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Photoinduced Electron-Transfer Reaction of Cyclic Oligosilanes and Polysilanes in Solution

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ABSTRACT: *Photoinduced electron-transfer (PET) reactions were investigated for the cyclic oligosilanes and high molecular weight polysilanes in the presence of 9-cyanoanthracene (CA), 9,10-dicyanoanthracene (DCA), and triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$) using chemical and spectroscopic methods in solution. For the cyclic oligosilanes, the pyranyl radical (TPP·) and silane radical cation were observed as direct evidence of the PET from silanes to $TPP^+BF_4^-$, and the reaction quantum yields showed that the ring opening of the radical cation of the cyclic oligosilane competed with the nucleophilic attack on the radical cation by the counter ion of the pyrylium salt and a back electron transfer (BET). For the high molecular weight polysilane, the observation of the transient absorptions of TPP· and the radical cation of polysilane is evidence of the PET, and the extremely long lifetime observed for the radical cation indicates the inefficient BET and reactivities.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:269–275, 2001

INTRODUCTION

The fluorescence quenching rate constants of 9,10-dicyanoanthracene (DCA) increased with increasing the number of silicon atoms in the silane compounds [$Me(SiMe_2)_nMe$, $n = 2–6$] [1,2]. This is explained by changing the oxidation potentials of the oligosilanes with the chain length of the silicon atoms, and the exothermicity of the electron-transfer process increases as n increases. DCA [3], acridinium salts [4], or pyrilium salts [5] sensitized the decomposition of the monosilanes or disilanes, and the silyl cations were supposed to be generated. In some cases, radical cations of silanes were trapped by alcohol intramolecularly or intermolecularly to give characteristic products [6–9], or they were observed spectroscopically [10,11]. For the high molecular weight polysilanes, radical ions were observed by pulse radiolyses [12], and direct evidence of the photo-induced electron transfer (PET) reaction was obtained recently by laser flash photolyses. Miller et al. [13] and our group [14] have independently reported that the fluorescence of a sensitizer such as DCA was quenched by polysilanes with relatively small rate constants. The small quenching rate constants suggest that the chromophore involved in the quenching processes has very long silicon chain units. Especially in the case of triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$), the pyranyl radical was observed as direct evidence of the electron transfer [14]. Watanabe et al. [15] then observed the radical cations of polysilanes in the near-IR region by C_{60} sensitization using nanosecond laser flash photolysis.

In this article, we would like to report our investigation of the mechanistic aspects of the PET of polysilanes in the presence of electron-deficient sensitizers (such as 9-cyanoanthracene [CA], DCA, and $TPP^+BF_4^-$), and of the nature of the silane cation rad-

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Dedicated to Prof. Emeritus Naoki Inamoto on his 72nd birthday.

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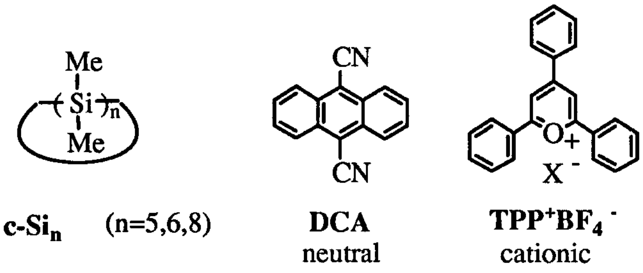


FIGURE 1 Cyclic oligosilanes and DCA and TPP$^+$BF$_4^-$.

icals (Figure 1). We successfully observed radical cations and a pyranyl radical directly as evidence for electron transfer in the case of TPP$^+$BF$_4^-$ sensitization. The formed silane radical cation induces the degradation by scissions of the silicon chain. However, the hole (cation site) migration along the chain could not be observed, and thus the mobility must be small. Failure to observe radical cations in the presence of DCA indicates that the back electron transfer is very fast. In addition, to clarify the mechanisms, the PET reaction of the cyclic oligosilanes was also examined as a reference. In the case of the cyclic oligosilanes, ring opening competes with the back electron transfer, and the disappearance quantum yields of cyclic oligosilane depend on the sensitizers and ring sizes.

RESULTS AND DISCUSSION

Initial Photoinduced Electron-Transfer Process

The fluorescence spectra and lifetimes of sensitizers in the presence or absence of the silanes were measured using a fluorometer and a single-photon-counting apparatus in argon-purged CH$_2$Cl$_2$. The overall reaction sequence is shown in Equations 1–5. In the equation, sensitizer and silanes are expressed as Sens and Si, respectively, for convenience. The asterisk and superscripted numbers indicate singlet and triplet excited states. The lifetime of the excited state (τ) and fluorescence intensity (I) of the sensitizer in the absence (indicated by subscript 0) and presence of the silane are shown in Equations 6–9. Using these equations and plotting either τ_0/τ or I_0/I vs. the silane concentration, a linear relation with slope $k_q\tau_0$ was obtained by the Stern-Volmer relationship shown by Equation 10. The k_q can be determined using the value of τ_0 measured by single-photon counting (12.2, 14.5, and 2.9 ns for DCA, CA, and TPP$^+$BF$_4$$_-$, respectively). For TPP$^+$, which is a cationic sensitizer, the neutral TPP· is generated by an electron-transfer reaction (Equation 5b).

$$\text{Sens} \xrightarrow{h\nu} {}^1\text{Sens}^* \tag{1}$$

$${}^1\text{Sens}^* \xrightarrow{k_d} \text{Sens} \tag{2}$$

$${}^1\text{Sens}^* \xrightarrow{k_f} \text{Sens} + h\nu \tag{3}$$

$${}^1\text{Sens}^* \xrightarrow{k_{isc}} {}^3\text{Sens}^* \tag{4}$$

$${}^1\text{Sens}^* + \text{Si} \xrightarrow{k_q^S[\text{Si}]} \text{Sens}^{-}\cdot + \text{Si}\cdot^{+} \tag{5a}$$

$${}^1\text{TPP}^{+*} + \text{Si} \xrightarrow{k_q^S[\text{Si}]} \text{TPP}\cdot + \text{Si}\cdot^{+} \tag{5b}$$

$$\tau_0 = 1/(k_d + k_f + k_{isc}) \tag{6}$$

$$\tau = 1/(k_d + k_f + k_{isc} + k_q^S[\text{Si}]) \tag{7}$$

$$I_0 = k_f\tau_0 \tag{8}$$

$$I = k_f\tau \tag{9}$$

$$\tau_0/\tau = I_0/I = 1 + k_q^S\,\tau_0\,[\text{Si}] \tag{10}$$

The observed k_q values are listed in Table 1. The electron-transfer processes are expected to be exothermic [16] by the consideration of the reduction potentials of the sensitizers (E_{red}, $\Delta E_{0,0}$, and $^*E_{red}$ are -0.89, 2.86, and 1.97 for DCA, -1.70, 3.10, and 1.40 for CA, and -0.29, 2.82, and 2.53 for TPP$^+$BF$_4^-$, respectively) [17], and the oxidation potentials of the silanes [18,19]. The quenching rate constants for a series of oligosilanes are listed in Table 1. Note that, for the disilanes and hexasilanes, the quenching rate constants of the TPP$^+$BF$_4^-$ fluorescence are consistent with the diffusion-controlled quenching rate. This is not the case for the DCA quenching where the disilanes have significantly slower rate constants than the hexasilanes. This is consistent with previous reports of DCA quenching in which a decrease in the quenching rate constant from hexasilane to disilane correlated with the corresponding increase in the oxidation potential [20,21]. The low oxidation potentials of the high molecular weight polysilanes would be expected to result in a very exothermic electron transfer; however, the quenching rate constants are quite smaller (10^8 mol^{-1} dm^3 s^{-1}) than the diffusion-controlled quenching rate constant that is expected to be by the redox potentials. Part of this discrepancy is due to the way in which we have evaluated the polymer concentration in terms of monomer units since silicon chains should be the actual quenching chromophore. The trans-gauche model reported [22] for the singlet excited state might not be important in the ground state since a very long chain acts as a chromophore. The decreased mobility of the polysilane polymer will also result in a decrease in the quenching constant. The steric effect of the bulky side-chain substituent should also result in differences in the quenching rate constant. In addi-

TABLE 1 Quenching Rate Constants[a] of Fluorescence (k_q^S) and *T-T* Absorption (k_q^T) of Sensitizers by Polysilanes

	k_q^S			k_q^T
Silanes	*DCA* $(\tau_0/\tau)^b$	*CA* $(\tau_0/\tau)^b$	*TPP*$^+$*BF*$_4^-$ $(\tau_0/\tau)^b$	*TPP*$^+$*BF*$_4^-$ $(\tau_0/\tau)^c$
Poly[4-methoxyphenylmethylsilane][d]	0.57	0.47	1.5	1.6
Poly[methylphenylsilane][d]	0.58	0.54	0.73	0.53
Poly[methyl-β-phenethylsilane][d]	0.35	0.28	0.30	0.68
Poly[propylmethylsilane][d]	0.33	0.35	0.43	0.58
$\text{-[SiMe}_2\text{(CH}_2)_2\text{SiMe}_2\text{-(SiMe}_2)_6]_n^-$[e]	30	23	25	
Decamethylcyclopentasilane[f]	25	5.6	12	
Dodecamethylcyclohexasilane[f]	27	2.1	27	14
Hexadecamethylcyclooctasilane[f]	21	2.3	32	
n-Tetradecamethylhexasilane[f]	22	8.9	25	18
Tetramethyl-1,2-diphenyldisilane[f]	7.9	4.8	20	6.1

[a] Listed as $k_q^S/10^9\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$:

[b] From Stern-Volmer plot of fluorescence lifetime, τ_0 of DCA, CA, and $\text{TPP}^+\text{BF}_4^-$ (14.5, 12.2, and 2.9 ns, respectively) in argon-purged CH_2Cl_2.

[c] Determined from Stern-Volmer plot of *T-T* absorption lifetime, τ_0 of $\text{TPP}^+\text{BF}_4^-$ (8.7 μs) in argon-purged CH_2Cl_2.

[d] Concentration based on molecular weight of monomeric unit.

[e] Concentration based on the unit of $\text{-[SiMe}_2\text{(CH}_2)_2\text{SiMe}_2\text{-(SiMe}_2)_6]_n^-$.

[f] Concentration based on the molecular weight.

tion, we were unable to obtain any evidence of a static quenching component (the Stern-Volmer plots were linear over the concentration range studied) nor evidence of any change in the absorption or fluorescence spectra due to the charge transfer (CT) complexation observed in the case of teteracyanoethylene (TCNE) and polysilanes [23].

In addition to the fluorescence quenching measurements described previously, we also examined the quenching of the $T_n \leftarrow T_1$ absorption of $\text{TPP}^+\text{BF}_4^-$ since it has a large intersystem crossing quantum yield. $\text{TPP}^+\text{BF}_4^-$ (2.5×10^{-4} mol dm^{-3}) was excited by laser excitation ($\lambda = 425$ nm) in the presence of silanes and in argon purged CH_2Cl_2, and quenching was observed ($^3\text{TPP}^{+*}$ at $\lambda = 850$ nm, $\tau_T = 1/k_d^T = 10\ \mu$s). The excited state reduction potential ($^*E_{\text{red}}$) for $^3\text{TPP}^{+*}$ is expected to be 2.53 V (the same as for $^1\text{TPP}^{+*}$).

$$^3\text{TPP}^{+*} \xrightarrow{k_d^T} \text{TPP}^+ \tag{11}$$

$$^3\text{TPP}^{+*} + \text{Si} \xrightarrow{k_q^T\,[\text{Si}]} \text{TPP}\cdot + \text{Si}\cdot^+ \tag{12}$$

PET Reaction of Cyclic Oligosilanes

Dodecamethylcyclohexasilane (CHS) is reported to give dimethylsilylane through the decreasing ring size reaction by direct photolysis, while CHS gives 1,6-dichlorododecamethylhexasilane in the presence DCA as an electron-deficient sensitizer in a CH_2Cl_2 and CCl_4 mixed solvent [6]. In addition to this, 1,6-difluorododecamethylhexasilane is produced in the presence of $\text{TPP}^+\text{BF}_4^-$ as a sensitizer in CH_3CN [24]. These reaction mechanisms are proposed to proceed through a single electron-transfer reaction from CHS to the sensitizers, generating the radical cation of CHS. We question whether the excited state DCA could be quenched by CCl_4 to generate Cl^- and the trichloromethyl radical ($\text{Cl}_3\text{C}\cdot$) and how the difluoro-compound could be generated.

The PET reaction of CHS in CH_2Cl_2 was investigated in the presence of $\text{TPP}^+\text{BF}_4^-$ as a sensitizer. The major product was 1-chloro-6-fluorododecamethylhexasilane. The product was easily converted to cyclohexasilasiloxane after exposing the sample to air or using a solvent containing water.

$$^1\text{DCA}^* + \text{Si} \xrightarrow{k_q^S\,[\text{Si}]} \text{DCA}^-\cdot + \text{Si}\cdot^+ \tag{5c}$$

$$\text{Si}\cdot^+ \xrightarrow{k_r} \text{product} \tag{13}$$

$$\text{DCA}^-\cdot + \text{Si}\cdot^+ \xrightarrow{k_b} \text{DCA} + \text{Si} \tag{14}$$

The Stern-Volmer plot of $1/\Phi_r$ versus the reciprocal of the concentration of CHS in the presence of DCA in CH_2Cl_2 under argon is shown in Figure 2. The Φ_r has a relation to the quenching efficiency and reactivity efficiency versus the BET, as in the following equation $\Phi_r = \{k_q[\text{silane}]/(k_d + k_q[\text{silane}])\}\{k_r/(k_r + k_b)\}$. Therefore, $1/\Phi_r = (1 + k_b/k_r)\ \{1 + k_d/(k_q[\text{silane}])\}$. The value $1/\Phi_r$ has a linear relationship versus 1/[silane]. The limiting reaction quantum yield, $\Phi_r^{\text{limit}} = 1/(\text{intercept})$, indicates the reaction efficiency when 100% of excited sensitizer is quenched by silanes, and k_b/k_r is derived from the 1 minus intercept value. The Φ_r^{limit} and k_b/k_r values were 0.29 and 2.5, respectively.

Equation 14 may include the BET from $\text{DCA}^-\cdot$

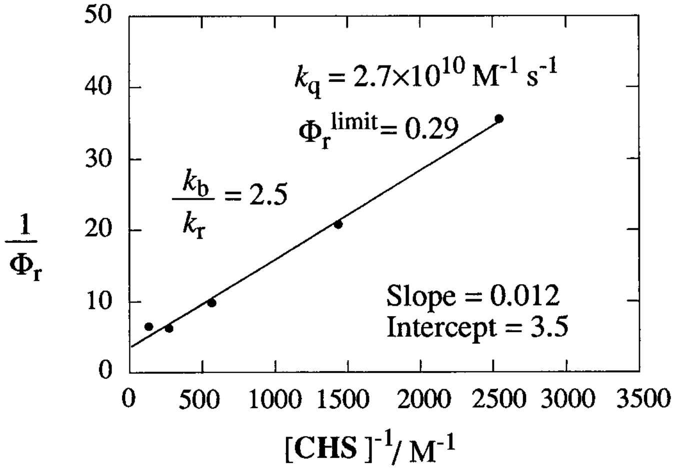


FIGURE 2 The Stern-Volmer type plot of the $1/\Phi_r$ against the inverse of concentration of CHS in the presence of DCA in CH_2Cl_2 under argon.

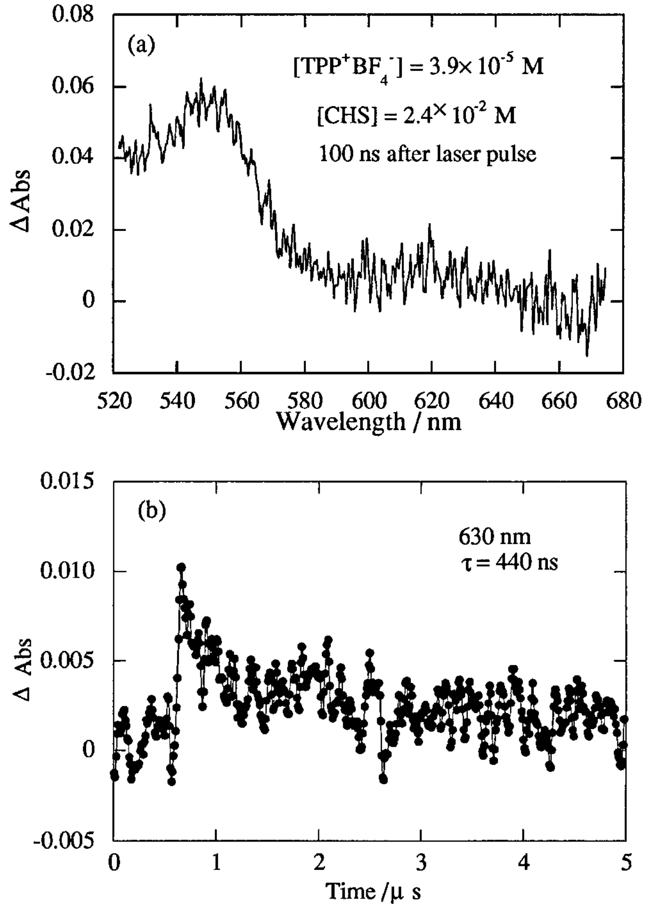
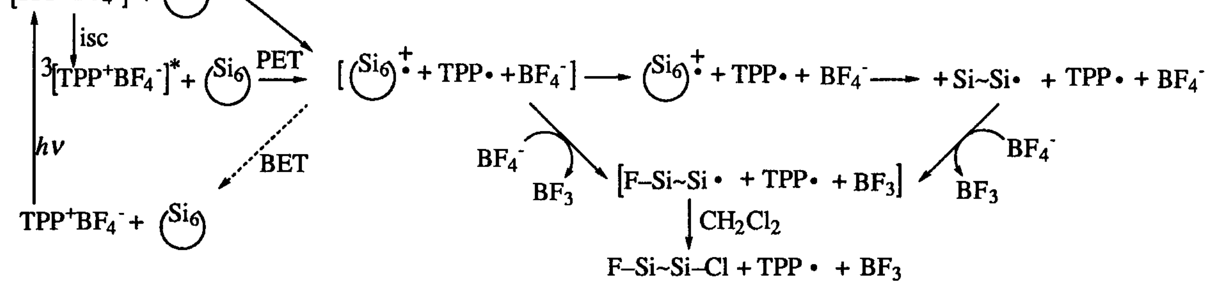


FIGURE 3 (a) Transient absorption spectra derived from laser excitation of $TPP^+BF_4^-$ in the presence of CHS (24 mmol dm^{-3}) in CH_2Cl_2 under argon; (b) its time profile at 630 nm.

to a radical cation of CHS to give CHS or to a radical cation of the ring cleaved CHS to give the 1,6-biradical intermediate that finally gives CHS by recombination of products. To make clear the mechanism, decamethylcyclopentasilane (CPS) and hexadecamethylcyclooctasilane (COS) could be used to obtain Φ_r^{limit} and k_b/k_r. These values were 0.33 and 2.0 for CPS, and 0.37 and 1.7 for COS, respectively. These results indicate that the ring size changing from 6 to 5 or 8 leads to a slight increase in Φ_r^{limit} due to the difference in the relative stability of the ring. However, these results are insufficient to distinguish between two back electron transfer (BET) processes (BET before ring opening to give the starting material, or BET after ring opening to generate biradical intermediates that easily recombine to give the starting material).

In the case of the reaction of CHS with $TPP^+BF_4^-$, Φ_r^{limit} and k_b/k_r were found to be 0.81 and 0.43, respectively. These values are quite different from those obtained for DCA. The large Φ_r^{limit} may reflect the smaller k_b due to the smaller coulomb interaction between the pyranyl radicals (neutral) and silane radical cation (+ charge) than the DCA radical anion (− charge) and silane radical cation (+ charge). In addition, there is the possibility that the counter anion (BF_4^-) directly reacts with the cyclic silane radical cation. This is now under investigation



SCHEME 1 Proposed reaction mechanism for the PET of CHS (denoted as Si_6) in the presence of $TPP^+BF_4^-$.

using triphenylpyrylium salts that have various counter ions.

For the transient absorption spectra of these systems, the pyranyl radicals (TPP·) were observed by laser excitation in the presence of CHS in argon-purged CH_2Cl_2. The spectra can be assigned to the pyranyl radicals (TPP·) at around 550 nm and the radical cation of CHS at around 620 nm by comparison with the reported spectrum (Figure 3) [11,25,26]. The lifetime of the radical cation of CHS was 440 ns when observed at 620 nm.

For the DCA sensitization, the transient absorption spectra of $DCA^{-}\cdot$ or radical cation of CHS were not observed by laser excitation in argon-purged CH_2Cl_2. This might correspond to the result of a faster BET in the case of DCA than in the case of $TPP^{+}BF_4^{-}$.

PET Reaction of Polysilanes

In our earlier report, some high molecular weight polysilanes, including poly[di-*n*-hexylsilane], poly[methylphenylsilane], poly[di-*n*-butylsilane], and poly[methylpropylsilane], in the presence of DCA or $TPP^{+}BF_4^{-}$ are photodegraded in argon-purged CH_2Cl_2. For example, decreases and shifts in the absorption band at 317 nm of poly[di-*n*-hexylsilane] to a shorter wavelength were observed upon prolonged irradiation of the sensitizer at 425 nm. This is interpreted as being due to a decrease in the average length of the silicon atom chain and is similar to the spectral bleaching observed upon direct irradiation [1].

Only the pyranyl radical was observed as evidence of PET in our earlier report [14]; however, this time, we successfully observed radical cations of the polysilanes in the presence of $TPP^{+}BF_4^{-}$ as a sensitizer (Figure 4a). Under the conditions employed in this article, poly(methylphenylsilane) (0.12 mol dm^{-3}) quenches only 20% of excited $TPP^{+}BF_4^{-}$ singlets; however, TPP· was observed in a fairly high optical density at 550 nm (Figure 4a), because the absorption of $^{3}TPP^{+*}$ at 900 nm was quenched with a rate constant (k_q^T) of 5×10^8 mol^{-1} dm^3 s^{-1}, and this corresponds to >99% of triplets being quenched. The absorption of the radical cation of polysilane was observed in the near-IR region at greater than 800 nm [15]. Figure 4b shows the time profile at 900 nm. The $T_n \leftarrow T_1$ absorption of $TPP^{+}BF_4^{-}$ decreased in intensity, and the absorption of the polysilane radical cation increased with the same rate constant (Figure 4c). The lifetime of the polysilane radical cation is 83 μs which is quite long, and it might indicate delocalization of the charge and spin along the polysilane chain.

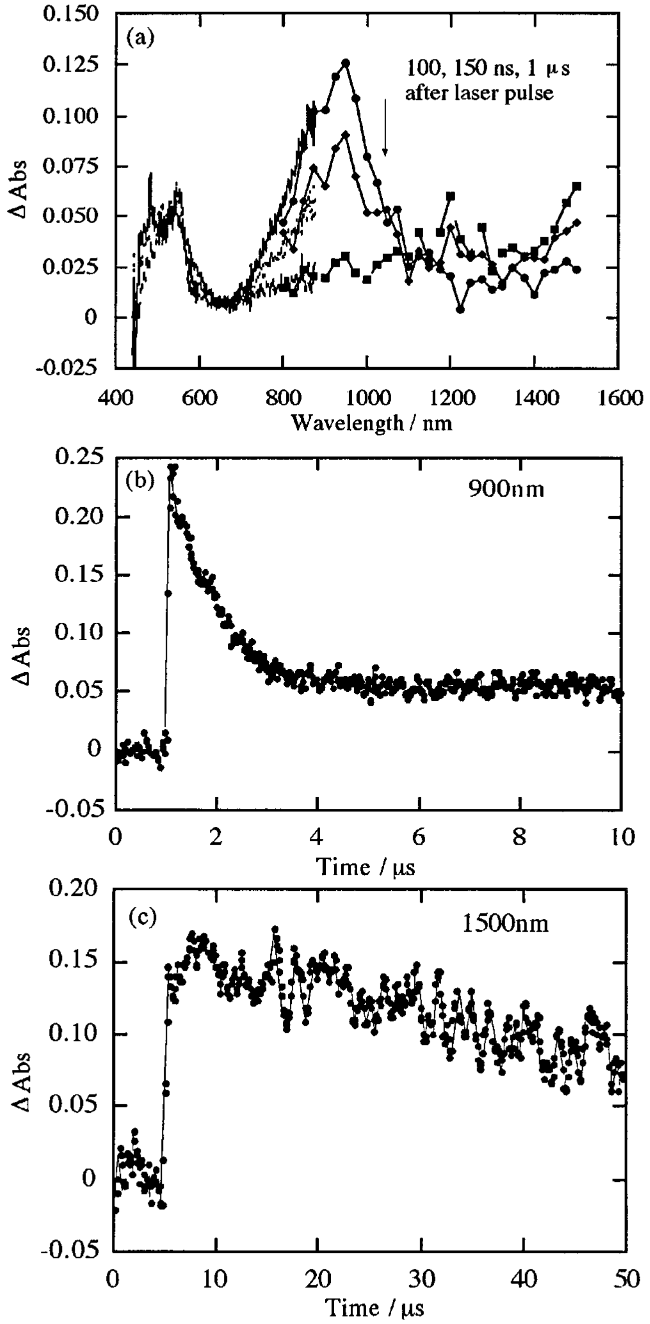


FIGURE 4 (a) Transient absorption spectra derived from laser excitation of $TPP^{+}BF_4^{-}$ in the presence of PMPS (1.2 mmol dm^{-3}) in CH_2Cl_2 under argon; (b) its time profile at 900 nm; (c) its time profile at 1500 nm. The spectra below 800 nm was obtained by a photodiode array detector and that above 800 nm was obtained by a Ge diode detector.

To date, we have been unable to detect the polysilane radical cation or the radical anions of DCA in CH_2Cl_2. This may be a consequence of the fast BET since inefficient separation of the radical cation and the radical anions compared to the case of neutral TPP· in these systems. Also, if charge separation by a migration of a hole along the silicon chain is fast, we can observe the absorption of radical ions; however, we did not. This indicates such a charge separation along the chain must be slower than the BET.

CONCLUSION

The reaction mechanism of PET between silanes and electron-deficient sensitizers was investigated in solution using product analysis and transient absorption spectroscopy. The efficiencies of the PET and BET are dependent on the type of sensitizers used, and the reactivity and stability of the silane radical cations are also dependent on the structure of the silanes. We are now performing research to clarify the effect of counter ions of the salt-type sensitizers.

EXPERIMENTAL

Materials

All the high molecular weight polysilanes were synthesized by the Wurtz-type coupling reaction from the corresponding dichlorosilanes in the presence of sodium in toluene as already reported [27,28]. CHS was synthesized [29] or purchased (Shinetsu or Petrarch). CPS was obtained by the photolysis of CHS at 254 nm (an Arion 15 W low-pressure mercury lamp being used) in nitrogen-saturated cyclohexane in the presence of triethylsilane and purified by a preparative GC (Ohkura Model-802, column; silicone OV-17, 15%, 2 m). COS was prepared by a previously reported method [19] and separated from the cyclic oligosilanes (mainly $n = \sim 5–9$) by gas chromatography (GC).

Tetradecamethyl-*n*-hexasilane was synthesized as previously reported [21] and purified by GC. The molecular weight (MW) of the polysilane high polymers was characterized by gel permeation chromatography (GPC) with polystyrene standards as listed in Table 2.

The sensitizers were purified by recrystallization. The CH_2Cl_2 solvent was washed with conc. H_2SO_4 overnight, washed with water, dried over anhydrous $CaSO_4$, and then finally distilled over LAH. Commercially available CH_2Cl_2 contains olefins such as methylbutene as a stabilizer. However, this acts as an electron acceptor from these sensitizers.

Spectroscopy

The absorption and fluorescence spectra were measured in argon-purged CH_2Cl_2 (Dotite) using a Hitachi U-3000 and an F-4010 spectrometers, respectively. The fluorescence lifetime was measured using a Horiba NAES-550 time-resolved fluorometer (single-photon counting).

The transient absorption spectra were measured using the systems based on an excimer laser (XeCl, Lambda Physik COMPex)-pumped dye laser (LAS GMBH LDL 205, Stilbene-3 dye, $\lambda = 425$ nm) with a photomultiplier detection system (Hamamatsu Photonics R928) or the system based on a Nd^{3+}:YAG laser (Continuum SL I-10, 355 nm, 6 ns full width at half-maximum [fwhm], 18–24 mJ/pulse) [30]. The absorption in the near-IR (NIR) region was measured using an NIR abaranche Ge photodiode (Hamamatsu Photonics C5331-SPL-B2834) with a suitable glass filter (Hoya R-60).

Quenching Studies

The quenching rate constants (k_q) of the fluorescence of the sensitizers (CA, DCA, and $TPP^+BF_4^-$) and the $T_n \leftarrow T_1$ absorption of $TPP^+BF_4^-$ (k_q^T) by the silanes were determined by a Stern-Volmer type plot of the lifetimes versus the concentrations of the silanes in argon or nitrogen-purged CH_2Cl_2.

Oxidation Potentials

The oxidation potentials of the sensitizers and silanes were measured by cyclic voltammetry (BAS CV-1B) at a platinum electrode in argon-saturated dry CH_3CN with 0.10 M tetrabutylammonium perchlorate as the supporting electrolyte. The scan speed

TABLE 2 Characteristics of High Molecular Weight Polysilanes

Polysilanes	λ_{max}	ε^a	*MW*	*MW/Mn*	*n*
Poly[4-methoxyphenylmethylsilane]	346	1.1×10^4	5.2×10^3	1.9	35
Poly[methylphenylsilane]	336	8.2×10^3	1.6×10^4	1.9	130
Poly[methyl-β-phenethylsilane]	305	1.1×10^4	9.4×10^4	3.4	640
Poly[di-n-butylsilane]	315	1.5×10^4	5.8×10^4	2.8	410
Poly[di-n-hexylsilane]	317	1.7×10^4	1.5×10^5	3.8	760
Poly[methylpropylsilane]	306	5.5×10^3	7.4×10^4	2.6	860
$-[SiMe_2(CH_2)_2SiMe_2-(SiMe_2)_6]_n-$	275	2.4×10^4	9.9×10^3	2.5	18

[a] ε, molar extinction coefficient, $M^{-1}cm^{-1}$ ($M = mol\ dm^{-3}$), concentration based on $-SiR_2-$ unit.

was 200 mV sec^{-1} and the reference electrode was the Ag/AgCl and converted to the value versus an saturated calorrel electrode. The oxidation potentials were determined from the half-peak potentials if it were irreversible.

Photochemistry of Oligocyclosilane

The solution of CHS, CPS, or COS in the presence of DCA or TPP^+ in dry CH_2Cl_2 was irradiated by 405 nm light isolated from a 1 kW medium pressure mercury lamp through a $CuSO_4 + NaNO_2 + NH_4OH$ solution filter [31] or L-39 glass filter in a merry-go-round apparatus. Product isolation was carried out by an appropriate method typically using preparative GC, and the structures were determined by gas chromatography–mass spectrometry (GC-MS) (Shimadzu QP-2000) and ^{1}H NMR (JEOL SR-400). The ^{1}H NMR data of the photochemical products are as follows. 1,6-Dichlorododecamethylhexasilane: ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 0.240$ (12H, s), 0.245 (12H, s), 0.515 (12H, s); 1-Chloro-6-fluorododecamethylhexasilane: ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 0.209$ (6H, s), 0.227 (6H, s), 0.235 (12H, s), 0.357 (6H, d, $J = 8.90$Hz), 0.513 (6H, s); 1,6-Difluorododecamethyl-hexasilane: ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 0.205$ (12H, s), 0.218 (12H, s), 0.357 (12H, d, $J = 8.24$Hz).

Decomposition Quantum Yield (Φ_{obs})

The decomposition quantum yields of the silanes were determined by irradiation at 405 nm through a filter in a merry-go-round apparatus. The light intensity was determined by potassium tris(oxalato)-ferrate (III) actinometry [31], and the conversion ($<20\%$) of the silanes was determined from the gas–liquid chromatography or UV–vis absorption spectra. The silane solutions in the presence of sensitizers in dry CH_2Cl_2 were degassed by three freeze-pump-thaw cycles.

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