Extremely efficient photoisomerization of water-soluble diphenylbutadiene dendrimers

Yousuke Miura [a], Atsuya Momotake [a], Yoko Kanna [b], Yoshinobu Nishimura [a], Tatsuo Arai [a,*]

[a] Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan
[b] Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan

A B S T R A C T

A water-soluble diphenylbutadiene-cored poly(aryl ether) dendrimer, together with a corresponding lipophilic diphenylbutadiene dendrimer and a standard compound, (1E,3E)-1,4-bis(3,5-dimethoxyphenyl) buta-1,3-diene, were prepared and their photochemical properties were examined. The water-soluble dendrimer in aqueous solution exhibited an extremely high photoisomerization quantum yield ($\Phi_{iso} = 0.64$), whereas the quantum yield of the bis(3,5-dimethoxyphenyl)butadiene reference compound in THF was much lower ($\Phi_{iso} = 0.26$). The excitation spectra of the water-soluble dendrimer strongly depended on the emission wavelength and the fluorescence lifetime contained several components. These results indicate that the core unit in the water-soluble dendrimer adopts multiple conformations, one of which is distorted and can undergo photoisomerization quite easily.

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1. Introduction

The excited-state behavior of arylethenes such as stilbenes is well characterized and has become an important area of study because of a number of practical and potential applications [1]. Among a number of deactivation pathways, photoisomerization around a C=C double bond has been studied since the 1960s [2,3] because it is an especially good model for the photoisomerization of retinal in rhodopsin, accounting for both its high selectivity and efficiency [4]. A retinal molecule that is covalently attached to an opsin protein through a Schiff base moiety undergoes photoisomerization from its 11-*cis* to its all-*trans* form with a remarkable quantum yield ($\Phi_{iso} = 0.65 \pm 0.02$) [5–7]. Generally, development of chromophores in which the photoisomerization quantum yield exceeds 50%, as seen in the rhodopsin system, has not been straightforward with respect to isomerization around the C=C double bond. For instance, for excited-state *trans*-stilbene, only one half of the molecules isomerizes to the *cis* form, and the other half reverts back to the original *trans* form (Fig. 1, energy diagram). Despite this, some C=C double bonded molecules that control the direction of photoisomerization have been reported [8–11]. For example, we have developed styrylanthracene, which exhibits one-

way *cis*-to-*trans* photoisomerization [12,13]. One-way *trans*-to-*cis* photoisomerization has also been observed in a water-soluble stilbene dendrimer [14], but the photoisomerization quantum yield was still less than 50% [15]. However, during the course of our research on photoresponsive dendrimers, the isomerization efficiency of stilbenes [14–16] or azobenzenes [17] was found to change significantly within water-soluble dendrimers in aqueous media compared to those in conventional organic solvents [18–20]. We report here the first synthesis of a water-soluble diphenylbuta-diene-cored dendrimer (Chart 1) that exhibits an extremely high photoisomerization quantum yield ($\Phi_{iso} = 0.64$). This dendrimer may serve as a model compound for a photoresponsive biomolecule.

2. Experimental section

2.1. Materials

2.1.1. Preparation of 1

A solution of *trans*-3,5-dimethoxycinnamaldehyde (0.75 g, 3.9 mmol) in THF (5 mL) was added to a mixture of diethyl 3,5-dimethoxybenzylphosphonate (1.15 g, 4.0 mmol) and NaH (0.3 g, 12.5 mmol) in THF (20 mL) at 0 °C under nitrogen atmosphere. The mixture was stirred for 48 h at room temperature. The reaction mixture was quenched with water (100 mL) and extracted with dichloromethane (100 mL × 2). The solvent was removed by
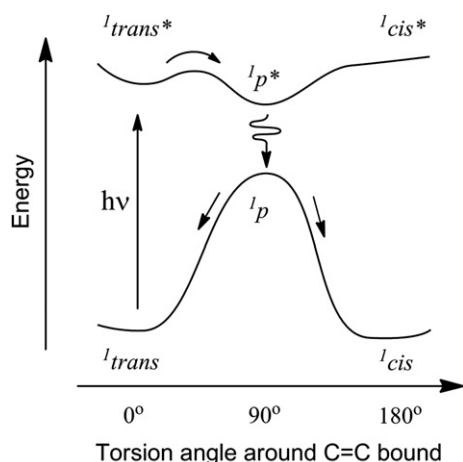
Fig. 1. Potential energy diagram of *trans-cis* photoisomerization around C=C double bonds.

evaporation under reduced pressure. The residue was purified via silica gel column chromatography (hexane/ethyl acetate = 4/1) and recrystallized from hexane/ethyl acetate to give **1** as colorless crystals (0.43 g, 1.32 mmol) in 36% yield. m.p. 118–119 °C ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.91 (m, 2H), 6.61 (m, 2H), 6.60 (d, J = 2.2 Hz, 4H), 6.38 (t, J = 2.2 Hz, 2H), 3.82 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.9, 139.3, 133.1, 129.6, 104.5, 100.1, 55.4. Anal. Calcd. for C$_{20}$H$_{22}$O$_4$: C, 73.60; H, 6.79; O, 19.61. Found: C, 73.33; H, 6.76; O, 19.91.

2.1.2. Preparation of **BD**

(1E,3E)-1,4-bis(3,5-dihydroxyphenyl)buta-1,3-diene (48 mg, 0.178 mmol) and G1-Br [21] (410 mg, 0.82 mmol) in a mixed solvent of THF (6 mL) and DMF (2 mL) were added to a mixture of 18-crown-6-ether (33 mg, 12.5 μmol) and K$_2$CO$_3$ (173 mg, 1.3 mmol) under a nitrogen atmosphere, and the mixture was stirred at 60 °C

Chart 1. Chemical structures of **G1-Br**, **1** and diphenylbutadiene-cored dendrimers (**BD** and **WBD**).

for 90 h. The solvent was evaporated after the resulting salts were filtered. The residue was purified via silica gel column chromatography (dichloromethane/ether = 20/1), followed by GPC column (TOSOH G2500H$_{xL}$) using chloroform as an eluent, to give **BD** as a pale yellow solid (70 mg, 36 μmol) in 20% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00 (d, J = 8.6 Hz, 32H), 7.43 (d, J = 8.6 Hz, 32H), 6.83 (br s, 2H), 6.64 (d, J = 2.2 Hz, 24H), 6.63 (d, J = 2.0 Hz, 4H), 6.51 (br s, 2H), 6.50 (t, J = 2.2 Hz, 12H), 6.47 (t, J = 2.0 Hz, 2H), 5.04 (s, 32H), 4.95 (s, 24H), 3.88 (s, 48H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 52.2, 69.5, 69.9, 101.7, 105.8, 106.5, 127.0, 129.7, 129.8, 129.9, 133.1, 139.4, 139.5, 141.9, 159.89, 159.94, 166.8. MALDI-TOF-MS (m/z): [M + Na]$^+$ calcd for C$_{116}$H$_{102}$O$_{28}$, 1942.66; found, 1943.57.

2.1.3. Preparation of **WBD**

A solution of **BD** (37 mg, 19 μmol) in mixed solvent (1 M KOH/THF/MeOH = 1/4/1, 12 mL) was stirred at 60 °C for 8 h under nitrogen atmosphere. The mixture was then acidified by the addition of 1 M HCl. The resulting precipitate was filtered and washed with distilled water to give **WBD** as a pale yellow solid (32 mg, 17.5 μmol) in 92% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95 (d, J = 8.4 Hz, 16H), 7.54 (d, J = 8.4 Hz, 16H), 7.11 (br s, 2H), 6.76–6.56 (br s × 4, 20H), 5.18 (s, 16H), 5.04 (s, 8H). MALDI-TOF-MS (m/z): [M + Na]$^+$ calcd for C$_{108}$H$_{86}$O$_{28}$, 1831.82; found, 1831.32.

2.2. Instrumental analysis

^{1}H and ^{13}C NMR spectra were measured with a Bruker ARX-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometer in solutions of CDCl$_3$ or DMSO-d_6 with tetramethylsilane as an internal standard. Absorption and fluorescence spectra were recorded on a Shimadzu UV-1600 spectrophotometer and a Hitachi F-4500 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with a Horiba NAES-1100 time-resolved spectrofluorometer or a time-correlated single-photon counting method as reported previously [22].

2.3. Photoirradiation

For ultraviolet–visible spectroscopic studies, 3.00 mL of sample solution was added to a 1 cm path length quartz cuvette. The absorbance at the peak wavelength of irradiated sample was 0.2. Deaerated solutions were prepared by bubbling the solutions with dry argon for 10–15 min to reach a 3.0 mL volume. The quantum yield of photoisomerization was determined by irradiation at 325 nm from a 150 W xenon lamp through a monochrometer using diphenylbutadiene ($\Phi_{tt \to tc}$ = 0.11 in cyclohexane) [23] as a standard. Note that the quantum yield of photoisomerization of **WBD** is defined as an isomerization quantum yield for *trans,trans* form-to-*cis,trans* or *cis,cis* form, since the product ratio (*cis,trans/cis,cis*) has not been determined. In these experiments the total conversion was always <10%.

3. Results and discussion

3.1. Photoisomerization

The photoisomerization quantum yield of **WBD** in aqueous solution was unpredictably high (Φ_{iso} = 0.64) in terms of the conventional photoisomerization mechanism of C=C double bonds as mentioned above (Table 1). Upon illumination of light at the maximum absorption wavelength, the absorption band due to the diphenylbutadiene core drastically decreased while a peak in the shorter wavelength region increased (Fig. 2a). This manner of spectral change during photoisomerization is different from that of well-known diphenylbutadiene (DPB) in which the mutual
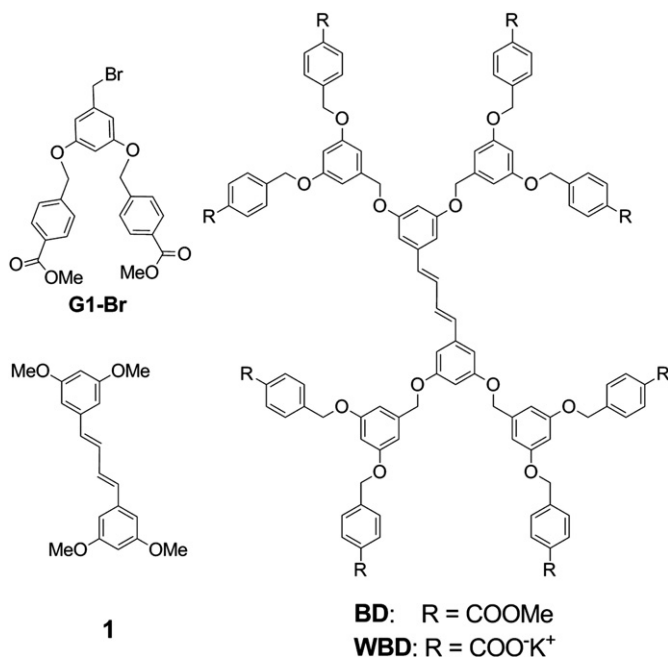
Table 1
Photochemical properties of **1** and **WBD**.

	λ_{abs}/nm	ε/M^{-1} cm^{-1}	τ_s/ns	Φ_{iso}
1	338	51500	1.2	0.26
WBD	275, 335	16900, 28600	0.15, 1.6, 9.1	0.64

isomerization takes place between the *trans,trans* (*tt*) form and the *cis,trans* (*ct*) form [23].Photoisomerization of **WBD** may produce the *cis,cis* (*cc*) form along with the *ct* form (Scheme 1).In contrast, the spectral change during the photoisomerization of **1** in THF (Fig. 2b), with a quantum yield of $\Phi_{iso} = 0.26$, is similar to that of DPB. This spectral difference between **WBD** and **1** probably originates from the difference in the ground state conformation, which is supported by the difference in the absorption spectra before irradiation. The band for the core of **WBD** is broadened and less intense compared to that of **1**. The extinction coefficient of **WBD** was determined at the maximum wavelength to be 28,600 M^{-1} cm^{-1}, which is almost half that of **1** (51,500 M^{-1} cm^{-1}, Table 1). In addition, the maximum wavelength of **WBD** was 3 nm shorter than that of **1**. These results suggest the shrinking of **WBD** in water due to the hydrophobic interactions of the dendrimer interior, which induces a twisted or distorted state of the diphenylbutadiene core around the C=C double bond or a different $\pi-\pi$ dihedral angle.

3.2. Fluorescence lifetime

Compound **1** should adopt a single planar conformation in THF. This is supported by the analysis of the single-component decay
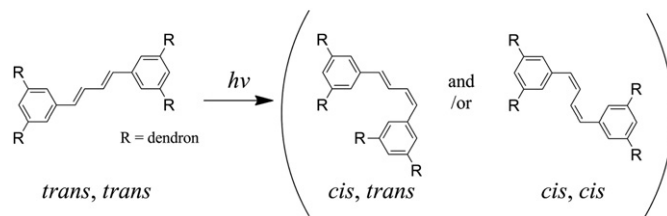
Scheme 1. Photoisomerization in **WBD**.

curve. On the other hand, the fluorescence decay curve of **WBD** was fitted to a three-component exponential decay (Fig. 3), likely due to the diphenylbutadiene core in water-soluble dendrimers adopting multiple conformations in the ground state, thus producing a multi-emission state. The estimated lifetime is 1.2 ns for **1** and 0.15, 1.6, and 9.1 ns for **WBD** (Table 1). The lifetime of 1.6 ns is assigned to the planar conformation, and the shorter component of 0.15 ns may be attributed to the distorted conformer [24]. The longer lifetime (9.1 ns) component is assigned to the s-*cis* form, which has been reported to have a longer lifetime than that of the planar conformation [25].
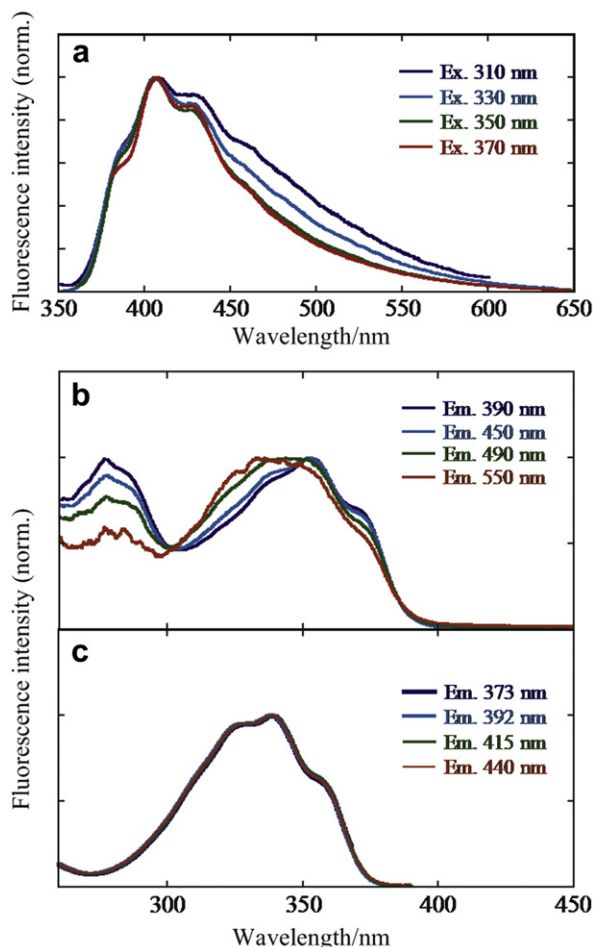
3.3. Fluorescence excitation spectra

As expected from the fluorescence lifetime analysis, the fluorescence (Fig. 4a) and the fluorescence excitation (Fig. 4b) spectra of **WBD** are largely dependent on the monitoring wavelength, indicating that the diphenylbutadiene core in **WBD** adopts multiple conformations in the ground state. A structured excitation spectrum was observed when monitored around 400 nm, whereas a broadened excitation spectrum was observed with monitoring at wavelengths longer than 450 nm. The structured excitation bands could be assigned to diphenylbutadiene with a planar conformation because the spectral shape is similar to the absorption band of **1**. The broadened spectra likely originated from the non-planar (distorted) conformation. The wavelength dependence of the excitation spectra indicates that the absorption spectrum of **WBD** represents the sum of the bands for multiple components in the ground state. Unlike **WBD**, the excitation spectrum of **1** is similar to the absorption spectrum (Fig. 4c) and did not depend on the monitoring wavelength, which is consistent with a single-component fit in the fluorescence decay analysis.
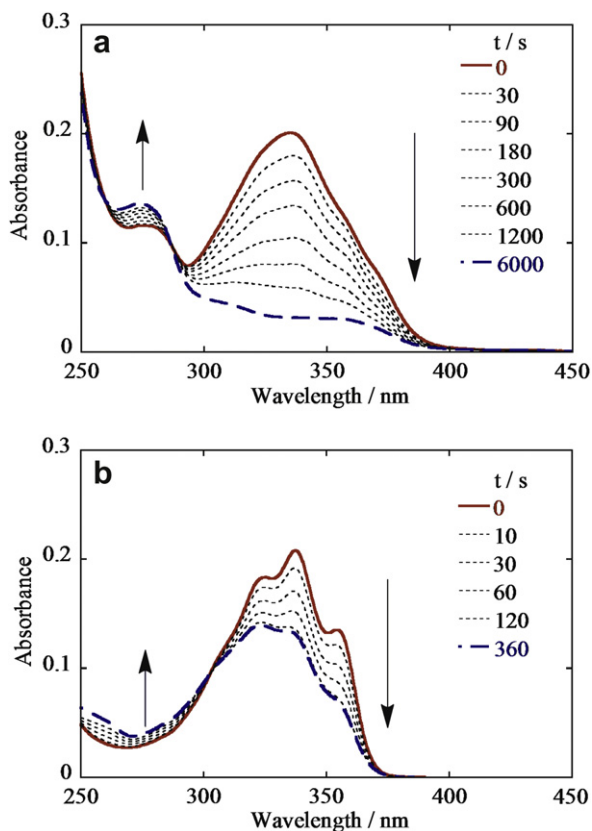
Fig. 2. Change in the absorption spectra of WBD with irradiation at 334 nm in 2 mM KOH aqueous solution (a) and 1 with irradiation at 338 nm in THF (b) under Ar.
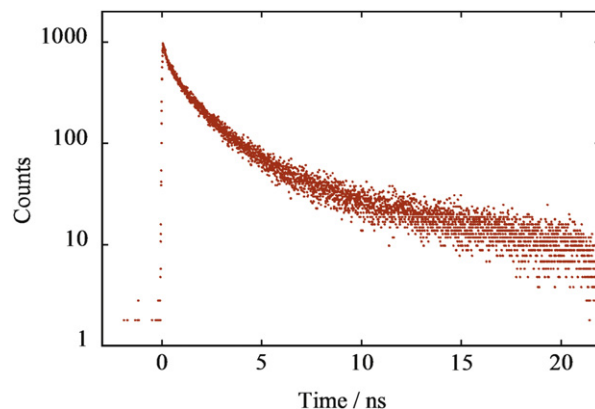
Fig. 3. Fluorescence decay curve of WBD in 2 mM KOH aqueous solution with excitation wavelength at 375 nm.

Fig. 4. Wavelength dependence of (a) fluorescence and (b) excitation spectra of WBD in 2 mM KOH aqueous solution and (c) 1 in THF under Ar.

3.4. Comparison with stiff diphenylbutadienes

To gain more insight on the photochemical and photophysical behaviors of **WBD**, we compared it to the photophysics of various "stiff" diphenylbutadienes by Lee et al. [24], where the two phenyl rings are held in a rigid conformation by alkyl chains connecting the 2-position of the phenyl ring to the polyene unit (Chart 2). The absorption spectrum of planar (E,E)-diindanylidenylethane (5-DPB) is structured, but the spectra are unstructured for other stiff diphenylbutadienes (6-DBP and 7-DPB), which are considered to adopt more distorted structures. In addition, the energy barriers for isomerization of 6-DBP and 7-DPB are smaller than for other DPBs, indicating that photoisomerization is favorable in more distorted DPBs. In the case of **WBD**, high-efficiency photoisomerization may be caused by the diphenylbutadiene core with a distorted conformation, which can be formed specifically within the water-soluble dendrimer in aqueous solution.

5-DPB: n = 1
6-DPB: n = 2
7-DPB: n = 3
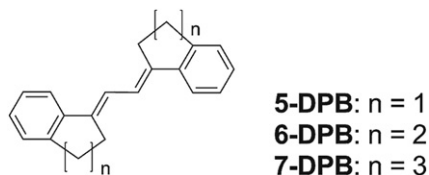
Chart 2. Chemical structures of stiff diphenylbutadiene.

4. Conclusions

In conclusion, the diphenylbutadiene-cored poly(aryl ether) dendrimer **WBD** undergoes photoisomerization with an extremely high quantum yield in aqueous solution. Fluorescence lifetime analysis and excitation spectra suggest that the core diphenylbutadiene adopts multiple conformations within the dendrimer and one of the conformers with a distorted structure may isomerize very efficiently. This is the highest isomerization quantum yield of diphenylbutadienes reported to date and also the highest isomerization quantum yield of a dendrimer. These findings using a water-soluble dendrimer system may be useful for controlling photoisomerization efficiency and developing new models of photoresponsive biomolecules.

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