

Photosensitized Oxygenation of Sulfides within an Amphiphilic Dendrimer Containing a Benzophenone Core

Yasuhiro Shiraishi,* Hisao Koizumi, and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

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Photosensitized oxygenation of sulfides within amphiphilic dendrimers, **Gn** [$n(\text{generation}) = 1-3$], consisting of a benzophenone (BZP) sensitizing core, apolar interior based on n -undecane spacer, and polar dendron exterior based on 2,2-bis(hydroxymethyl)propionic acid, has been investigated in O_2 -saturated methanol. Sulfoxide formation occurring via reaction of O_2 with triplet excited-state sulfide ($^3\text{sulfide}^*$), which is formed by a triplet energy transfer (TET) from photoformed $^3\text{BZP}^*$ to sulfide, was accelerated by the dendric sensitizers, where **G2** showed the highest yields of alkylaryl and dialkyl sulfoxides. Laser photolysis studies revealed that enhanced access of sulfide to the $^3\text{BZP}^*$ core inside the apolar microenvironment accelerates the TET to sulfide, whereas prompt migration of polar sulfoxide to the polar outer shell of the dendrimer suppresses a competitive TET to sulfoxide, thus resulting in effective $^3\text{sulfide}^*$ formation. Another notable feature of the dendric sensitizer appears in oxygenation of diaryl sulfide, which is promoted by a persulfoxide intermediate formed by photooxygenation of dialkyl sulfide; photoirradiation of a mixture of diethyl sulfide (**1a**) and diphenyl sulfide (**4a**) with **G2** gave 17-fold higher diphenyl sulfoxide (**4b**) yield than that obtained with unmodified BZP. The apolar microenvironment within the dendric sensitizer encapsulates a large quantity of **4a**, which is oxidized effectively by the persulfoxide of **1a**, thus resulting in high **4b** yield. The BZP core within the dendric sensitizer is stable even by photoexcitation in protic solvent, suggesting potential utilities of this dendric system for effective and selective photosensitized oxygenation of sulfides.

1. Introduction

Dendrimers are hyperbranched macromolecules with well-structured three-dimensional architecture, consisting of core, building blocks, and external surface groups.¹⁻⁴ The structural features and the associated molecular and supramolecular properties of dendrimer have attracted a wide variety of investigations in a number of chemical, biological, and material related studies.^{5,6} Especially, application of dendrimer as a catalyst has received a great deal of attention. Constructing the catalytic active site on several positions of dendrimer triggers various unique catalytic activities, which are scarcely realized for catalysts based on traditional random, linear, and cross-linked polymers.^{7,8} Meanwhile, application of dendrimer as a photo-functional material has also attracted considerable attention.⁹⁻¹¹ In this case, numerous light-collecting chromophores, placed on the periphery of the dendrimer, enable a smooth transfer of the absorbed light energy to a core molecule. Future artificial light-harvesting systems may well be based upon such “energy sink” type dendric structures.

Besides the above broadened application of dendrimer, there are only few reports of dendric structure utilized as a photocatalyst (photosensitizer) for conversion of molecules.¹²⁻¹⁵ Among the reports, the amphiphilically designed dendric photosensitizers, which are synthesized by Hecht and Fréchet,¹² demonstrate unique photosensitizing activity. These dendric sensitizers employ benzophenone (BZP), a typical triplet photosensitizer, as a core molecule, which is modified with apolar n -undecane spacers and then surrounded by polar aliphatic

polyester dendrons based on 2,2-bis(hydroxymethyl)propionic acid [Figure 1; **Gn**; $n(\text{generation}) = 1-3$]. These are utilized for photosensitized oxygenation of cyclopentadiene into 2-cyclopentene-1,4-diol in O_2 -saturated methanol (MeOH) in the presence of thiourea. In that, singlet oxygen ($^1\text{O}_2$), formed via a triplet energy transfer (TET) from a triplet excited-state BZP ($^3\text{BZP}^*$) core to O_2 , is stabilized in apolar microenvironment inside the dendrimer,¹⁶ thus promoting effective $^1\text{O}_2$ -addition to diene. Another emphasized aspect of this dendric system is smooth transfer of the apolar diene into the apolar interior and of the resulting polar diol to the polar outer shell of the dendrimer. This enhanced diene transfer into the interior assists the effective $^1\text{O}_2$ -addition to diene. The above photosensitizing “pump” system, inspired by the amphiphilically designed dendric sensitizers, may well be applicable to several photo-reactions, which are associated with a large polarity difference between substrate and product.

Sulfoxides are the materials used extensively as a synthetic intermediate and chiral auxiliary.^{17,18} These are synthesized photochemically by three main reactions: (1) sulfide with $^1\text{O}_2$,¹⁹⁻²¹ (2) O_2 with triplet excited-state sulfide ($^3\text{sulfide}^*$),²²⁻²⁴ and (3) cation radical of sulfide ($\text{sulfide}^{\bullet+}$) with superoxide radical ($\text{O}_2^{\bullet-}$), both formed via photoinduced electron transfer by electron-deficient photosensitizers (e.g., 9,10-dicyanoanthracene).²⁵⁻²⁷ The sulfoxides are highly polarized compounds as compared to the corresponding sulfides.^{24,26} Therefore, the above amphiphilically designed dendric sensitizers, **Gn**, if employed for the photosensitized oxygenation of sulfides, may demonstrate unique sensitizing properties involving the “pump” function. In the present work, photooxygenation of sulfides

* Corresponding author. Tel.: +81-6-6850-6271. Fax: +81-6-6850-6273. E-mail: shiraish@cheng.es.osaka-u.ac.jp.

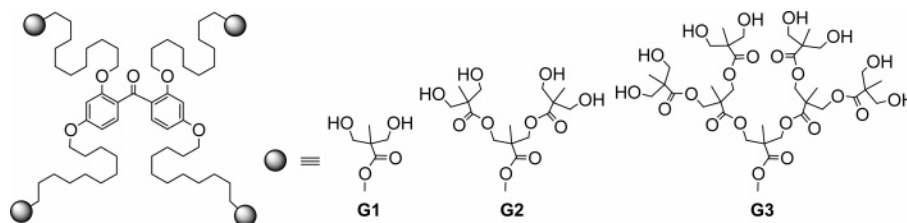
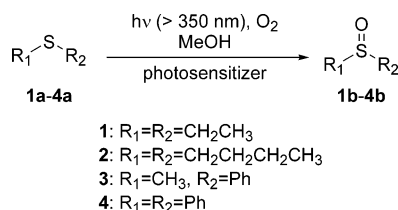


Figure 1. Structure of the dendritic photosensitizers.

SCHEME 1



promoted by the dendritic sensitizers, **Gn** [$n(\text{generation}) = 1-3$], was investigated in O_2 -saturated MeOH (Scheme 1). The sensitizing activities of the dendritic sensitizers were studied in comparison with those of unmodified BZP. The photochemical and photophysical properties of the dendritic sensitizers were examined in detail by means of laser flash photolysis. We describe here a role of the apolar microenvironment inside the dendritic sensitizers as a reaction cavity promoting effective and selective photosensitized oxygenation of sulfides.

2. Experimental Section

2.1. Materials. The dendritic photosensitizers, **Gn** [$n(\text{generation}) = 1-3$], were synthesized and characterized according to the literature procedure.¹² Unmodified BZP and 2,2',4,4'-tetramethoxybenzophenone (TMBZP) were also used as photosensitizers for comparison, both which were purchased from Sigma-Aldrich and used without further purification. Sulfides and sulfoxides were purchased from Sigma-Aldrich, Tokyo Kasei, and Wako and were used as received. Benzene, ethanol, and MeOH (Wako), of highest spectroscopic grade, were used as received.

2.2. Photooxygenation General Procedure. Photoreaction experiments were carried out as follows: each photosensitizer (1.5 μmol) was dissolved in dry MeOH (15 mL) containing an individual sulfide (1.5 mmol) within a Pyrex glass tube (capacity: 20 mL), and each tube was sealed using a rubber septum cap. O_2 was bubbled through the solution for 10 min at 273 K to avoid the solvent evaporation. The samples were then photoirradiated by a 2 kW Xe lamp (Ushio Inc.), filtered through an aqueous $CuSO_4$ (10 wt %) solution to give light wavelengths of $\lambda > 350$ nm with magnetic stirring [light intensity at 350–420 nm (through the filter), 65.1 mW/m^2]. It was confirmed that photooxygenation of all of the sulfides used scarcely occurred in the absence of sensitizers. The temperature of the solution during photoirradiation was 313 K. The concentrations of substrates and products in MeOH were determined by a capillary GC equipped with a flame ionization detector (Shimadzu; GC-1700) in comparison with authentic samples.

2.3. Laser Flash Photolysis. The measurements were carried out in MeOH (or benzene) under dry Ar at 298 K, where the respective concentrations of 1×10^{-4} M for **Gn** and 5×10^{-3} M for the other BZP derivatives were employed. The sample (5 mL) in a 10 mm path length quartz cell was degassed by two freeze–pump–thaw cycles on a high vacuum line. The third harmonics of a nanosecond Nd^{3+} :YAG laser (355 nm) from

Surelite 10 (Continuum; pulse width, 4–6 ns; laser power, 10 mJ/pulse) were used for photoexcitation. The detection system consists of a streak camera (Hamamatsu Photonics K. K.; C2830) and a 150 W Xe short arc lamp (Ushio Inc.; UXL-150-D-O). The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance after the laser flash at intervals of 5–10 nm over the spectral range 400–600 nm, averaging at least 10 decays at each wavelength. The transient signals were analyzed by the least-squares best-fitting method.²⁸

2.4. Fluorescence and Phosphorescence Measurements.

The measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. Respective excitation wavelengths of 355 nm for sensitizers and 265 nm for sulfides and sulfoxides were employed. The measurements were carried out in ethanol–ether glass (2/1 v/v) at 77 and 298 K,²⁹ using a 4 mm cylindrical quartz tube, where the respective concentrations of 1×10^{-4} M for **Gn** and 5×10^{-3} M for the other BZP derivatives, sulfide, and sulfoxide were employed. The analytical conditions for the phosphorescence measurements were as follows: pulse width, 2 ms; delay time, 2 ms; cycle, 40 Hz. The singlet energy (E_S) and triplet energy (E_T) of sensitizers and substrates were determined by the literature procedures.^{30–32} The fluorescence quantum yield (Φ_f) of the sensitizers was determined by a comparison of the integrated corrected emission spectrum of standard quinine, which was excited at 366 nm in 0.1 M H_2SO_4 ($\Phi_f = 0.55$).³³ The phosphorescence quantum yield (Φ_p) was determined by a comparison of the integrated corrected emission spectrum of unmodified BZP ($\Phi_p = 0.74$).³⁴

3. Results and Discussion

3.1. Photosensitized Oxygenation of Sulfides. Photoirradiation of sulfides (**1a–4a**) in O_2 -saturated MeOH with respective photosensitizers gave the corresponding sulfoxides (**1b–4b**) as the sole product (Scheme 1). In all runs, neither sulfones nor C–S cleaved products were detected by GC analysis, and the quantity of the converted sulfides agreed reasonably well with that of the sulfoxides formed. Figure 2 summarizes the sulfoxide yields, obtained following photoirradiation (24 h) of sulfides with respective sensitizers, where the yields of alkylaryl and dialkyl sulfoxides (**1b–3b**), obtained with the dendritic sensitizers, are clearly higher than those obtained with unmodified BZP. Highest sulfoxide yields (**1b–3b**) were obtained with **G2**, where the **2b** yield is 4-fold higher than that obtained with BZP. **G1** and **G3** showed lower activity than **G2**. As described,¹² the sensitizing activity of the dendritic sensitizers in the cyclopentadiene photooxygenation in O_2 -saturated MeOH lies in the order of **G3** > **G2** > **G1**, whose order is inconsistent with that of the present sulfide photooxygenation. Figure 3a shows the change in **2b** yield during photoirradiation of **2a** with the respective sensitizers. The **2b** formation with all of the dendritic sensitizers occurs over the entire photoirradiation time, whereas the formation with the unmodified BZP is almost saturated in 12 h photoirradiation.

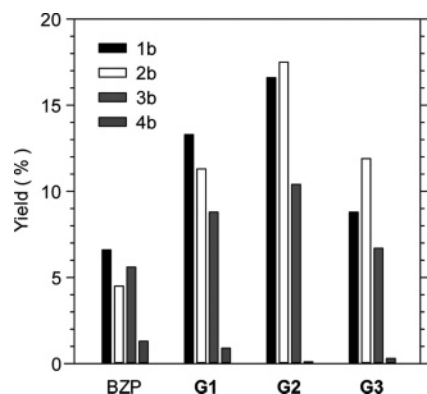


Figure 2. Sulfoxide (**1b**–**4b**) yields obtained by photoirradiation (24 h) of respective sulfides (**1a**–**4a**) with respective photosensitizers in O_2 -saturated MeOH.

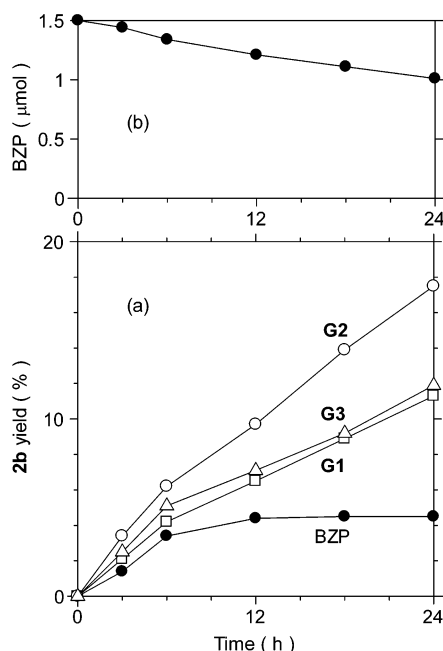


Figure 3. Changes in (a) **2b** yield during photoirradiation of **2a** in O_2 -saturated MeOH with respective photosensitizers and (b) the quantity of BZP during photoirradiation.

3.2. Reaction Mechanism. As shown in Figure 4a, the dendric sensitizers show a red-shifted absorption band at 300–400 nm as compared to the unmodified BZP. This is because of substitution of electron-donating ether oxygen on the BZP. These dendric sensitizers show weak fluorescence at 360–420 nm at 298 K, whereas the unmodified BZP does not show fluorescence.³⁵ The quantum yield of the fluorescence (Φ_f) of the dendric sensitizers (298 K) is, however, less than 0.03 (Table 1). As shown in Figure 4b, phosphorescence spectra (77 K) of the dendric sensitizers appear at >420 nm, which are slightly red-shifted but almost the same as that of the unmodified BZP. As shown in Table 1, the E_T values of the dendric sensitizers were estimated to be 285–286 kJ/mol, whose values are only about 3–4 kJ/mol less than that of the unmodified BZP (289 kJ/mol). These results suggest that the photosensitized oxygenation of sulfides in the dendric system may occur via the formation of $^3BZP^*$ core, as was also the case for unmodified BZP.

The present photooxygenation systems may involve two reaction mechanisms: (1) reaction of sulfide with 1O_2 formed via TET from $^3BZP^*$ to O_2 ^{19–21} and/or (2) reaction of O_2 with 3 sulfide* formed via TET from $^3BZP^*$ to sulfide.^{22–24} When

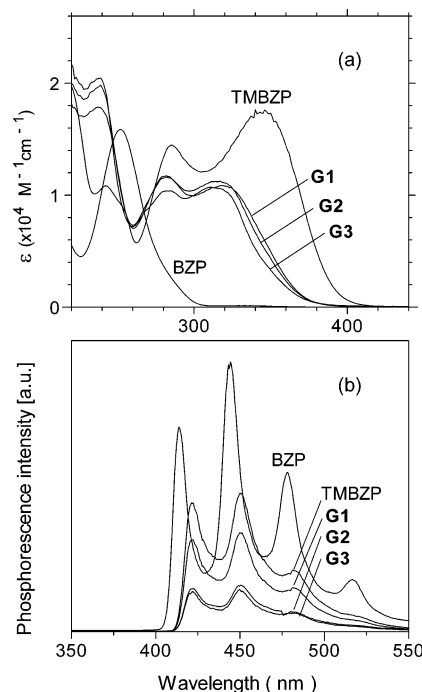


Figure 4. (a) Absorption spectra (298 K) and (b) phosphorescence spectra (77 K; $\lambda_{ex} = 355$ nm) of the respective photosensitizers in ethanol–ether (2/1 v/v).

TABLE 1: Photophysical Properties of the Photosensitizers

sensitizer	E_S (kJ/mol) ^a	E_T (kJ/mol) ^a	Φ_f (298 K) ^a	Φ_p (77 K) ^a	τ_p (77 K) (ms) ^a	τ_T (μ s) ^b
BZP	297	289	<i>c</i>	0.74	5.2	<i>d</i>
TMBZP	305	286	0.02	0.58	4.1	<i>d</i>
G1	299	286	0.02	0.39	3.2	1.31
G2	317	286	0.03	0.24	2.4	0.68
G3	316	285	0.03	0.22	2.1	0.48

^a Measured in ethanol–ether (2/1 v/v). ^b Measured in MeOH. ^c Not observed. ^d Triplet excited-state BZP moieties were decomposed by laser excitation (355 nm), as shown in Figure 5a and e.

TABLE 2: The Triplet Energy of Sulfides and Sulfoxides and Rate Constant for Quenching of the $^3BZP^*$ and $^3BZP^*$ Core of the Dendric Sensitizers by Sulfides and Sulfoxides

substrate	E_T (kJ/mol) ^a	k_q (10^7 M ⁻¹ s ⁻¹)			
		BZP ^b	G1 ^c	G2 ^c	G3 ^c
1a	281	0.18	0.23	0.82	1.92
2a	279	0.22	0.30	3.12	4.87
3a	279	0.34	0.49	3.67	5.64
4a	280	0.59	0.62	4.11	10.23
1b	285	0.12	0.06	0.03	0.01
2b	286	0.17	0.04	0.02	<0.01
3b	284	0.29	0.06	0.02	<0.01
4b	286	0.39	0.03	0.01	<0.01

^a Measured in ethanol–ether (2/1 v/v). ^b Measured in benzene to avoid the photodecomposition of sensitizer. ^c Measured in MeOH.

3a was photoirradiated with respective sensitizers in the presence of DABCO (1.5 mmol), an efficient 1O_2 quencher,³⁶ only a slight decrease in the **3b** yield was observed: the respective decrease in the yield (24 h photoirradiation) is 6% (BZP), 7% (**G1**), 3% (**G2**), and 2% (**G3**) based on the yield obtained in the absence of DABCO (Figure 2). This suggests that the former pathway involving the 1O_2 formation is ruled out of the main mechanism for the present sulfide photooxygenation. As shown in Tables 1 and 2, the E_T values of all of the sulfides used (279–281 kJ/mol) are lower than those of the sensitizers (285–289 kJ/mol), such that the TET from $^3BZP^*$ or $^3BZP^*$ core to sulfide

occurs exothermically. When **3a** was photoirradiated with the respective sensitizers together with 4-phenylbenzophenone ($E_T = 254$ kJ/mol; $E_S = 321$ kJ/mol; $50 \mu\text{mol}$),³⁵ a significant decrease in the **3b** yield was observed: the respective decrease in the yield is 91% (BZP), 93% (**G1**), 95% (**G2**), and 91% (**G3**) based on the yield obtained in the absence of 4-phenylbenzophenone (Figure 2). This is because the $^3\text{sulfide}^*$, formed via the TET from the $^3\text{BZP}^*$ or $^3\text{BZP}^*$ core to sulfide, is deactivated subsequently by TET from $^3\text{sulfide}^*$ to 4-phenylbenzophenone of rather lower E_T .²³ The above findings indicate that the sulfide photooxygenation, sensitized by the present BZP-based sensitizers, proceeds mainly via the latter mechanism involving the $^3\text{sulfide}^*$ formation, via the TET from $^3\text{BZP}^*$ to sulfide, and subsequent reaction with O_2 .

3.3. Properties of Dendric Sensitizer. As shown in Figure 4a, the dendric sensitizers show a rather higher molar extinction coefficient than unmodified BZP at 300–400 nm. This enhanced absorption might contribute to the higher sensitizing activity of the dendric sensitizers. When a spectral irradiance from the light source was measured through a MeOH solution (15 mL) containing BZP or **G1** sensitizer ($1.5 \mu\text{mol}$; the same concentration used for the photooxygenation reactions) (Supporting Information), light intensity absorbed by the solution at 350–420 nm was estimated by the integration of the spectrum to be 30.4 (BZP) and 34.7 mW/m^2 (**G1**) (14% difference). As shown in Figure 2, the sulfoxide yields (**1b–3b**) obtained with **G1** are, however, >50% higher than those obtained with BZP. The difference of the photon number adsorbed by the sensitizers may therefore be ruled out of the higher sensitizing activity of the dendric sensitizers. As shown in Figure 4a, TMBZP shows a red-shifted absorption band similar to that of the dendric sensitizers. Due to the higher absorption of TMBZP at 380–420 nm, the light intensity absorbed by the TMBZP solution was estimated to be 50.1 mW/m^2 , whose value is >40% higher than that of the solution containing BZP or **G1**. However, the use of TMBZP as photosensitizer demonstrates almost the same sulfoxide yields as those obtained with the unmodified BZP: the yields (24 h photoirradiation) are 5.2% (**1b**), 5.8% (**2b**), and 4.1% (**3b**), respectively. The enhanced absorption of the dendric sensitizers can therefore be excluded from the reason for the higher sulfoxide yields (Figure 2). The enhanced sensitizing activity of the dendric sensitizers is therefore attributed to the structural effect derived from the dendric sensitizers.

Figure 5 shows time-resolved transient absorption spectra, observed after 355 nm laser excitation of the respective sensitizers dissolved in MeOH. All of the dendric sensitizers show a triplet–triplet (T–T) transient absorption band centered at 470 nm (Figure 5b–d), attributed to the $^3\text{BZP}^*$ core, whereas the unmodified BZP show T–T absorption at 520 nm (Figure 5a). All of the transient bands decrease with a lapse of time. For the spectrum of BZP (Figure 5a), the T–T absorption band at 520 nm disappeared within 0.2 μs , and new transient absorption appeared at 540 nm. GC analysis of the MeOH solution, obtained following 24 h photoirradiation of **2a** with unmodified BZP (Figure 3), confirmed a decrease in the BZP concentration and the corresponding formation of diphenyl methanol, indicating that BZP is decomposed during photoexcitation in MeOH. The photodecomposition of BZP in MeOH proceeds via the formation of a ketyl radical, occurring via H abstraction from protic MeOH solvent by $^3\text{BZP}^*$,^{37,38} as below:

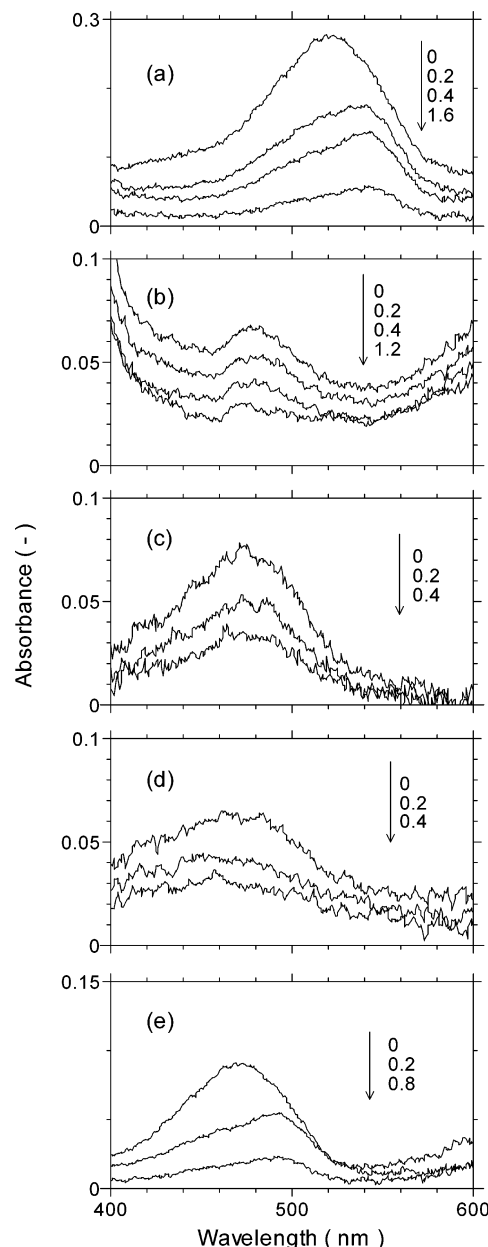
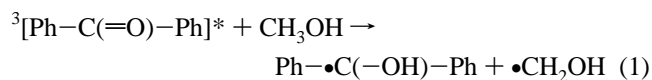


Figure 5. Time-resolved transient absorption spectra of (a) BZP, (b) **G1**, (c) **G2**, (d) **G3**, and (e) TMBZP photosensitizers after 355 nm laser excitation in MeOH at 298 K. The numeric numbers in the figure denote the lapsed time (μs) after the excitation.

The new transient absorption at 540 nm (Figure 5a) is therefore due to the formation of the ketyl radical of BZP.^{37,38} However, upon photoexcitation of the dendric sensitizers (Figure 5b–d) in MeOH, such red-shifted transient absorption, attributed to the ketyl radical, was not observed, suggesting that the BZP core within the dendric sensitizers is stable even by photoexcitation in MeOH. As reported,^{39,40} alkoxy-substituted aromatic ketones with the lowest π, π^* triplet state are less reactive for the H abstraction than unsubstituted aromatic ketones with the n, π^* triplet state. The enhanced stability of the BZP core within the dendric sensitizers is therefore due to the substitution of the alkoxy groups on the BZP core. However, as shown in Figure 5e, upon photoexcitation of TMBZP, new red-shifted transient absorption, attributed to the ketyl radical, was observed at 490 nm. The enhanced photostability of the BZP core within the dendric sensitizers may therefore be assisted by the apolar inner environment constructed by the long alkyl-chains of the

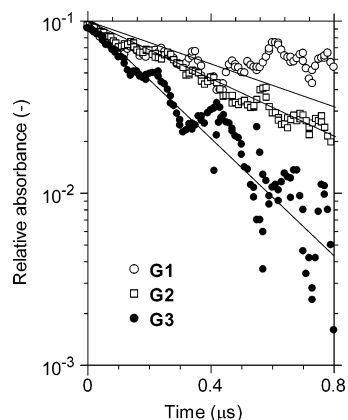


Figure 6. Change in the T–T absorption of the dendric photosensitizers (470 nm) with a lapse of time after 355 nm laser excitation in MeOH at 298 K.

n-undecane spacers. This enhanced core stability may be one of the reasons for the higher sensitizing activity of the dendric sensitizers. However, as shown in Figure 3b, although 80% of BZP added remains in the solution following 12 h photoirradiation, the **2b** formation is almost saturated (Figure 3a), indicating that the enhanced core stability is a minor factor for the high sensitizing activity of the dendric sensitizers.

Figure 6 shows the time profile for the T–T absorption decays of the dendric sensitizers at 470 nm upon 355 nm laser excitation in MeOH. The absorption decay rate increases with an increase in the dendron generation of the sensitizers. According to the first-order kinetics (slope = $-k_0$), the lifetime of the $^3\text{BZP}^*$ core within the dendric sensitizers ($\tau_T = 1/k_0$) was found to lie in the order of **G1** (1.31 μs) > **G2** (0.68) > **G3** (0.48), as summarized in Table 1. It is well known that the lifetime of the unmodified $^3\text{BZP}^*$ decreases with a decrease in solvent polarity.³⁵ The number of polar –OH groups on the periphery of the sensitizers increases with an increase in the dendron generation (Figure 1), thus promoting a polarity difference between the external surface and the internal apolar environment of the dendric sensitizer. As a consequence of this, the polarity of the inner environment decreases, thus possibly causing the decrease in the lifetime of the $^3\text{BZP}^*$ core. As shown in Table 1, the phosphorescence quantum yield (Φ_p) and the lifetime (τ_p) at 77 K also decrease with the dendron generation advance. These findings support the generation-induced decrease in the polarity of the inner environment within the dendric sensitizers. Although the lifetime of the $^3\text{BZP}^*$ core decreases with the dendron generation advance, the sensitizing activity of **G2** is higher than that of **G1** (Figure 2). The above findings are contradictory to each other.

Considering the apolar interior of the dendric sensitizers, O_2 concentration in the interior must be taken into account. As described,³⁵ solubility of O_2 in *n*-decane and MeOH at partial pressure of 101.3 kPa O_2 (at 298 K) is 11.2 and 10.2 mM, respectively, indicating that the O_2 solubility in apolar medium is relatively higher than that in polar medium. The O_2 concentration in the apolar microenvironment inside the dendrimer is therefore expected to be higher than that in bulk solution. However, as shown in Figure 2, the sensitization activity of **G3** dendrimer, having a more apolar inner environment, is lower than that of the other dendrimers of lower generation. This suggests that the difference of the O_2 concentration inside the dendrimer is a minor factor for the photooxygenation efficiency.

3.4. Sulfide and Sulfoxide Transfer. Considering the apolar interior of the dendric sensitizers, the transfer of apolar sulfide

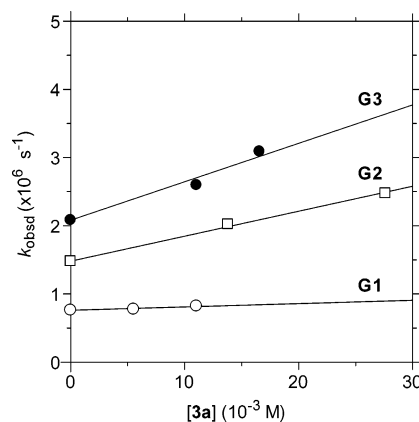


Figure 7. Stern–Volmer plots for the first-order decay rate (k_{obsd}) of the $^3\text{BZP}^*$ core of the dendric photosensitizers as a function of the concentration of **3a**, obtained by 355 nm laser excitation in MeOH at 298 K.

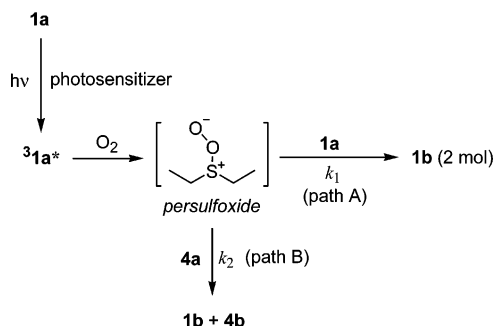
into the interior may affect the photooxygenation efficiency, as was also the case for the cyclopentadiene photooxygenation.¹² To clarify the TET efficiency from the $^3\text{BZP}^*$ core to sulfide, laser photolysis studies of the dendric sensitizers in the presence of respective sulfides were carried out, and the first-order decay rate constant of the $^3\text{BZP}^*$ core, k_{obsd} , was determined. As shown in Figure 7, the plots of k_{obsd} against the concentration of all of the substrates (in this case: **3a**) gave straight lines. From the slopes, the quenching rate constant of the $^3\text{BZP}^*$ core by the respective substrates, k_q , was determined by the Stern–Volmer equation,²⁸ eq 2:

$$k_{\text{obsd}} = k_0 + k_q[\text{sulfide}] \quad (2)$$

where k_0 denotes the decay rate constant of the $^3\text{BZP}^*$ core in the absence of substrate, and [sulfide] denotes the sulfide concentration in the solution. The TET efficiency from unmodified $^3\text{BZP}^*$ to substrate is reported to increase with an increase in solvent polarity.⁴¹ The polarity of the inner environment of the dendric sensitizer decreases with the dendron generation advance, such that the TET efficiency from $^3\text{BZP}^*$ core to sulfide is expected to become lower with the dendron generation advance. However, as summarized in Table 2, the k_q values of the dendric sensitizers with all of the sulfides increase with the dendron generation advance. The enhancement of the TET efficiency may result because the transfer of the apolar sulfide into the interior of the dendric sensitizer is accelerated because of the decrease in the polarity of the inner environment. As a consequence, the local concentration of sulfide around the $^3\text{BZP}^*$ core increases, thus accelerating the TET from $^3\text{BZP}^*$ core to sulfides.

As is shown in Tables 1 and 2, the E_T values of sulfoxides (**1b–4b**) are higher than those of the corresponding sulfides (**1a–4a**),³¹ but are lower than those of the sensitizers. The TET from the $^3\text{BZP}^*$ or $^3\text{BZP}^*$ core to sulfoxides therefore occurs exothermically, as also for the TET to sulfides. The k_q value of the unmodified BZP with **2b** (in benzene) is $1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, whose value is only 13% lower than that with the corresponding sulfide **2a**. When the photoreaction (24 h) of **2a** with BZP was carried out in the presence of the same molar amount of **2b**, the conversion of **2a** scarcely occurred. This indicates that, in the photosensitizing reaction with BZP, the TET from $^3\text{BZP}^*$ to sulfoxide occurs competitively with the TET to sulfide, thus suppressing the sulfide conversion. This is the reason for the saturation of the sulfoxide **2b** formation (Figure 3a) when using BZP as sensitizer. However, as shown

SCHEME 2



in Table 2, the k_q values of the ${}^3\text{BZP}^*$ core of the dendritic sensitizers with sulfoxides are significantly lower than those with the corresponding sulfides. In addition, the k_q values with sulfoxides decrease with the dendron generation advance, whereas the values with sulfides increase with the advance. This is because the transfer of sulfoxides into the apolar environment within the dendritic sensitizers is suppressed because of their high polarity.^{23,25} The local concentration of sulfoxide within the inner environment is therefore lowered, thus resulting in the ineffective TET from ${}^3\text{BZP}^*$ core to sulfoxide. The decrease in the TET efficiency to sulfoxide with the dendron generation advance results because the sulfoxide transfer is suppressed more significantly, due to the decrease in the inner polarity. Based on the above findings, in the sulfide photooxygenation within the dendritic sensitizer, the sulfoxide formed may be transferred promptly to the polar outer shell of the dendrimer, although the transfer rate of the sulfoxide could not be determined in the present experiment. The TET from the ${}^3\text{BZP}^*$ core to sulfoxide is therefore suppressed, thus promoting effective TET to sulfide. The continuous sulfoxide **2b** formation, when using the dendritic sensitizers (Figure 3a), is therefore attributed to the suppression of the competitive TET to sulfoxide because of the prompt sulfoxide transfer out of the dendritic shell. The above results clearly explain the high sensitizing activity of the dendritic sensitizer (Figure 2), as follows: (1) high photostability of the BZP core, (2) prompt sulfoxide transfer out of the dendritic shell, and (3) increased local concentration of sulfide around the BZP core due to the acceleration of sulfide transfer into the inner environment. The sensitizing activity of the dendritic sensitizer, of higher dendron generation, is suffered from the shortened lifetime of ${}^3\text{BZP}^*$ core, due to the decrease in the inner polarity (Table 1). The **G2** sensitizer, having a relatively longer lifetime of the ${}^3\text{BZP}^*$ core, encapsulates a relatively higher quantity of sulfide and lower quantity of sulfoxide, thus showing the highest sensitizing activity for sulfide photooxygenation.

3.5. Diaryl Sulfide Oxygenation by Persulfoxide. As shown in Table 2, the k_q values of the ${}^3\text{BZP}^*$ core of the dendritic sensitizers with diaryl sulfide **4a** are higher than those with alkylaryl and dialkyl sulfides (**1a–3a**), indicating that TET from ${}^3\text{BZP}^*$ core to **4a** occurs more effectively. However, as shown in Figure 2, the **4b** yields obtained by photoirradiation of **4a** with all of the sensitizers are significantly lower than the yields of alkylaryl and dialkyl sulfoxides. Diaryl sulfides are also inert in the oxygenation by ${}^1\text{O}_2$.^{19–21,25} The low **4b** yield may therefore be due to lower electron density of the sulfur atom on diaryl sulfide **4a**, as was also the case for ${}^1\text{O}_2$ oxygenation. As shown in Figure 2, the **4b** yields with dendritic sensitizers are lower than that with unmodified BZP. This may be due to the shorter lifetime of the ${}^3\text{BZP}^*$ core within the apolar environment. As shown in Scheme 2, photooxygenation of sulfides (for example, **1a**) in protic solvent proceeds via formation of a persulfoxide intermediate,^{19–21} which oxidizes

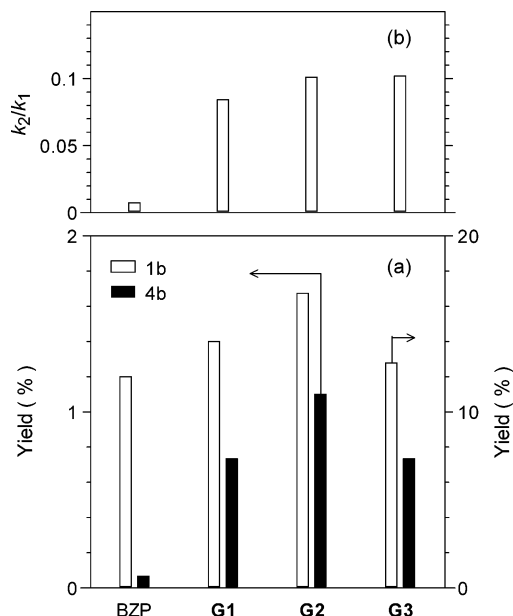


Figure 8. (a) Sulfoxide (**1b** and **4b**) yields obtained by photoirradiation (24 h) of a mixture of **1a** (0.3 mmol) and **4a** (1.5 mmol) with respective photosensitizers (1.5 μmol) in O_2 -saturated MeOH and (b) the ratio of the trapping rate (k_2/k_1) of **4a** and **1a** by persulfoxide of **1a** formed during photoirradiation, which was calculated according to eq 3.

another sulfide molecule **1a**, producing 2 mol of sulfoxide **1b** per mol of O_2 (path A). When **4a** is added to this photoreaction system containing **1a**, the **4a** is trapped by the persulfoxide of **1a** and oxidized effectively into **4b** (path B).^{19,20} Figure 8a shows the **1b** and **4b** yields obtained by photoirradiation (24 h) of a mixture of **1a** (0.3 mmol) and **4a** (1.5 mmol) with respective sensitizers (1.5 μmol) in O_2 -saturated MeOH. As expected, the **1b** yield obtained with dendritic sensitizers is higher than that obtained with unmodified BZP; the yield lies in the order of **G2** > **G1** > **G3** > BZP. The **4b** yield lies in the same order as the **1b** yield. Surprisingly, the **4b** yield obtained with **G2** is 17-fold higher than that obtained with the unmodified BZP. The molar ratio of **4b/1b** obtained with BZP is 0.28, whereas the ratio obtained with **G2** is 3.29, indicating that the path B (Scheme 2) is significantly accelerated with **G2**. The reaction pathways, shown in Scheme 2, give a steady-state kinetic expression with the rate constants, k_1 and k_2 , for the respective pathways A and B, as below:^{19,20}

$$\frac{[1b]}{[4b]} = 1 + \frac{2k_1[1a]}{k_2[4a]} \quad (3)$$

Based on eq 3, the ratio of the rate constant for the respective pathways of A and B, k_2/k_1 , for the respective sensitizers can therefore be estimated, as summarized in Figure 8b. The k_2/k_1 value is found to increase with an increase in the dendron generation of the sensitizer, where the value obtained with **G2** and **G3** is 20-fold higher than that obtained with unmodified BZP. This suggests that **4a** is trapped very effectively by the persulfoxide of **1a** within these dendritic sensitizers. The **4a** trapping by the persulfoxide of **1a** occurs competitively with the **1a** trapping (Scheme 2),^{19,20} such that the trapping rate (k_1 and k_2) depends on the quantity of sulfides (**1a** and **4a**) around the persulfoxide formed. As shown in Table 2, the k_q value of **G2** and **G3** sensitizers with **1a** is 3.6- and 8.3-fold higher than that of **G1**, whereas the values of **G2** and **G3** with **4a** are 6.6- and 16.5-fold higher than that of **G1**. This indicates that the **4a** transfer into the inner environment is accelerated more signifi-

cantly than the **1a** transfer, because of the low polarity of **4a**, and the ratio of the concentration of **4a** to **1a** within **G2** and **G3** sensitizers is higher than that within **G1**. The persulfide of **1a**, formed via the reaction of $^3\text{1a}^*$ with O_2 inside the **G2** and **G3** sensitizers, therefore enables one to oxidize **4a** more preferentially, thus resulting in high **4b** yield. The above findings indicate that the present amphiphilically designed dendric system provides an apolar reaction cavity, which enables an effective encapsulation of targeted apolar sulfide, thus allowing the selective oxygenation of the targeted sulfide.

4. Conclusion

The amphiphilically designed dendric photosensitizers, **G_n** [$n(\text{generation}) = 1-3$], consisting of a BZP triplet sensitizing core, apolar interior, and polar dendric exterior, were utilized for photosensitized oxygenation of sulfides into sulfoxide in O_2 -saturated MeOH. The sulfoxide formation occurring via the reaction of O_2 with $^3\text{sulfide}^*$, formed via TET from $^3\text{BZP}^*$ to sulfide, is accelerated within the dendric sensitizer; the sulfoxide yield lies in the order of **G2** > **G1** \approx **G3** > unmodified BZP. The polarity of the inner microenvironment within the dendric sensitizer decreases with the dendron generation advance. This accelerates the transfer of apolar sulfide into the interior and the exclusion of polar sulfoxide to outer shell of the dendrimer. This "pump" function enhances the TET from $^3\text{BZP}^*$ core to sulfide, while suppressing the competitive TET to sulfoxide, thus promoting effective $^3\text{sulfide}^*$ formation. The lifetime of the $^3\text{BZP}^*$ core decreases with the dendron generation advance. The **G2** sensitizer, of relatively longer lifetime for the $^3\text{BZP}^*$ core and higher encapsulation ability for sulfide and lower encapsulation ability for sulfoxide, demonstrates the highest sulfoxide yield. Another notable feature of the dendric sensitizer is preferential encapsulation of apolar sulfides within the inner environment; photoirradiation of a mixture of diaryl sulfide and dialkyl sulfide allows selective oxygenation of diaryl sulfide. This occurs because apolar diaryl sulfide, which is transferred preferentially inside the interior, is oxidized effectively by the persulfide of the dialkyl sulfide. These sensitizing features imply that the present dendric sensitizers provide apolar photosensitizing reaction cavity, controlling selective inclusion and/or exclusion of substrates and products. The dendric sensitizers show high photostability even in protic solvents, indicating the potential application of this dendric system for photosensitized oxygenation of sulfides.

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Supporting Information Available: Spectral irradiance from the light source through the solutions containing respective sensitizers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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