

# A Photoresponsive Silicon Radical within a Porphyrin $\pi$ -Cloud: Photolysis of Organo- and Nitroxysilicon Porphyrins with Visible Light

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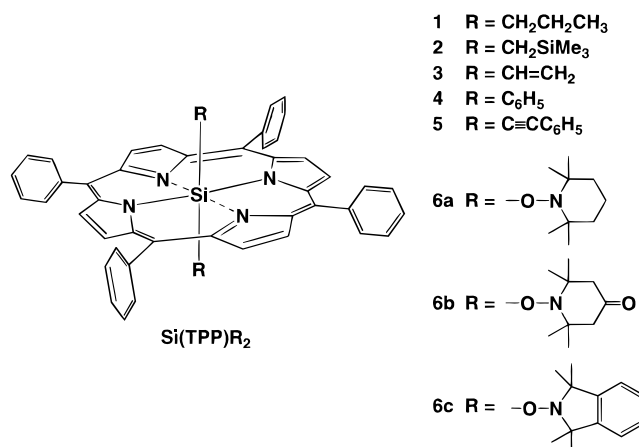
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**Abstract:** Upon irradiation with visible light ( $\lambda > 420$  nm) in  $C_6D_6$  under Ar, dialkylsilicon porphyrins Si(TPP) $R_2$  (TPP = 5,10,15,20-tetraphenylporphinato) ( $R = CH_2CH_2CH_3$  (**1**) and  $CH_2TMS$  (**2**)) reacted with nitroso compounds, such as 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO), 4-oxo-2,2,6,6-tetramethylpiperidiny-1-oxy, and 1,1,3,3-tetramethylisoindoliny-2-oxy, to give dinitroxysilicon porphyrins **6**. In the absence of nitroso compounds, photolysis of **1** resulted in the formation of a long-lived ( $>50$  days at 25 °C) EPR-active silicon diradical with a  $g$ -value of 2.0026, which did not react with nitroso compounds in the dark but was smoothly trapped by TEMPO to give **6a** upon excitation with visible light. Irradiation of **6** with visible light in the presence of free nitroso compounds resulted in reversible axial ligand exchange, which proceeded, in response to the switching on and off of the light, to reach an equilibrium.

## Introduction

Photochemical properties of porphyrin complexes have attracted continuing attention not only in relation to biological photosynthetic reactions but also for molecular design of light-harvesting materials, photoresponsive switches, photocatalysts, and so forth. Although extensive studies have been made on photoexcited metalloporphyrins with a variety of transition and nontransition metals,<sup>1,2</sup> the photochemical behaviors of porphyrin complexes of nonmetal elements are much less explored to date.<sup>3,4</sup>

Silicon porphyrin is a representative of nonmetal porphyrin complexes,<sup>3,5</sup> which accommodates a hexacoordinate silicon atom at a geometric center of four pyrrole nitrogen atoms. Very recently, we have succeeded in the synthesis of a series of organosilicon porphyrins (**1–5**) and have found by crystallographic studies that their two axial ligands are in a trans configuration to each other.<sup>6</sup> Although the porphyrin rings in silicon porphyrins are highly nonplanar when the axial ligands



are of electron-withdrawing character such as fluoride and triflate,<sup>5</sup> these organosilicon porphyrins have a strong tendency to adopt a planar conformation as for the porphyrin ring, indicating an electronic interaction between the axial ligands and the porphyrin ring via the central silicon atom. In the course of this study, we noticed that some of the organosilicon porphyrins are labile under illumination with room light. This observation prompted us to investigate the photochemical properties of organosilicon porphyrins.

In the present paper, we report results of studies on the photochemical reaction of a series of organosilicon porphyrins **1–5** with radical scavengers such as nitroso compounds and highlight the formation of a long-lived silicon diradical with a unique photoswitchable reactivity.

## Results and Discussion

**(I) Reaction of Organosilicon Porphyrins with Nitroso Compounds upon Irradiation with Visible Light.** Irradiation of dialkylsilicon porphyrins (Si(TPP) $R_2$ , **1** and **2**; TPP = 5, 10,15,20-tetraphenylporphinato) with visible light in the presence of nitroso compounds resulted in a quantitative formation

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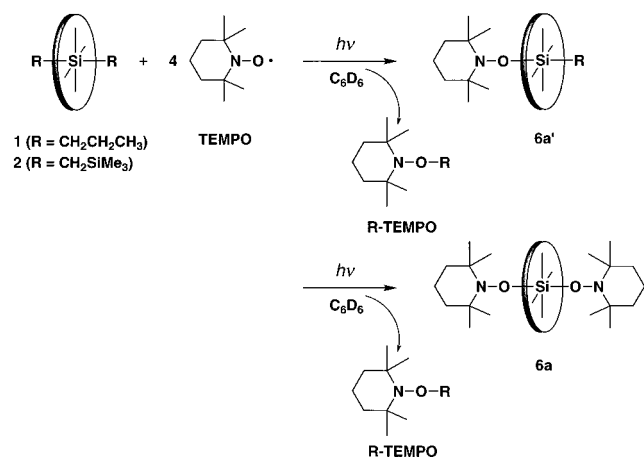
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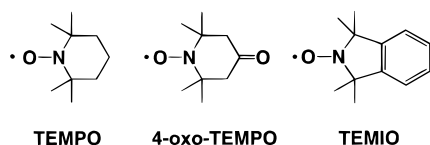
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## Scheme 1



of the corresponding dinitroxide complexes **6** (Scheme 1).<sup>7,2</sup> For example, when a mixture of dipropyl complex (**1**) (5.0  $\mu$ mol) and 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) (20  $\mu$ mol)



in C<sub>6</sub>D<sub>6</sub> (0.5 mL) under Ar was exposed to a xenon arc light ( $\lambda > 420$  nm) at 25 °C for 20 min, <sup>1</sup>H NMR signals due to the axial propyl groups of **1** [ $\delta$  -1.38 (f, CH<sub>3</sub>),  $\delta$  -4.24 (e, MeCH<sub>2</sub>),  $\delta$  -6.51 (d, CH<sub>2</sub>Si(TPP)); Figure 1a] disappeared completely. On the other hand, new signals assignable to a bis(TEMPO) complex **6a** [ $\delta$  -1.24, -2.41 (g, (CH<sub>3</sub>)<sub>2</sub>C-NOSi(TPP))] appeared together with a set of new signals due to [1-(1'-propoxy)-2,2,6,6-tetramethylpiperidine [Pr-TEMPO;  $\delta$  4.03 (D, EtCH<sub>2</sub>-ON)] (Figure 1c), which was identified by comparison with the authentic sample prepared from TEMPO and 1-propylmagnesium bromide.<sup>8</sup> From the relative intensity of the signal at  $\delta$  4.03 (Pr-TEMPO) to that at  $\delta$  -1.24 (**6a**), Pr-TEMPO was found to be formed twice as much as **6a**, as illustrated in Scheme 1. The trans configuration of the two TEMPO ligands in **6a** with respect to the silicon atom is evident from a single signal due to the ortho protons ( $\delta$  8.32) of the meso phenyl groups of the porphyrin ring, as in cis complexes of tetravalent metalloporphyrins, the ortho protons on the coordinated and noncoordinated faces of the porphyrin ring are not equivalent to each other and provide two signals.<sup>9</sup> In sharp contrast, the reaction of **1** with TEMPO in the dark hardly took place even at 90 °C for 168 h, indicating that photoexcitation of the porphyrin ring of **1** is essential for the formation of **6a**. When the reaction upon selective excitation of **1** at its Q-band (638  $\pm$  10 nm) was followed by means of UV-visible spectroscopy ([**1**]<sub>0</sub>/[TEMPO]<sub>0</sub> = 0.1/0.4 mM), characteristic absorption bands at 455.0 and 656.5 nm decreased in intensity with time, while two new absorption bands assignable to **6a** appeared at 425.5 and 561.0 nm and became predominant (Figure 2).<sup>10</sup> From the change in absorbance at 656.5 nm, the conversion of **1** during the initial

30-s irradiation was determined to be 23%, from which the quantum yield of the reaction was evaluated to be 13%.

The UV-visible spectral profile in Figure 2 also showed the appearance of a shoulder around 450 nm, assignable to the Soret band of monopropyl mono-TEMPO complex **6a'**, which however decayed upon further irradiation. In the <sup>1</sup>H NMR spectrum of the reaction mixture ([**1**]<sub>0</sub>/[TEMPO]<sub>0</sub> = 10/40 mM) after 4-min irradiation (Figure 1b), signals assignable to **6a'** were observed at  $\delta$  -1.33, -2.47 (g', (CH<sub>3</sub>)<sub>2</sub>C-NOSi(TPP)),  $\delta$  -1.15 (f', CH<sub>3</sub>CH<sub>2</sub>), -4.00 (e', MeCH<sub>2</sub>), and -6.09 (d', CH<sub>2</sub>Si(TPP)). Plots of the mole fractions of **6a** and **6a'**, as determined from the intensities of the corresponding signals ( $\delta$  -4.00 and -1.24), versus irradiation time (Figure 3) show that the yield of **6a'** once reached a maximum in 4-min irradiation and then decreased, while that of **6a** increased sigmoidally with irradiation time. Therefore, the formation of dinitroxide complex **6a** from **1** and TEMPO is likely to occur via a stepwise mechanism involving **6a'** as intermediate.

In addition to TEMPO, other nitroso compounds such as 4-oxo-2,2,6,6-tetramethylpiperidyl-1-oxy (4-oxo-TEMPO) and 1,1,3,3-tetramethylisoindolyl-2-oxy (TEMIO) also reacted with dipropylsilicon porphyrin (**1**) ([**1**]<sub>0</sub>/[4-oxo-TEMPO or TEMIO]<sub>0</sub> = 10/40 mM), upon irradiation with visible light ( $\lambda > 420$  nm) for 30 min, to give quantitatively the corresponding silicon dinitroxide complexes **6b** [ $\delta$  -1.59, -2.08 ((CH<sub>3</sub>)<sub>2</sub>C-NOSi(TPP)), 8.24 (o-H)], and **6c** [ $\delta$  -1.11, -1.63 ((CH<sub>3</sub>)<sub>2</sub>C-NOSi(TPP)), 8.40 (o-H)]. As for other organosilicon porphyrins, a dialkyl complex such as **2** (R = CH<sub>2</sub>SiMe<sub>3</sub>) also reacted with TEMPO ([**2**]<sub>0</sub>/[TEMPO]<sub>0</sub> = 10/40 mM) under irradiation with visible light ( $\lambda > 420$  nm), giving **6a** in a quantitative yield in 30 min. On the other hand, no reaction took place with organosilicon porphyrins bearing axial Si-C (sp<sup>2</sup>) and Si-C (sp) bonds such as **3** (R = CH=CH<sub>2</sub>), **4** (C<sub>6</sub>H<sub>5</sub>),<sup>6</sup> and **5** (C $\equiv$ CC<sub>6</sub>H<sub>5</sub>)<sup>6</sup> under similar conditions. In relation to the low reactivities of **3** - **5** toward TEMPO, our previous study has shown that the Si-C bond distances in **3** and **5** (1.83 and 1.82 Å) are shorter than that in **2** (1.95 Å), suggesting a possible d $\pi$ -p $\pi$  interaction between the central silicon atom and the unsaturated axial ligands.<sup>6,11</sup>

**(II) Photolysis of Dipropylsilicon Porphyrin (1) in the Absence of Nitroso Compounds.** As described in the above section, the photochemical generation of silicon dinitroxides **6a**-**6c** from dialkylsilicon porphyrins **1** and **2** and nitroso compounds is accompanied by the simultaneous formation of 2 equiv of O-alkylated nitroso compounds ( $\Delta$ , Figure 3). This observation indicates that the axial Si-C bond is cleaved homolytically to generate a (porphinato)silyl radical and an alkyl radical, both of which are subsequently trapped by the nitroso compound. In relation to this mechanism, we investigated photolysis of Si(TPP)Pr<sub>2</sub> (**1**) in the absence of nitroso compounds: When a C<sub>6</sub>D<sub>6</sub> solution of **1** (10 mM) was irradiated with visible light ( $\lambda > 420$  nm) at 25 °C under Ar, the color of the solution gradually turned from green to brown. TLC trace of the reaction mixture on a silica gel plate with CH<sub>2</sub>Cl<sub>2</sub> as eluent showed a complete disappearance of **1** ( $R_f$  = 0.7) within 10 min to give a major spot with an  $R_f$  of 0.05. The <sup>1</sup>H NMR spectrum of the reaction mixture showed a complete disappearance of the signals at an upfield region ( $\delta$  -1 to -7 ppm) due to the axial propyl groups, indicating the photolysis of the axial Si-C bonds of **1**. On the other hand, absorption spectral trace of the reaction in C<sub>6</sub>H<sub>6</sub>

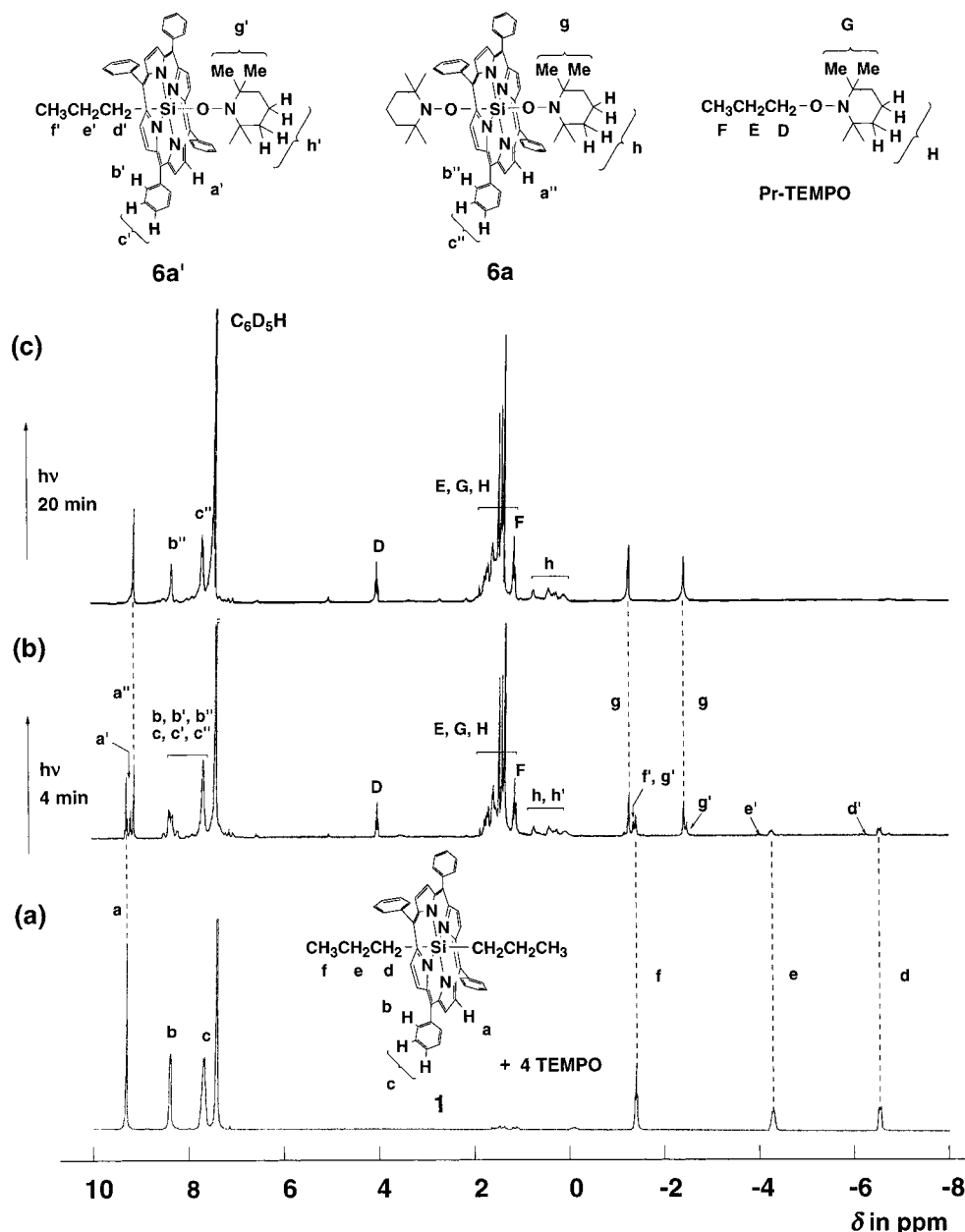
(7) For cleavage of Si-C bonds in silicon compounds, see: (a) Reference 3. (b) Tamao, K.; Akita, M.; Kato, H.; Kumada, M. *J. Organomet. Chem.* **1988**, *341*, 165 and references therein.

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(10) The spectral profile is very similar to those of dialkoxysilicon porphyrins.

(11) For d $\pi$ -p $\pi$  interactions in silicon compounds, see: Buell, G. R.; Corriu, R.; Guerin, C.; Spialter, L. *J. Am. Chem. Soc.* **1970**, *92*, 7424.



**Figure 1.** Reaction of Si(TPP)Pr<sub>2</sub> (**1**, 10 mM) with TEMPO (40 mM) in C<sub>6</sub>D<sub>6</sub> at 25 °C under Ar. <sup>1</sup>H NMR spectra before irradiation (a) and after irradiation with visible light (λ > 420 nm) for 4 (b) and 20 min (c). Free TEMPO is NMR-silent.

([**1**]<sub>0</sub> = 0.1 mM) at 25 °C upon selective excitation at 638 ± 10 nm showed that the Q-band at 656.0 nm, characteristic of **1**, disappeared in 1 min, while the Soret band at 455.0 nm shifted to 425.5 nm. Furthermore, an absorption band at 444.5 nm, assignable to an intermediate monopropyl complex, was observed at the initial stage of the reaction (~10 s), suggesting that the photolysis of **1** in the absence of nitroso compounds also occurs in a stepwise fashion.

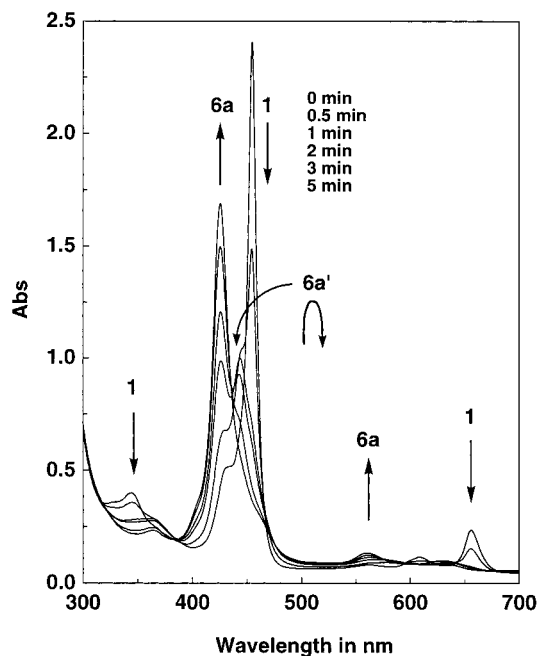
The EPR spectrum of a C<sub>6</sub>D<sub>6</sub> solution of **1** (10 mM) after 10-min irradiation displayed a strong single band with a *g*-value of 2.0026 at 25 °C (Figure 4a). Although this signal was significantly broad without any hyperfine splitting, the *g*-value is characteristic of those reported for silyl radicals (2.002–2.006).<sup>12</sup> Quite interestingly, the EPR-active species lasted for a long period of time without significant decay at 25 °C in the dark, so long as the reaction mixture was kept under Ar: The signal retained 95 and 86% of the original intensity in 1 and 50

days, respectively (Figure 4b,c). Of further interest to note is the fact that this EPR-active species does not react with TEMPO in the dark: Upon addition of 10 equiv of TEMPO with respect to **1** after the complete photolysis of **1** in C<sub>6</sub>D<sub>6</sub>, no <sup>1</sup>H NMR signals due to **6a** were detected throughout observation for 4 h in the dark. However, upon exposure of this mixture to visible light (λ > 420 nm) for 10 min, **6a** was formed in 43% yield.<sup>13</sup>

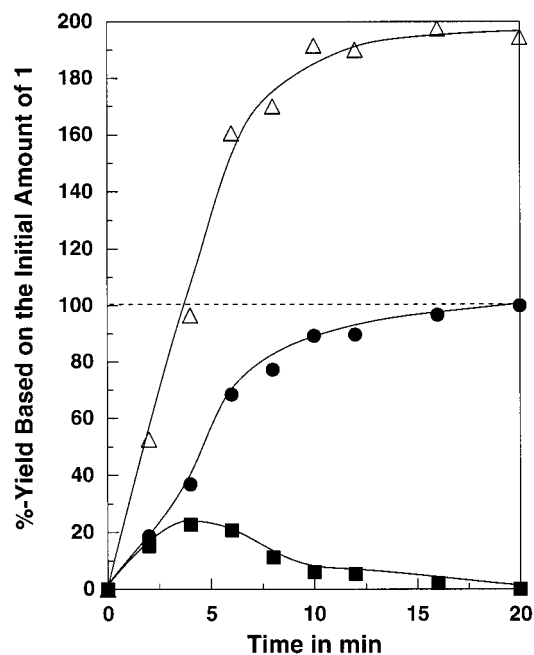
The formation of bis(TEMPO) complex **6a**, thus observed, indicates that the EPR-active species, generated upon photolysis of **1**, is most likely to be a silicon diradical. However, considering its low reactivity toward TEMPO in the dark, the unpaired electrons at the ground state are considered to be partially delocalized over the surrounding π-cloud of the porphyrin ring (**7**, Scheme 2). On the other hand, when the porphyrin ring is excited with visible light, such an electronic delocalization may be switched off, resulting in the generation

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(13) Determined from the <sup>1</sup>H NMR signal intensity at δ -1.24 (12H) relative to that of the pyrrole-β protons (8H).



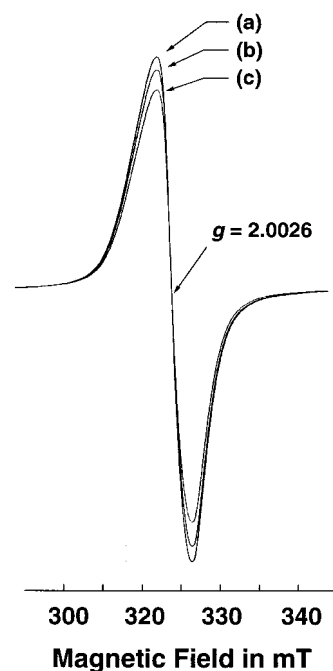
**Figure 2.** Reaction of Si(TPP)Pr<sub>2</sub> (**1**, 0.1 mM) with TEMPO (0.4 mM) in C<sub>6</sub>H<sub>6</sub> at 25 °C under Ar. Absorption spectral change upon irradiation with 150-W xenon arc light at 638 ± 10 nm.



**Figure 3.** Reaction of Si(TPP)Pr<sub>2</sub> (**1**, 10 mM) with TEMPO (40 mM) in C<sub>6</sub>D<sub>6</sub> at 25 °C upon irradiation with visible light ( $\lambda > 420$  nm) under Ar. Time courses of the formation of monopropyl mono-TEMPO complex (**6a'**, ■), bis(TEMPO) complex (**6a**, ●), and Pr-TEMPO ( $\Delta$ ), as evaluated from the intensities of the <sup>1</sup>H NMR signals at  $\delta$  -2.41 (12H) for **6a**,  $\delta$  -4.00 (2H) for **6a'**, and  $\delta$  4.03 (2H) for Pr-TEMPO, relative to the sum of those of the pyrrole- $\beta$  protons ( $\delta$  9.1–9.3, 8H).

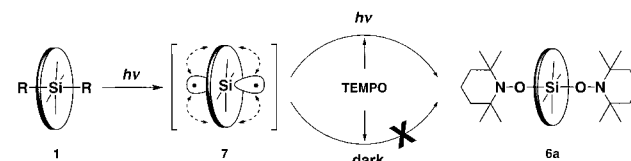
of a silicon-centered diradical species with sufficient reactivity toward TEMPO. Therefore, the silicon diradical within a porphyrin  $\pi$ -cloud is a “photoswitchable radical”, whose reactivity can be controlled by visible light.

**(III) Reaction of Dinitrosilicon Porphyrins with Nitroxy Compounds.** To obtain further insight into the photochemical properties of the (porphinato)silyl radical, we investigated photolysis of dinitrosilicon porphyrin **6a** in the presence of free nitroxy compounds. Quite interestingly, the axial nitroxy

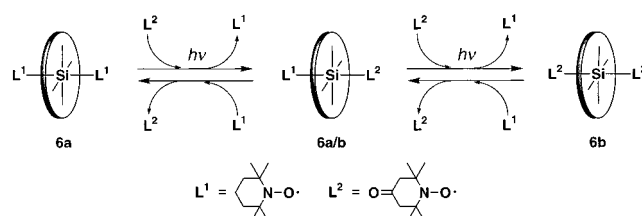


**Figure 4.** EPR spectra at 25 °C of a C<sub>6</sub>D<sub>6</sub> solution of **1** (10 mM) kept in the dark for 10 min (a), 24 h (b), and 50 days (c) after irradiation with visible light ( $\lambda > 420$  nm) for 10 min at 25 °C under Ar.

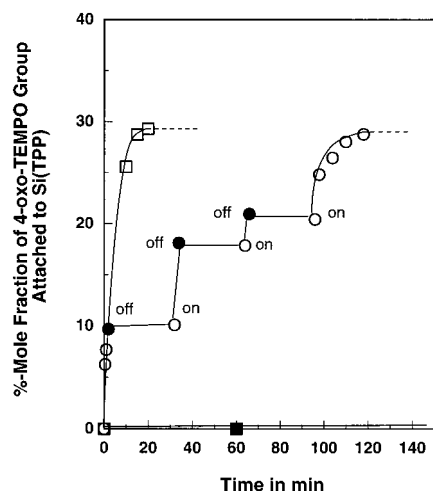
#### Scheme 2



#### Scheme 3



groups in **6a** underwent ligand exchange with the nitroxy compounds, for which the effect of visible light was again essential (Scheme 3): When a C<sub>6</sub>D<sub>6</sub> solution of **6a** containing a mixture of TEMPO and 4-oxo-TEMPO ([**6a**]<sub>0</sub>/[TEMPO]<sub>0</sub>/[4-oxo-TEMPO]<sub>0</sub> = 10/40/60 mM) was irradiated with visible light ( $\lambda > 420$  nm) at 25 °C under Ar, the <sup>1</sup>H NMR signals due to the methyl groups in the nitroxy ligands of **6a** decreased with time, while new signals at  $\delta$  -1.59 and -2.08 assignable to those of a 4-oxo-TEMPO group attached to Si(TPP) (4-oxo-TEMPO–Si(TPP)) appeared. As shown in Figure 5 (□), the mole fraction of 4-oxo-TEMPO–Si(TPP) reached a plateau at 30% within 30-min irradiation. When **6b** was used in place of **6a** for the above reaction ([**6b**]<sub>0</sub>/[TEMPO]<sub>0</sub>/[4-oxo-TEMPO]<sub>0</sub> = 10/60/40 mM), a similar photoinduced ligand exchange occurred, where the mole fraction of the TEMPO ligand reached a plateau at 70% within 30 min. Therefore, the photoinduced exchange of the nitroxy groups is fully reversible. In sharp contrast, no exchange of the axial nitroxy ligands occurred in the dark throughout an observation over a period of 1 h under otherwise conditions identical to the above (■). The essential effect of visible light was nicely demonstrated by a light on



**Figure 5.** Irradiation of Si(TPP)(TEMPO)<sub>2</sub> (**6a**, 10 mM) with visible light in the presence of a mixture of TEMPO and 4-oxo-TEMPO ([**6a**]<sub>0</sub>/[TEMPO]<sub>0</sub>/[4-oxo-TEMPO]<sub>0</sub> = 10/40/60 mM) in C<sub>6</sub>D<sub>6</sub> at 25 °C under Ar. Changes in mole fraction of the 4-oxo-TEMPO group attached to Si(TPP) ([4-oxo-TEMP-Si(TPP)]/[TEMPO-Si(TPP)] + [4-oxo-TEMPO-Si(TPP)]) under irradiation (□), in the dark (■), and under light on/off conditions (○, ●).

(○)/off (●) experiment (Figure 5), where the ligand exchange proceeded only when the reaction mixture was exposed to visible light, whereas the exchange totally stopped when the light was switched off.

The photoinduced ligand exchange of the axial nitroxy groups, thus observed, is considered to occur via homolysis of the Si–O bonds in the nitroxide complex, followed by competitive recombination of the resulting (porphinato)silyl radical with free nitroxy compounds (TEMPO and 4-oxo-TEMPO). Therefore, the nitroxide complexes **6** are silyl radical equivalents, which can reversibly photodissociate into free radicals upon excitation of the porphyrin ring. The cleanliness of the reaction in Figure 5 suggests a long lifetime of the silyl radical intermediate.

## Conclusion

Silylenes including silicon diradicals with unpaired electrons<sup>14,15</sup> have attracted considerable attention not only from a fundamental interest in relation to carbenes<sup>16</sup> but also as new potential intermediates in organic synthesis and materials science. In the present study, we have demonstrated that dialkylsilicon porphyrins, upon excitation of the porphyrin ring with visible light, undergo homolytic cleavage of the axial Si–C bonds to generate a highly stable silicon diradical at the ground state, which can be activated by visible light to react with nitroxy compounds. Furthermore, we have also shown that the axial Si–O bonds in the resulting dinitroxy silicon porphyrins are cleaved homolytically to afford free radicals upon irradiation with visible light. These results indicate an interesting possibility that the silicon diradical within a porphyrin  $\pi$ -cloud serves as a “photoswitchable radical”, whose reactivity can be

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(15) Ground-state triplet silylenes have only been predicted theoretically by computational studies: (a) Gordon, M. S. *Chem. Phys. Lett.* **1985**, *144*, 138. (b) Grev, R. G.; Schaefer, H. F.; Gaspar, P. G. *J. Am. Chem. Soc.* **1991**, *113*, 5638. (c) Cramer, C. J.; Falvey, D. E. *Tetrahedron Lett.* **1997**, *38*, 1515.

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controlled by visible light. Studies on reactivities of dialkyl- and dinitroxy silicon porphyrins with unsaturated compounds may be one of the subjects worthy of further investigation.

## Experimental Section

**General Information.** Organosilicon porphyrins **1–5** were synthesized according to the method reported in a previous paper.<sup>6</sup> Nitroxy compounds such as TEMPO and 4-oxo-TEMPO were purchased from Tokyo Kasei and used as received. TEMIO was synthesized according to the literature method<sup>17</sup> [mp 130–131 °C (lit.<sup>17</sup> mp 128–129 °C). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>NO: C, 75.75; H, 8.48; N, 7.36. Found: C, 75.19; H, 8.38; N, 7.53. Pr-TEMPO was synthesized from TEMPO and 1-propylmagnesium bromide according to the literature method.<sup>8</sup> <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.03 (t, 2H, CH<sub>2</sub>–O), 1.8–1.3 (m, overlapped, 20H, C(CH<sub>2</sub>)<sub>3</sub>C, C(CH<sub>3</sub>)<sub>2</sub>, and CH<sub>2</sub>CH<sub>3</sub>), 1.16 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>). C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub> were distilled over sodium wire in the presence of benzophenone ketyl and stored under Ar. <sup>1</sup>H NMR spectra were recorded in C<sub>6</sub>D<sub>6</sub> at 25 °C on a Jeol type GSX-270 spectrometer operating at 270 MHz, where chemical shifts (ppm) were determined with respect to residual C<sub>6</sub>D<sub>5</sub>H ( $\delta$  7.40) as internal standard. UV–visible spectra were recorded in C<sub>6</sub>H<sub>6</sub> at 25 °C on a Jasco type V-560 spectrophotometer. EPR spectra were recorded at 25 °C on a Jeol FE-1X X-band spectrometer using following parameters: magnetic field, 3280  $\pm$  50 G; modulation, 100 kHz and 0.063 G; amplitude, 5; response, 0.3 s.

**Photolysis of Organosilicon Porphyrins in the Presence of Nitroxy Compounds.** Typically, to a 10-mL round-bottomed flask, fitted with a three-way stopcock, containing dipropylsilicon complex **1** (14.5 mg, 20  $\mu$ mol) was added a C<sub>6</sub>D<sub>6</sub> solution (2 mL) of TEMPO (12.5 mg, 80  $\mu$ mol), and the mixture was stirred in the dark at room temperature for 5–10 min. An aliquot (0.8 mL) of the above solution was transferred to a NMR tube, which was then sealed off. The NMR tube was exposed to a 150-W xenon arc light from a distance of 8 cm at 25 °C through a thermal-cut filter and a glass filter to cut out light with a wavelength shorter than 420 nm. The reaction was followed by means of <sup>1</sup>H NMR spectroscopy.

**6a.** <sup>1</sup>H NMR:  $\delta$  9.11 (s, 8H, pyrrole- $\beta$ ), 8.32 (br, 8H, Ph-*o*), 7.7–7.5 (br, 12H, Ph-*m, p*), 0.75–0.15 (br, 12H, C(CH<sub>2</sub>)<sub>3</sub>C), –1.24 and –2.41 (s  $\times$  2, 24H, (CH<sub>3</sub>)<sub>2</sub>C–NOSi(TPP)).

**6b.** <sup>1</sup>H NMR:  $\delta$  9.07 (s, 8H, pyrrole- $\beta$ ), 8.24 (br, 8H, Ph-*o*), 7.7–7.5 (br, 12H, Ph-*m, p*), 0.75–0.15 (br, 8H, C(CH<sub>2</sub>)–CO), –1.59 and –2.08 (s  $\times$  2, 24H, (CH<sub>3</sub>)<sub>2</sub>C–NOSi(TPP)).

**6c.** <sup>1</sup>H NMR:  $\delta$  9.20 (s, 8H, pyrrole- $\beta$ ), 8.40 (d, 8H, Ph-*o*), 7.7–7.5 (br, 12H, Ph-*m, p*), 6.70 and 6.22 (br  $\times$  2, 8H, C<sub>6</sub>H<sub>4</sub>), –1.11 and –1.63 (s  $\times$  2, 24H, (CH<sub>3</sub>)<sub>2</sub>C–NOSi(TPP)).

**Determination of Quantum Yield.** To a quartz cell of 1-cm path length, fitted with a three-way stopcock, were successively added a mixture of **1** (10 mM) and TEMPO (40 mM) in C<sub>6</sub>D<sub>6</sub> (0.02 mL) and dry C<sub>6</sub>H<sub>6</sub> (2 mL) under Ar. Then, the cell was exposed to a 150-W xenon arc light from a distance of 8 cm at 25 °C through a band-path filter ( $\lambda$  = 638 nm, bandwidth 10 nm) coupled with UV-cut (<330 nm) and thermal-cut filters. The reaction was followed by means of UV–visible spectroscopy (Figure 2). The light intensity transmitted through the cell during the initial 30 s was continuously monitored by an optical power meter (Anritsu model ML96B) directly attached to the backside of the cell. Quantum yield was determined from the number of the molecules of converted **1**, as evaluated from

(17) Griffiths, P. G.; Moad, G.; Rizzardo, E.; Solomon, D. H. *Aust. J. Chem.* **1983**, *36*, 397.

the change in absorbance at 650 nm, versus that the absorbed photons calculated from the light intensity and the detection area of the power meter.

**Photolysis of Dipropylsilicon Porphyrins (Si(TPP)Pr<sub>2</sub>, 1) in the Absence of Nitroxy Compounds.** To a 10-mL round-bottomed flask, equipped with a three-way stopcock, containing **1** (7.3 mg, 10  $\mu$ mol) was added C<sub>6</sub>D<sub>6</sub> (2 mL), and the mixture was stirred in the dark at room temperature for 5 min. Then, the flask was exposed to a 150-W xenon arc light at 25 °C for 10 min in a manner similar to that described above. An aliquot of the reaction mixture was taken out from the flask by a hypodermic syringe and subjected to TLC, UV-visible, and <sup>1</sup>H NMR analyses to confirm complete cleavage of the axial Si-C bonds. Then, another aliquot (0.5 mL) was transferred from the residual solution to an EPR tube and subjected to EPR spectroscopy at 25 °C. The residue (0.5 mL) was transferred into an NMR tube containing TEMPO (7.8 mg, 50  $\mu$ mol) under Ar, and the yield of **6a** was determined from the <sup>1</sup>H NMR signal intensity at  $\delta$  -1.24 (12H) relative to that of the pyrrole- $\beta$  protons (8H).

**Photolysis of Dinitroxysilicon Porphyrin (Si(TPP)(TEMPO)<sub>2</sub>, 6a) in the Presence of Nitroxy Compounds.** A C<sub>6</sub>D<sub>6</sub> solution (4 mL) of a mixture of **1** (29.1 mg, 40  $\mu$ mol) and TEMPO (49.9 mg, 320  $\mu$ mol) was exposed to visible light ( $\lambda$  > 420 nm) in a manner similar to the above, to give a solution of **6a** (40  $\mu$ mol) containing free TEMPO (160  $\mu$ mol). To this solution was added a C<sub>6</sub>D<sub>6</sub> solution (0.2 mL) of 4-oxo-TEMPO (40.8 mg, 240  $\mu$ mol), and an aliquot (0.5 mL) of the mixture was transferred to a NMR tube, which was then sealed off. The tube was exposed to a xenon arc light (150 W) at 25 °C, and the reaction was followed by means of <sup>1</sup>H NMR spectroscopy. The mole fraction of the 4-oxo-TEMPO group attached to Si-(TPP) ([4-oxo-TEMP-Si(TPP)]/([TEMPO-Si(TPP)] + [4-oxo-TEMPO-Si(TPP)])) was determined from the intensity of the signal at  $\delta$  -1.24 (12H) due to the TEMPO ligand relative to that at  $\delta$  -1.59 (12H) due to the 4-oxo-TEMPO ligand.

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