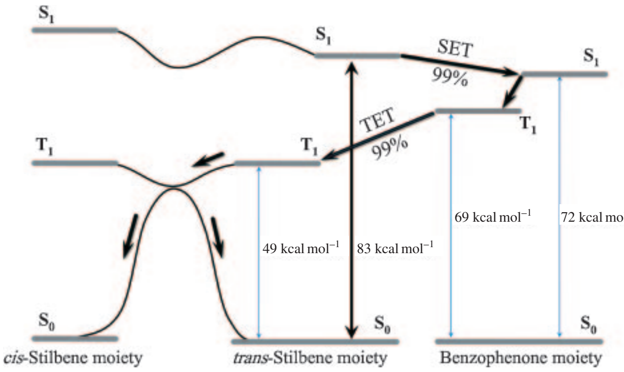

Figure 1. Energy round trip in stilbene-cored benzophenone dendrimers.

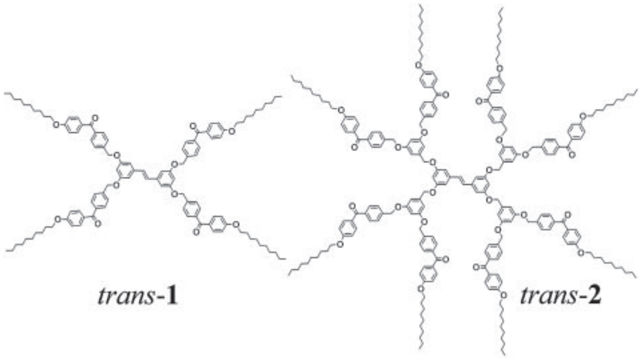

Figure 2. Chemical structures of *trans*-**1** and *trans*-**2**.

In the course of our study of photoresponsive dendrimers, we have attempted to develop a new photoresponsive aggregate system using the above-mentioned efficient energy-transfer processes with high isomerization efficiency. In this respect we have prepared *trans*-**1** and *trans*-**2** having benzophenone peripheries with alkyl chains and reported their photochemical and photophysical behaviors (Figure 2).

The absorption spectra of dendrimers resulted from benzyl ether branching and peripheral benzophenone units along with a stilbene core. Figure 3 shows the absorption spectra of *trans*-**1** and *trans*-**2** measured in MCH and in benzene. In benzene the spectral profiles of *trans*-**1** and *trans*-**2** were similar to those of dendrimers without alkyl chains at the peripheries. However, as shown in Figure 3a, the characteristic vibrational structure was observed around 322 and 339 nm in MCH for *trans*-**1**, which is usually observed in solid state or in "cyclic" or "stiff" stilbenes where the vibrational structure is well pronounced even at room temperature.[4,5] On the other hand, in *trans*-**2**, the vibrational structures were not observed in MCH (Figure 3b).

In the case of *trans*-**1** the vibrational structure is probably due to the restriction of torsion around the single bond by formation of higher order structure in MCH. If this is the case, organogel can be formed when *trans*-**1** in MCH (10^{-2} M) is warmed to 60 °C and cooled to room temperature (Figure 3d). The absence vibrational structure in benzene where *trans*-**1** exists as monomer may support the above proposition that the restriction of the single bond rotation may cause the appearance of vibrational structure of the stilbene core. Furthermore, the vibrational structures observed in MCH diminished upon heating (Figure 3c) and the shape of the spectrum became similar to that measured in benzene. This result may indicate

Published on the web March 5, 2011; doi:10.1246/bcsj.20100318

decomposition of the high-order structure with increasing temperature. The lack of vibrational structure at 300–350 nm for *trans*-**2** in MCH (Figure 3b) also suggests the higher generation dendrimer has less possibility of forming high-order structure of the core in the aggregates.

The dynamic light scattering (DLS) measurement for *trans*-**1** and *trans*-**2** was performed at room temperature to investigate the aggregation behavior. Figure 4 shows the apparent diameter (D_a) distributions of *trans*-**1** (5×10^{-6} M, left) and *trans*-**2** (5×10^{-5} M, right) in MCH. The size distribution showed one peak: D_a at about 1 μm and 4 nm for *trans*-**1** and *trans*-**2**, respectively. This suggests that *trans*-**1** can form much larger aggregates at one-order lower concentration which can be consistent with the absorption spectra.

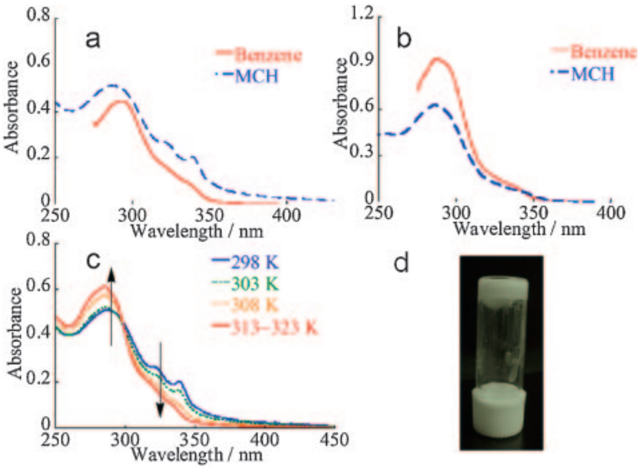

Figure 3. Absorption spectra of (a) *trans*-**1** (5.0×10^{-6} M) and (b) *trans*-**2** (5.0×10^{-6} M). (c) Change in the absorption spectra upon temperature for *trans*-**1** (5.0×10^{-6} M). (d) Organogel of *trans*-**1** in MCH.

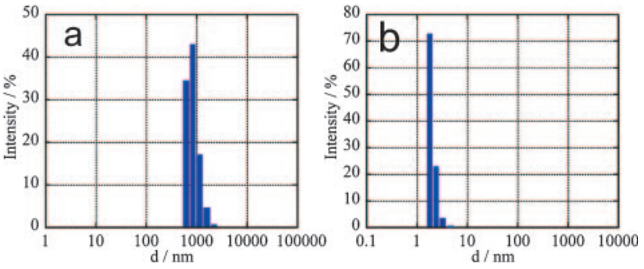

Figure 4. Size distribution and number-average hydrodynamic diameter estimated by dynamic light scattering measurements of *trans*-**1** (5 μM) (a) and *trans*-**2** (50 μM) (b) in MCH.

Although *trans*-**1** may form higher order structure at much diluted conditions in MCH, photoirradiation of *trans*-**1** (10^{-6} M) at 320 nm resulted in *trans*–*cis* photoisomerization, as revealed by the change in the absorption spectra (Figure 5). Under these conditions, only the stilbene core absorbs light. Upon irradiation, the absorbance at 300–350 nm decreased due to the formation of *cis*-isomer because the extinction coefficient of *cis*-isomer is smaller than that of *trans*-isomer. The $\Phi_{t\to c}$ value was determined to be 0.3 for *trans*-**1**, which is considerably high, despite a formation of higher order structure. *trans*-**2** formed smaller aggregates and also underwent photoisomerization and intermolecular reaction to give higher molecular weight compounds in MCH (Figure S1). In benzene, *trans*-**1** and *trans*-**2** also underwent clean *trans*–*cis* photoisomerization with higher $\Phi_{t\to c}$ values than in MCH (Figure S2 and Table 1).

It should be noted that in our system, stilbene can be directly excited to produce triplet stilbene through two-step energy transfer. After excitation, singlet energy transfer (SET) to the peripheral benzophenone units occurs with extremely high quantum yield, which can be estimated from the fluorescence spectra of dendrimers and of model compound *trans*-3,3′,5,5′-tetramethoxystilbene (TMST)[6] that were measured at room temperature (Figure S3). Upon excitation at the same wavelength (310 nm), *trans*-**1** and *trans*-**2** exhibited fluorescence spectra similar to that of TMST, but with very weak intensities (Figure S3, inset), due to intramolecular singlet energy transfer from the excited stilbene to the surrounding benzophenone

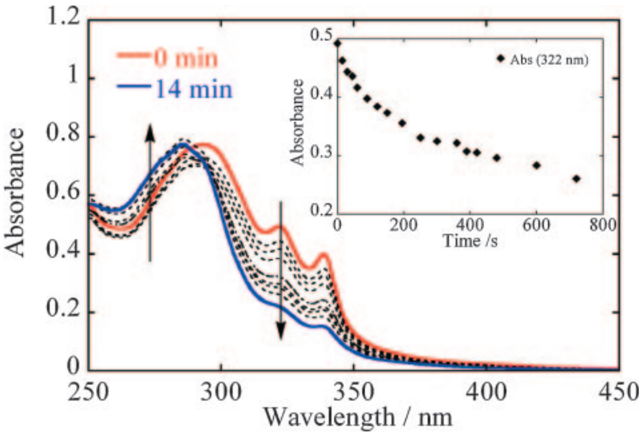

Figure 5. Change in the absorption spectra of *trans*-**1** (1.3×10^{-5} M) with irradiation at 320 nm light in MCH.

Table 1. Quantum Yields for *trans*–*cis* Photoisomerization ($\Phi_{t\to c}$), Fluorescence Quantum Yields (Φ_f), Quantum Yields for SET (Φ_SET), Lifetimes for Excited Singlet State (τ_s), Quantum Yields for TET (Φ_TET), Lifetimes for Excited Triplet State (τ_T), and ERT (Φ_ERT) of *trans*-**1** and *trans*-**2**

Substrate	Solvent	$\Phi_{t\to c}$	Φ_f	Φ_SET	τ_s/ns (%)	Φ_TET	τ_T/μs	Φ_ERT
trans-**1**	Benzene	0.42	0.0011	0.995	<0.5	>0.99	<0.02	0.99
	MCH	0.30	0.0008	0.996	<0.5 (99.2), 20 (0.08)	>0.99[b]	—[c]	0.99[d]
trans-**2**	Benzene	0.36	0.0036	0.985	<0.5	0.992	0.06	0.98
	MCH	0.07[a]	0.0015	0.993	<0.5 (99.6), 6.5 (0.04)	0.99[b]	—[c]	0.98[d]

a) Photoreaction including isomerization and intermolecular reaction. b) Estimated by phosphorescence spectra at 77 K (Figure S4). c) Less solubility for measuring the transient absorption spectra. d) Estimated from phosphorescence data at 77 K.

units, leading to quenching of fluorescence emissions. The fluorescence quantum yields (Φ_f) of the dendrimers were determined to be 0.0011 and 0.0036 for *trans*-**1** and *trans*-**2**, respectively, which were almost two orders of magnitude less than TMST ($\Phi_f = 0.24$). The quantum yield for SET (Φ_{SET}) was estimated to be 0.99 by comparing the Φ_f value.

The benzophenone units then undergo intersystem crossing, and the triplet energy comes back to the stilbene core by intramolecular triplet energy transfer (TET). Quantum yield for TET (Φ_{TET}) was estimated by comparing the phosphorescence spectra at 77 K in MCH (Figure S4). *trans*-**1** and *trans*-**2** exhibited phosphorescence upon excitation 370 nm. However the intensities were much weaker than those of model compound 4-methylbenzophenone (4-MeBP) due to triplet energy transfer from excited benzophenone to the core stilbene. The quantum yields (Φ_{TET}) were 0.99 estimated by comparing the phosphorescence intensities.

In benzene, the Φ_{TET} value was estimated by comparing the transient absorption spectra at 298 K (Figure S5). The T–T absorption spectra of 4-MeBP and *trans*-**2** were observed around 530 nm, whereas the absorption band of *trans*-**1** was not detected probably due to the short lifetime. The triplet lifetimes were determined to be 6.35 µs for 4-MeBP, <20 ns (less than the equipment limit) for *trans*-**1**, and 60 ns for *trans*-**2**. The short lifetime of triplet-state in the dendrimers strongly indicates the occurrence of intramolecular TET from the triplet benzophenone units to the stilbene core. Quantum yield (Φ_{TET}) at 298 K can be calculated from the triplet lifetime of *trans*-**1**, *trans*-**2**, and 4-MeBP. Thus, the quantum yield of the round-trip energy transfer (Φ_{ERT}) was estimated based on eq 1.

$$\Phi_{ERT} = \Phi_{SET} \cdot \Phi_{isc} \cdot \Phi_{TET} \qquad (1)$$

where Φ_{isc} represents the quantum yield of intersystem crossing in the benzophenone units and can be assumed to be quantitative ($\Phi_{isc} = 1$).[7] The Φ_{ERT} values for all dendrimers were calculated to be as high as 0.98–0.99. In this case, direct intersystem crossing of stilbene itself is negligible because the rate constant for SET ($k_{SET} = 10^{10}\,s^{-1}$) is probably much greater than those of other photochemical processes.[6] In addition self quenching did not occur even in aggregates because of rapid SET and TET. Finally the energy transfer ends with *trans–cis* isomerization of triplet stilbene.

In summary, stilbene-cored benzophenone dendrimers *trans*-**1** and *trans*-**2** showed efficient two-step energy transfer to give stilbene triplet. In benzene, both *trans*-**1** and *trans*-**2** exhibited clean photoisomerization. In diluted MCH solution, *trans*-**1** and *trans*-**2** formed aggregates with different size depending on the generation. *trans*-**1** underwent efficient and clean *trans–cis* isomerization in the aggregates whereas *trans*-**2** underwent intermolecular reaction to give higher molecular weight compounds in addition to isomerization.

Experimental

Apparatus. Sample solutions were prepared in benzene and MCH (Kanto Chemical) and deoxygenated by bubbling with highly purified argon (>99.999%) via a needle. Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4500 fluorescence spectrophotometer with a 1 cm × 1 cm quartz cuvette. Fluorescence lifetimes were determined using a Horiba NAES-1100 time-resolved spectrofluorometer. The excitation source of 355 nm for transient absorption measurement was generated by the third harmonic generator (Spectra Physics, DHS-2) from the fundamental of YAG laser (Spectra Physics, Quanta-Ray DCR-3) with a repetition rate of 10 Hz. The time profile of a pulse was FWHM of about 20 ns with 2.3 mJ/pulse. Xenon flash lamp (Hamamatsu Photonics, L2437) was used as a probe light, which was introduced into Spectrograph (Andor, SR-303i) and detected by ICCD camera (Andor, iStar 720) with a time resolution of 5 ns. The timing of the laser, flash lamp and ICCD camera was controlled by a digital delay generator (Stanford Research, DG535). iStar application software converted transmission to absorbance leading to absorption spectra at each time delay. Size distribution and number-average hydrodynamic diameter were measured by fiber-optic dynamic light scattering spectrophotometer (FDLS-3000, Otsuka Electronics, Co., Ltd., Japan).

This work was supported by Grants-in-Aid for Scientific Research in a Priority Area, “New Frontiers in Photochromism” (Nos. 471 and 19550176), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Supporting Information

Figures S1–S5 are change in the absorption spectra with irradiation, fluorescence, phosphorescence, and transient absorption spectra of *trans*-**1** and *trans*-**2**. Experimental section are synthesis, NMR, and MALDI-TOF MS data of *trans*-**1** and *trans*-**2**.

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