

Effects of Benzyl Ether Type Dendrons as Hole-Harvesting Antennas, and Shielding for the Neutralization of Stilbene Core Radical Cations with Chloride Ion during Two-Photon Ionization of Stilbene Dendrimers Having Stilbene Core and Benzyl Ether Type Dendrons

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Abstract: The two-photon ionization (TPI) process (308 and 266 nm) of stilbene dendrimers having a stilbene core and benzyl ether type dendrons has been investigated in an acetonitrile and 1,2-dichloroethane mixture (3:1) in order to elucidate the dendrimer effects. The quantum yield of the formation of stilbene core radical cation during the 308-nm TPI was independent of the dendron generation of the dendrimers, whereas a generation dependence of the quantum yield of the radical cation was observed during the 266-nm TPI, where both the stilbene core and benzyl ether type dendron were ionized, suggesting that the subsequent hole transfer occurs from the dendron to the stilbene core, and that the dendron acts as a hole-harvesting antenna. The neutralization rate of the stilbene core radical cation with the chloride ion, generated from the dissociative electron capture by 1,2-dichloroethane, decreased with the increase in the dendrimer generation, suggesting that the dendron is an effective shield of the stilbene core radical cation against the chloride ion.

Introduction

Recently, the usefulness of dendrimers as light-harvesting antennas, fluorescent chemosensors, and organic light-emitting diodes, and in drug delivery, has been demonstrated by many research groups because of the three-dimensional and site-isolated structure of dendrimers.^{1–10} The ability of the dendritic shell to create specific site-isolated nano-environments has been explored. Diederich et al. reported the iron porphyrin core with two tethered imidazolin ligands, providing intramolecular axial ligation. The reduction potential of the porphyrin core shifted to the anodic direction when the sufficient dendritic shielding was achieved.¹¹ Gorman and co-workers prepared cubic iron–

sulfur clusters with poly(aryl ether) dendrons through a ligand-exchange reaction. It has been reported that the electron transfer between the electrode and the core with the higher generation dendron was slower.¹² Newkome et al. displayed the interaction of “lock” and “key” dendritic segments mediated by a bis-(terpyridine)ruthenium(II) complex form, which indicated highly efficient shielding of the core.¹³ Kaifer et al. showed that the heterogeneous electron-transfer rate constants as well as the diffusion coefficients decreased with the increase in the generation number.¹⁴ Fréchet et al.¹⁵ and Ito et al.¹⁶ investigated fullerene dendrimers and observed intra- and intermolecular photoinduced electron transfer, respectively. Even though the shielding effects in dendrimers have been studied by some groups to prove specific site-isolated nano-environments and encapsulated functional core, kinetic studies on the reactive core are rather limited.^{16,17}

In the present study, the stilbene (ST) core was connected with the benzyl ether type dendrons (Scheme 1), i.e., 3,3',5,5'-

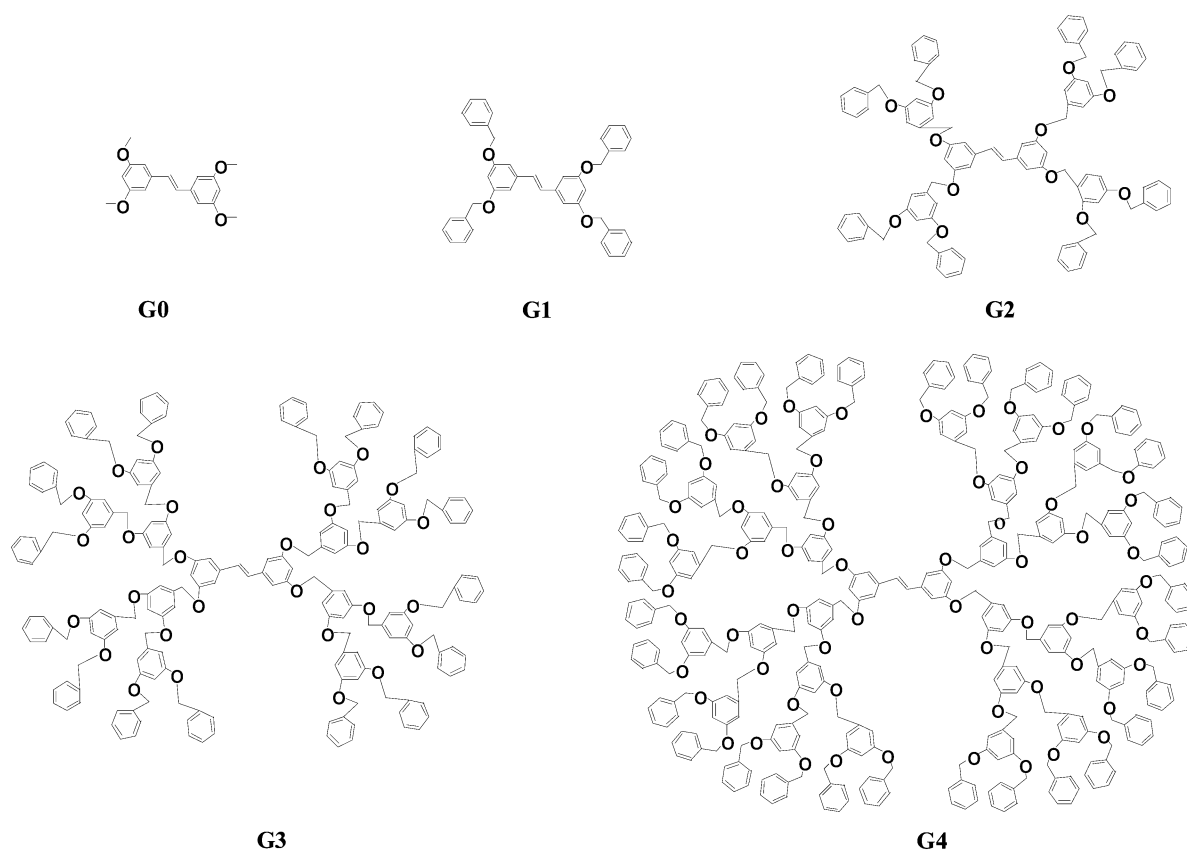
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Scheme 1. Stilbene Dendrimers



tetramethoxystilbene (**G0**) and **ST** with first generation (**G1**), second generation (**G2**), third generation (**G3**), or fourth generation (**G4**) dendrons.^{10,18} The photophysical and photochemical properties have been studied by means of laser flash photolysis with respect to the two-photon ionization (TPI) and the subsequent processes, depending on the dendrimer generation. In the case of 308-nm laser excitation, only the **ST** core is excited, while both the **ST** core and the dendron are excited upon 266-nm laser irradiation. Here, we first report that TPI of **G1–G4** occurs to give **ST** core radical cation through TPI of the **ST** core and benzyl ether moieties of the dendrons, that the subsequent hole-transfer process occurs quantitatively within the 5-ns laser pulse duration from the peripheral dendron to the **ST** core (hole-harvesting effect), and that the dendritic shielding effect of the dendrons works for the neutralization of **ST** core radical cation with chloride ion.

Experimental Section

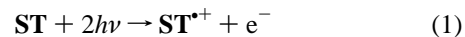
Materials. **G0–G4** (Scheme 1) were prepared according to the procedure previously described in the literature.¹⁹ Acetonitrile (AN) and 1,2-dichloroethane (DCE) (Wako spectroscopic grade) were used without further purification.

Nanosecond Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were carried out using a 308-nm flash from a XeCl excimer laser (Lambda Physik Compex102; pulse width of 25 ns fwhm) or a 266-nm laser flash from a Nd:YAG laser (Continuum Surelite-II; pulse width of 5 ns fwhm) as an excitation source. The monitor light was obtained from a 450-W Xe lamp (Osram XBO-450)

synchronized with the laser flash, and monitored using a photomultiplier (Hamamatsu Photonics R928) or a silicon photodetector (Hamamatsu Photonics S5343). The signal from the detector was digitized with an oscilloscope and transmitted to a personal computer via the GPIB interface. Transient absorption spectra were measured by a multichannel analyzer with an image intensifier having a 30-ns gate width. The dendrimer samples in a rectangular quartz cell (0.5 × 1.0 × 4.0 cm, monitor light path length of 1.0 cm) were prepared in an AN and DCE mixture (3:1) at room temperature.

Results and Discussion

TPI during 308-nm Laser Flash. A transient absorption spectrum with a peak at 470–510 nm was observed 500 ns after a 308-nm laser flash during the laser flash photolysis of **G0** in the AN and DCE mixture (3:1) (Figure 1). The observed absorption spectrum is assigned to the radical cation of the methoxy stilbene (**ST**^{•+}) generated by the TPI process (eq 1).



From $\Delta\text{OD}_{480} = 0.11 \pm 0.015$ and the molar absorption coefficient of **ST**^{•+} at 480 nm for **G0** ($\epsilon_{480} = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), estimated from the hole transfer from biphenyl radical cation to **G0** during laser flash photolysis of a mixture of **G0** ($1.7 \times 10^{-4} \text{ M}$), 9,10-dicyanoanthracene ($1.2 \times 10^{-4} \text{ M}$), and biphenyl (0.1 M) in an AN and DCE mixture (3:1), the concentration of **G0**^{•+} (**[G0**^{•+}]) was calculated to be $3.7 \times 10^{-6} \text{ M}$. The number of laser photons absorbed (N_p) by **G0** was measured to be $N_p = 2.8 \times 10^{-4} \text{ einstein L}^{-1}$ from actinometry

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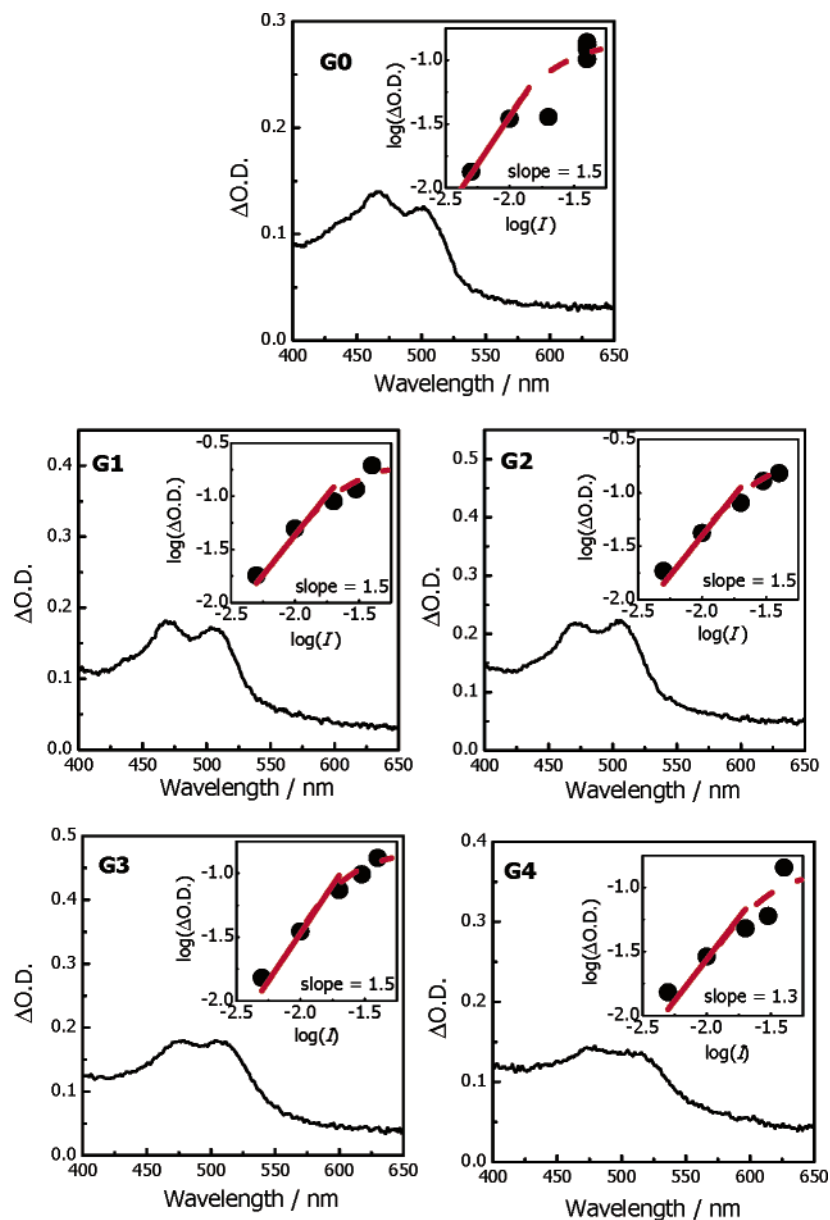


Figure 1. Transient absorption spectra assigned to $\text{G0}^+ - \text{G4}^+$ observed at 500 ns after a laser flash with the laser intensity of $I = 40 \text{ mJ pulse}^{-1}$ during the TPI of $\text{G0} - \text{G4}$ at 308 nm in an AN and DCE mixture (3:1). Absorbance at 308 nm was adjusted to be 1.0 for the laser path length of 0.5 cm. Insets are plots of $\log(\Delta\text{OD}_{480})$ vs $\log(I)$.

using the triplet–triplet absorption of benzophenone as a standard.²⁰ Thus, the quantum yield of the ionization of G0 by the 308-nm laser flash ($\Phi_{\text{ion } 308}$) was estimated to be 0.014.

Similar transient absorption spectra were observed during the 308-nm TPI of $\text{G1} - \text{G4}$ (Figure 1). The absorbance of $\text{G1} - \text{G4}$ at 308 nm was adjusted to be 1.0 for the laser path length of 0.5 cm, where the concentration of $\text{G1} - \text{G4}$ was $6.7 \times 10^{-4} \text{ M}$. Since only the ST core has absorption at 308 nm, the ST core can be selectively excited to cause TPI of the ST core. Since benzyl ether type dendrons have no absorption at 308 nm,¹⁹ it is not possible for TPI of benzyl ether type dendrons to occur under the present irradiation conditions. Therefore, the $\Phi_{\text{ion } 308}$ values of $\text{G0} - \text{G4}$ were calculated to be $(1.3 \pm 0.2) \times 10^{-2}$ (Table 1) on the basis of the molar absorption coefficients

Table 1. Formation of $\text{ST}^{+\bullet}$ Core and Neutralization during the 308-nm TPI of $\text{G0} - \text{G4}$ in an AN and DCE Mixture^a

generation	ΔOD_{480}	$[\text{G}^{\bullet+}]/10^{-6} \text{ M}$	$\Phi_{\text{ion } 308}/10^{-2}$	$k_{\text{N}}/10^9 \text{ M}^{-1} \text{ s}^{-1}$
G0	0.14	4.0	1.4	4.3
G1	0.13	3.7	1.3	3.3
G2	0.14	4.0	1.4	2.9
G3	0.11	3.1	1.1	1.6
G4	0.12	3.4	1.2	0.65

^a Quantum yields ($\Phi_{\text{ion } 308}$) of the formation of $\text{ST}^{+\bullet}$ core were calculated from ΔOD_{480} ($[\text{G}^{\bullet+}] = [\text{ST}^{+\bullet}]$). Neutralization rate constants (k_{N}) of $\text{ST}^{+\bullet}$ core with chloride ion were obtained from the decay time profiles of ΔOD_{480} .

of the $\text{ST}^{+\bullet}$ core of $\text{G0} - \text{G4}$ estimated from the hole transfer with biphenyl radical cation. The $\Phi_{\text{ion } 308}$ values of $\text{G0} - \text{G4}$ were higher than that of *trans*-stilbene ($\Phi_{\text{ion } 308} = 2.0 \times 10^{-3}$),^{21,22}

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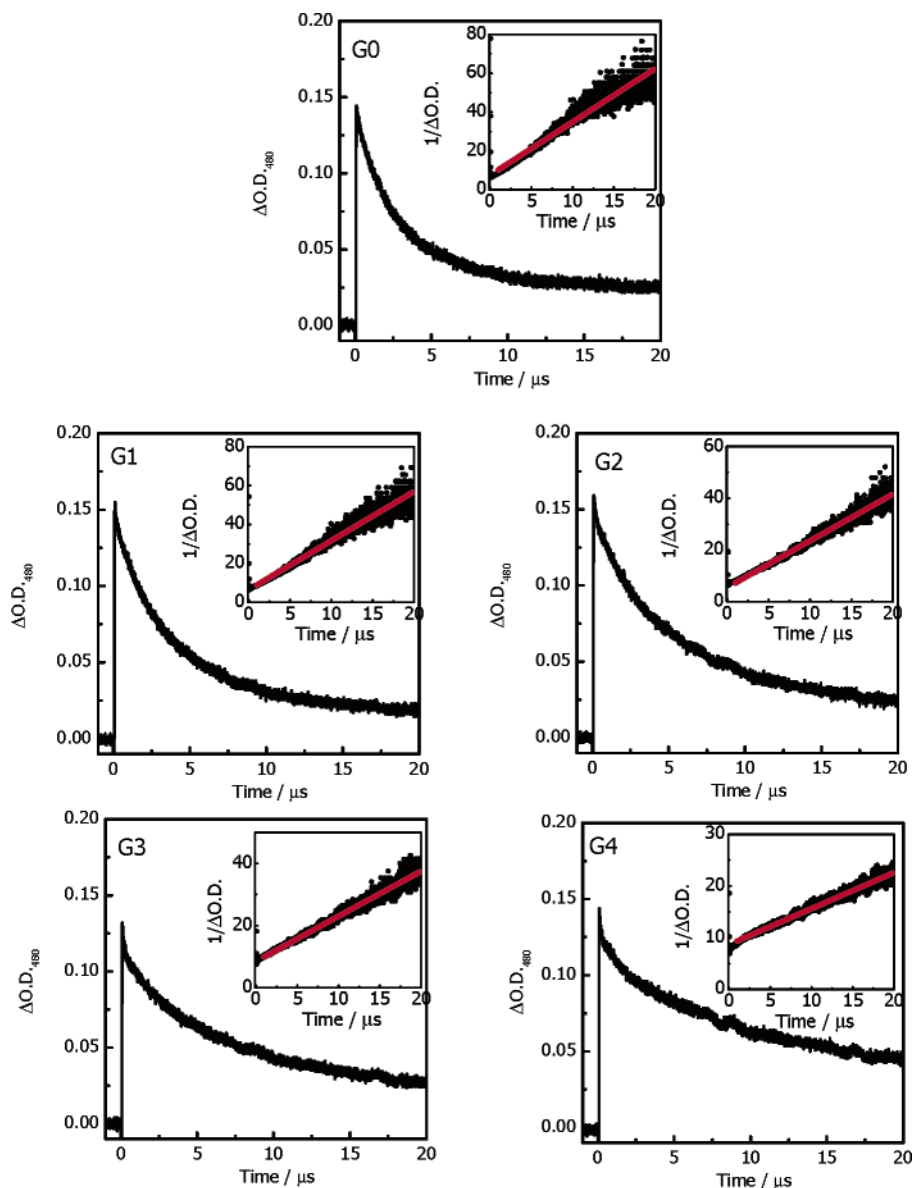


Figure 2. Time profiles of the transient absorption at 480 nm (ΔOD_{480}) assigned to $ST^{+\bullet}$ of **G0–G4** in AN and DCE mixture (3:1). Insets are time profiles of ΔOD_{480}^{-1} .

because the S_1 -state lifetimes of **G0–G4** (9.3–9.7 ns)¹⁹ were longer than that of *trans*-stilbene (40 ps).^{21,22} The $\Phi_{ion\ 308}$ value was independent of the dendron generation of the dendrimer, indicating that the formation of $ST^{+\bullet}$ via excitation of the **ST** core was not influenced by the dendron generation. Thus, **ST** and $ST^{+\bullet}$ cores were isolated from the benzyl ether type dendrons as site-isolated nano-environments in **G0–G4** and $G0^{+\bullet}$ – $G4^{+\bullet}$, respectively.

The TPI of stilbene and dimethoxy-substituted stilbene has been already investigated with laser flash photolysis at 308 nm in AN.²¹ Since the ionization potential (IP) of **ST** in AN is 7.1 eV,²³ the 308-nm photon energy (4.0 eV) is not sufficient to ionize the **ST** core. Formation of $ST^{+\bullet}$ clearly indicates that two-photon excitation must be involved in the 308-nm TPI of the **ST** core of **G0–G4** under the present irradiation conditions with the laser power of 40 mJ pulse⁻¹. Plots of $\log(\Delta OD_{480})$ vs $\log(\text{laser intensity})$ were linear lines with a slope of ap-

proximately 1.5 at the laser fluence of 0–10 mJ pulse⁻¹ (Figure 1, insets), indicating that two-photon excitation is involved in the formation of $ST^{+\bullet}$. The slopes were slightly smaller than 2 and became much smaller than 2 at laser intensity higher than 20 mJ pulse⁻¹. Previously, we found that the slope becomes much smaller than 2 when the absorption of the laser flash was saturated during the laser pulse width of 25 ns. For example, we observed slopes of 0.8–1.0 in the 308-nm TPI of substituted stilbenes.^{21,22} This is also the case with the 308-nm TPI of pyrene and its derivatives.²⁴

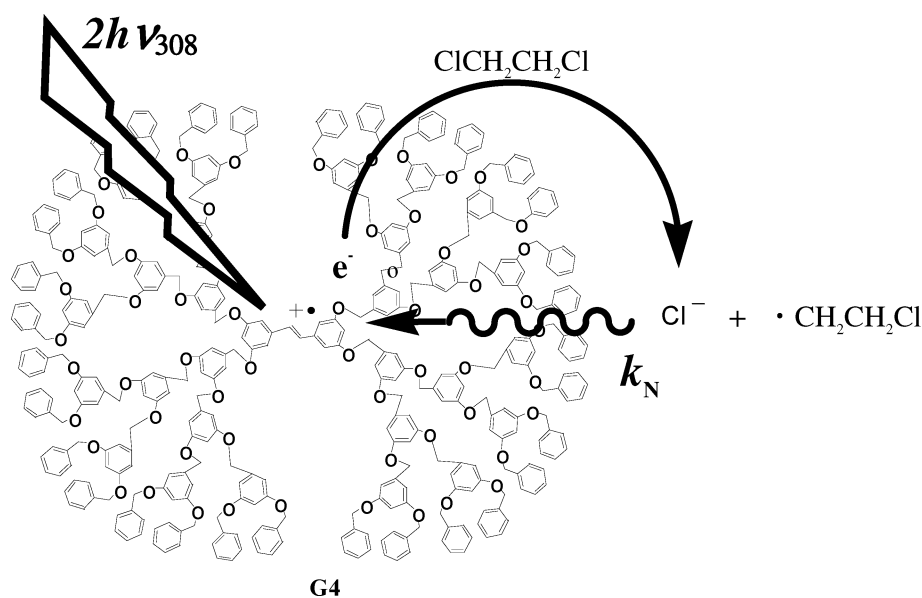
An electron must be generated together with the formation of $ST^{+\bullet}$ during the TPI of **G0–G4**. However, no transient absorption of AN radical anion ($AN^{\bullet-}$) and AN dimer radical anion ($(AN)_2^{\bullet-}$)²⁵ was observed, suggesting that the electron is mainly trapped by DCE to give chloride ion and

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Scheme 2

Table 2. Formation of $ST^{\bullet+}$ Core and Neutralization during the 266-nm TPI of G_0 – G_4 in an AN and DCE Mixture^a

generation	$\epsilon_{266} M^{-1} 10^3 cm^{-1}$	$f_{ST}/\%$	$\Delta OD_{480}/10^{-3}$	$[G^{\bullet+}]_{266}/10^{-6} M$	$\Phi_{ion\ 266}/10^{-2}$	$\Phi_{ion\ 266}^H/10^{-2}$	$k_N/10^9 M^{-1}$
G0	0.55	100	72 ± 3	2.0 ± 0.1	1.7 ± 0.1	1.7 ± 0.1	5.5
G1	0.71	77	60 ± 2	1.7 ± 0.1	1.4 ± 0.1	1.8 ± 0.2	4.4
G2	1.43	38	68 ± 2	1.8 ± 0.1	1.5 ± 0.1	3.9 ± 0.2	4.0
G3	2.29	24	41 ± 2	1.2 ± 0.1	1.0 ± 0.1	4.2 ± 0.4	1.8
G4	4.86	11	32 ± 2	0.92 ± 0.1	0.77 ± 0.1	6.9 ± 0.4	0.95

^a Molar absorption coefficients at 266 nm (ϵ_{266}), fraction of laser photons absorbed by ST core (f_{ST}), quantum yields of the formation of $ST^{\bullet+}$ core ($\Phi_{ion\ 266}$) calculated from ΔOD_{480} ($[G^{\bullet+}] = [ST^{\bullet+}]$), quantum yield of the formation of $ST^{\bullet+}$ core normalized with absorbed photons by ST core ($\Phi_{ion\ 266}^H$), and neutralization rate constants (k_N) of $ST^{\bullet+}$ core with chloride ion obtained from the decay time profiles of ΔOD_{480} . $[^3BP^*] = [I] = 1.2 \times 10^{-4} M$.

2-chloroethyl radical through the dissociative electron capture (eq 2).^{26,27}



The transient absorption bands of $ST^{\bullet+}$ of G_0 – G_4 decayed in the 20- μs time scale after the laser irradiation (Figure 2). The decay of $ST^{\bullet+}$ of G_0 – G_4 can be attributed to the neutralization of $ST^{\bullet+}$ with chloride ion (eq 3). Similar neutralization has been reported for *trans*-stilbene and aromatic compounds.²⁷



The decay of $ST^{\bullet+}$ obeyed second-order kinetics (Figure 2, inset). The rate constants of the neutralization of $ST^{\bullet+}$ core with chloride ion (k_N), listed in Table 1, decreased with the increase in the dendrimer generation from $k_N = 4.3 \times 10^9 M^{-1} s^{-1}$ for G_0 to $k_N = 6.5 \times 10^8 M^{-1} s^{-1}$ for G_4 . This finding was attributed to the enhanced shielding of $ST^{\bullet+}$ core by the dendrons, which inhibits the neutralization of $ST^{\bullet+}$ core with chloride ion (Scheme 2). In other words, the neutralization of $ST^{\bullet+}$ core with chloride ion is strongly prevented by the dendrons, resulting in the 85% decrease of the neutralization

rate constant by the dendritic shielding of G_4 . These results clearly illustrate the dendritic shell effect that inhibits approach of chloride ion toward $ST^{\bullet+}$ core in the neutralization process. Similarly, a 20% decrease of the back electron-transfer rate by the dendritic shielding has been observed for the bimolecular back electron transfer between C_{60} core radical anion and *N,N,N',N'*-tetramethylbenzidine radical cation during photoinduced electron transfer of C_{60} core dendrimers and *N,N,N',N'*-tetramethylbenzidine in benzonitrile.¹⁶ Dendritic shielding effects have been reported for the increase of redox potentials of the iron porphyrin core¹¹ and the electrochemical properties of the iron–sulfur core¹² in the cyclic voltammetry.

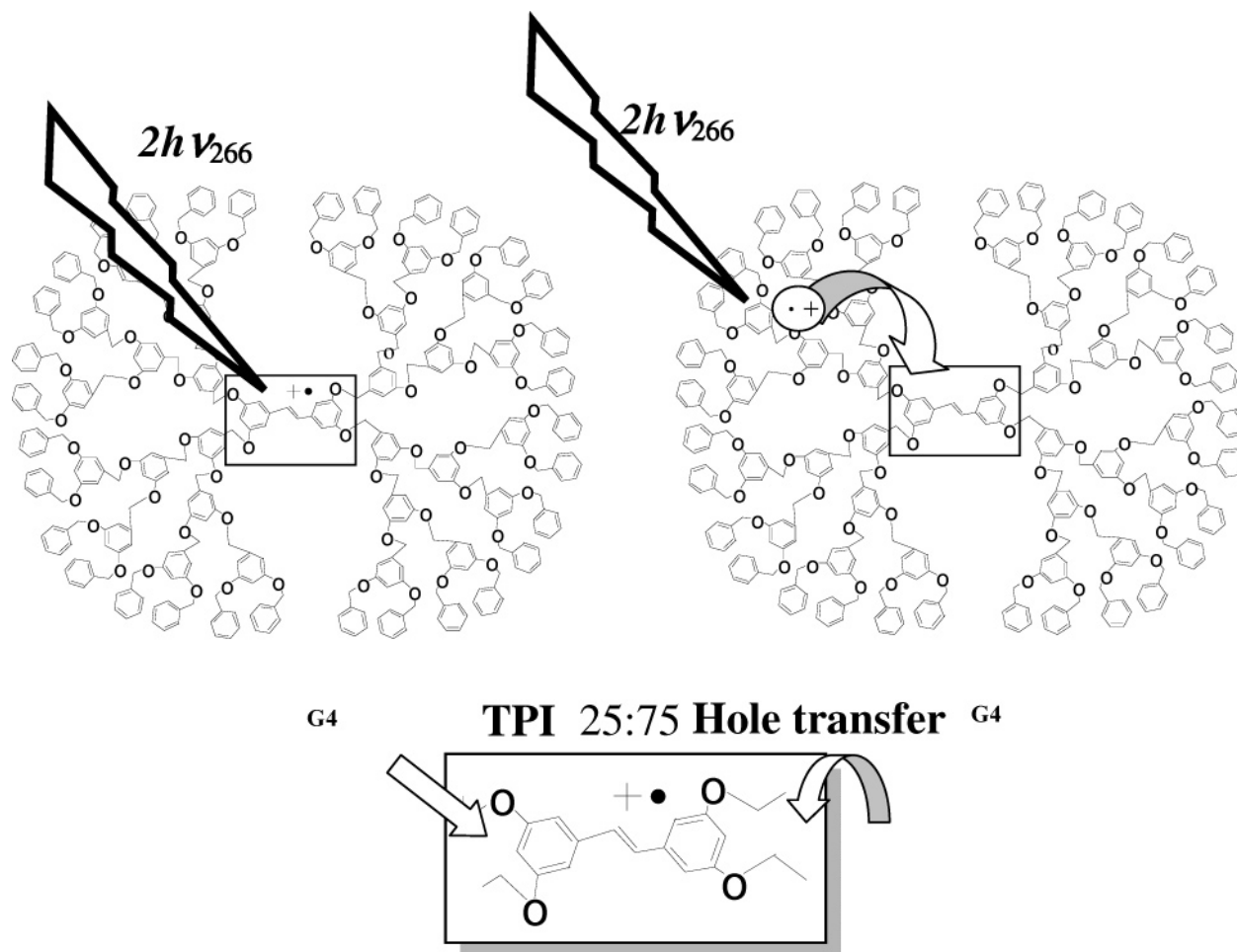
TPI during 266-nm Laser Flash. A similar transient absorption spectrum of $G_0^{\bullet+}$ was observed at 500 ns after a 266-nm laser flash during the laser flash photolysis in an AN and DCE mixture (3:1), indicating occurrence of the TPI. In the case of TPI with a 266-nm laser flash, the concentrations of G_0 – G_4 were adjusted to absorb 266-nm photons with 1.2×10^{-4} einstein L^{-1} . The quantum yields of the 266-nm TPI ($\Phi_{ion\ 266}$) for G_0 – G_4 were calculated to be $(1.7\text{--}0.77) \times 10^{-2}$ (Table 2), and were found to decrease with the increase in the dendrimer generation.

It should be noted that both the ST core and the dendron are excited with excitation at 266 nm. In the case of G_0 , the fraction of laser photons absorbed by the ST core (f_{ST}) is 100%. With the increase in the dendrimer generation,¹⁹ the f_{ST} values decrease to 77, 38, 24, and 11% for G_1 – G_4 , respectively (Table 2). The quantum yield of the formation of $ST^{\bullet+}$ core normalized

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Scheme 3



with absorbed photons by the **ST** core ($\Phi_{\text{ion } 266}^{\text{H}}$) was estimated from eq 4.

$$\Phi_{\text{ion } 266}^{\text{H}} = [\text{ST}^{\bullet+}] / (N_p f_{\text{ST}}) \quad (4)$$

The $\Phi_{\text{ion } 266}^{\text{H}}$ values of **G0–G4** were calculated to be $(1.7 \pm 0.1) \times 10^{-2}$, $(1.8 \pm 0.1) \times 10^{-2}$, $(3.9 \pm 0.2) \times 10^{-2}$, $(4.2 \pm 0.1) \times 10^{-2}$, and $(6.9 \pm 0.1) \times 10^{-2}$, respectively (Table 2). The variation of $\Phi_{\text{ion } 266}^{\text{H}}$ between **G0** and **G1** with and without phenyl group, respectively, was small, while the generation dependence of $\Phi_{\text{ion } 266}^{\text{H}}$ for **G1–G4** was obvious, as shown in Figure 3. In the previous section, it was revealed that the

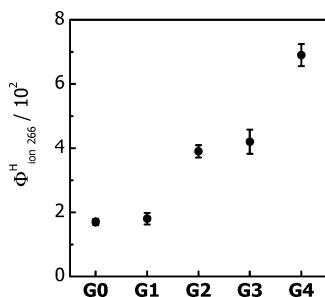


Figure 3. Dependence of the quantum yields of ionization, $\Phi_{\text{ion } 266}^{\text{H}}$, on dendrimer.

ionization yield from the excited **ST** core was independent of dendrimer generation. Thus, an additional mechanism should

be included in the formation of **ST**^{•+} during the 266-nm TPI of the dendrimer. Since benzyl ether moieties as the components of the dendron have absorption at 266 nm, the TPI of benzyl ether moieties may occur to give benzyl ether radical cations.

From the oxidation potentials of the components of the dendrimers [stilbene ($E^{\text{ox}} = 1.27$ V),²¹ methoxybenzene ($E^{\text{ox}} = 1.62$ V), methoxymethylbenzene ($E^{\text{ox}} = 1.55$ V), 1,3-dimethoxybenzene ($E^{\text{ox}} = 1.49$ V)],²³ exothermic hole transfer from the dendron to the **ST** core is possible after the formation of the benzyl ether radical cation of the dendron. Since the kinetics trace of **ST**^{•+} did not show any rise after a laser flash due to the hole transfer, the hole transfer seems to be completed within the laser flash duration of 5 ns. The increase of $\Phi_{\text{ion } 266}^{\text{H}}$ with the increase in dendrimer generation can be attributed to the hole transfer from the benzyl ether radical cation of the dendrons to the **ST** core (Scheme 3). The ratios of $\Phi_{\text{ion } 266}^{\text{H}}$ resulting from the hole transfer from the dendrons to the **ST** core (f_{H}) were estimated from $f_{\text{H}} = (\Phi_{\text{ion } 266}^{\text{H}}(\text{Gn}) - \Phi_{\text{ion } 266}^{\text{H}}(\text{G0})) / \Phi_{\text{ion } 266}^{\text{H}}(\text{Gn})$ to be 6, 56, 60, and 75% for $n = 1, 2, 3,$ and 4 , as dendrimer generation, respectively.

A hole generated in the dendron during the 266-nm TPI is considered to be quantitatively transported to the **ST** core during the laser pulse duration of 5 ns.²⁸ Therefore, ionization quantum yields of the dendrons ($\Phi_{\text{ion } 266}^{\text{D}}$) of **G1–G4** were calculated to be 0.36×10^{-2} , 1.5×10^{-2} , 1.3×10^{-2} , and 1.4×10^{-2} ,

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respectively, from $\Phi_{\text{ion}}^{\text{D}} = f_{\text{H}}[\text{G}^{\bullet+}]_{266}(\text{G0}) / (f_{\text{ST}}(\text{Gn}) - f_{\text{ST}}(\text{G0}))N_{\text{p}}$. Since the dendrons **G2–G4** have similar values of $\Phi_{\text{ion}}^{\text{D}} = (1.3\text{--}1.5) \times 10^{-2}$, and the benzyl ether moiety (1,3-dimethoxy-5-methylbenzene) is the common component for the dendron **G2–G4**, TPI of 1,3-dimethoxy-5-methylbenzene moieties can occur to give the radical cation.

Thus, we confirmed that benzyl ether moieties of the dendrons show the hole-antenna (harvesting) effect for the formation of $\text{ST}^{\bullet+}$ through the hole transfer from benzyl ether moieties of the dendrons to the **ST** core and that the dendrimer is a molecular lens in addition to the photo-antenna effect. From the decay profiles of $\text{ST}^{\bullet+}$, the neutralization rate constants were found to decrease with the increase in the dendrimer generation, similar to the former section (Table 2).

Conclusions

We have demonstrated that the peripheral dendron composed of benzyl ether moieties acts as an efficient hole-harvesting antenna for the **ST** core in the **ST** dendrimers (**G1–G4**). A hole generated in the dendron during the 266-nm TPI migrates

to the **ST** core. A 75% yield of $\text{ST}^{\bullet+}$ resulted from the hole transfer from the dendrons to the **ST** core during the 266-nm TPI of **G4**, and the remaining 25% of $\text{ST}^{\bullet+}$ was yielded by the direct TPI of the **ST** core. The rate constant of the neutralization of $\text{ST}^{\bullet+}$ core with chloride ion decreased with the increase in the dendrimer generation. For example, an 85% decrease of the neutralization rate was observed in the case of **G4**, indicating dendritic shielding for the neutralization of $\text{ST}^{\bullet+}$ core with chloride ion. Consequently, the ability of the dendritic shell to create specific site-isolated nano-environments, such as enhanced shielding of $\text{ST}^{\bullet+}$ core against the chloride ion, has been demonstrated. Thus, the present study provides a new strategy for molecular design of hole-harvesting materials.

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