Enhancement of Singlet Oxygen Sensitization of Tetraphenylporphyrin by Silylation

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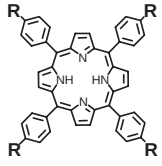
Photophysical and singlet oxygen sensitization processes of 5,10,15,20-tetrakis(4-trimethylsilylphenyl)porphyrin have been studied. It was found out that the quantum yield (Φ_Δ) of singlet oxygen production increased by the silylation of 5,10,15,20-tetraphenylporphyrin (TPP). The silylation does not affect the photophysical processes of TPP but enhances the sensitization efficiency of singlet oxygen by the triplet sensitizer ($f_\Delta{}^T$). This enhancement can be explained by the suppression of the process from the triplet encounter complex composed of the triplet sensitizer and ground-state oxygen to the ground-state sensitizer and oxygen.

Photodynamic therapy is one of novel treatments for cancer and certain noncancerous conditions that are generally characterized by overgrowth of unwanted or abnormal cells.[1] In this treatment, the photosensitizing drug is retained in tumor by the intravenous injection of the drug followed by the irradiation of the tumor with visible light. By the irradiation to the drug, singlet oxygen ($^1\Delta_g$) and other reactive oxygen species are formed directly in a tumor and destroy it from inside.[1,2] Porphynoid or their metal complexes are one of famous photosensitizers, and improvement of their photosensitization efficiency is one of the most important subjects for this therapy.

Introduction of silicon atom(s) to aromatic compounds is known to change remarkably their photophysical and photochemical properties. We reported that the silylation of anthracene[3] and naphthacene,[4] and triphenylene[5] remarkably enhanced the fluorescence and phosphorescence efficiency, respectively. We also reported that the introduction of silicon atom into the aromatic ring (e.g. 9,10-dihydro-9-silaanthracene,[6] 9,10-dihydro-9-silaphenanthrene,[7] and 9-silafluorene[8]) enhances the intersystem crossing efficiency. In this paper, we report photophysical and photochemical processes of 5,10,15,20-tetrakis(4-trimethylsilylphenyl)porphyrin (SiTPP) to study the effect of the silylation of porphynoid on the singlet oxygen production efficiency.

SiTPP was synthesized according to the literature.[9] To study the effect of the silylation, 5,10,15,20-tetraphenylporphyrin (TPP) and 5,10,15,20-tetrakis(4-tolyl)porphyrin (MeTPP) have also been studied (Scheme 1). Figure 1 shows emission spectra



R	Abbreviation
H	TPP
$SiMe_3$	SiTPP
Me	MeTPP

Scheme 1. Molecular structure of tetraphenylporphyrin derivatives.

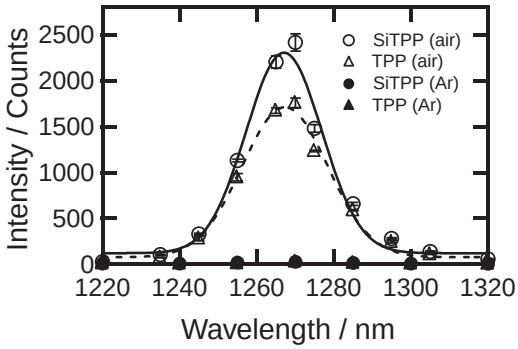


Figure 1. Phosphorescence spectra of singlet oxygen sensitized by TPP and SiTPP in air- and Ar-saturated tetrahydrofuran observed just after the laser excitation with 355-nm light pulse.

observed upon excitation of TPP and SiTPP in air-saturated tetrahydrofuran (THF) in near IR region. An emission band was observed with a maximum at 1270 nm, but in Ar-saturated THF this emission band was not observed (Figure 1), indicating that the emission band is ascribable to the phosphorescence of the singlet oxygen sensitized. The phosphorescence intensity observed for SiTPP is 1.3 times larger than that for TPP. This enhancement was not observed by the methylation of TPP (MeTPP). These facts indicate that the silylation of TPP enhances the singlet oxygen production efficiency. Quantum yields of singlet oxygen production (Φ_Δ) were determined relative to perinaphthenone[10] under air and are summarized in Table 1.

To clarify the mechanism of enhancement of the singlet oxygen production efficiency, photophysical processes of SiTPP were studied. Figure 2 shows UV–vis absorption, fluorescence, and phosphorescence spectra of SiTPP and TPP. The phosphorescence spectra were measured in 2-methyltetrahydrofuran at 77 K. Spectral features of SiTPP are essentially the same as those of TPP. Transient absorption spectrum of the triplet state was also measured. The spectral shape and lifetime of the triplet state of SiTPP are also very similar to those of TPP. Photophysical parameters determined are summarized in Table 1. Molar absorption coefficient (ε), fluorescence quantum yield (Φ_f), fluorescence lifetime (τ_f), quantum yield of the intersystem crossing (Φ_T), lifetime of the triplet state (τ_T), and triplet state energy (E_T) are also very similar to each other. These indicate that the silylation does not affect the photophysical processes of TPP.

Energy difference (0.46 eV) between the first excited singlet state ($^1M^*$) and triplet state ($^3M^*$) of the sensitizer is much smaller than that (0.98 eV) between O_2 ($^3\Sigma_g{}^-$) and O_2 ($^1\Delta_g$), so that the sensitization of the singlet oxygen by $^1M^*$ is energetically impossible. Therefore, the quantum yield of singlet oxygen

Table 1. Photophysical parameters, singlet oxygen sensitization efficiencies of TPP, SiTPP, and MeTPP in THF

Sample	Φ_Δ	$\varepsilon_{415\,nm}/M^{-1}\,cm^{-1}$	Φ_f	τ_f/ns	Φ_T	τ_T/μs	E_T/kJ mol^{-1}	$f_\Delta{}^T$	E_{ox}/V vs, SCE	ΔG^{CT}/kJ mol^{-1}
TPP	0.58	4.8×10^5	0.09	10.3	0.83	130	140	0.70	1.06	38
SiTPP	0.77	5.0×10^5	0.11	10.3	0.87	150	139	0.89	1.12	44
MeTPP	0.61	5.1×10^5	0.13	10.1	0.83	160	140	0.73	1.04	36

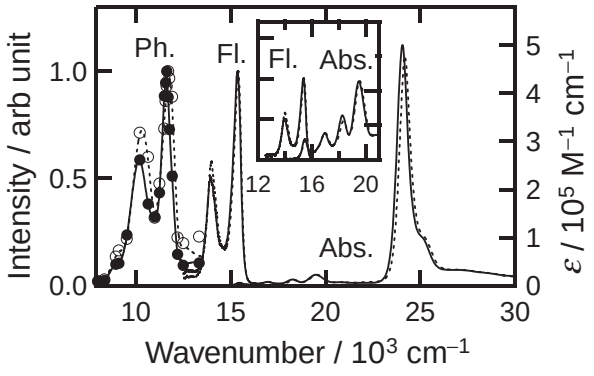


Figure 2. Absorption, fluorescence, and phosphorescence spectra of TPP (broken line) and SiTPP (full line): the inset is the absorption and fluorescence spectra in the region of 12000–20000 cm^{-1}.

production (Φ_Δ) can be described as $\Phi_\Delta = \Phi_T \times P_T{}^{O_2} \times f_\Delta{}^T$, where $P_T{}^{O_2}$ is quenching efficiency of the triplet sensitizer by oxygen and $f_\Delta{}^T$ is the fraction of the triplet sensitizer quenched by oxygen to yield singlet oxygen (sensitization efficiency).[11,12] In air-saturated THF, $P_T{}^{O_2}$ was 0.99 for three samples, so that $f_\Delta{}^T$ was determined to be 0.70, 0.89, and 0.73 for TPP, SiTPP, and MeTPP, respectively (Table 1). This indicates that only the sensitization efficiency ($f_\Delta{}^T$) is enhanced by the silylation.

Wilkinson et al. reported that singlet oxygen is produced from the singlet encounter complex $^1(^3M^*\cdots O_2(^3\Sigma_g{}^-))$ as shown in Scheme 2.[11,12] They also reported that process 2 from the triplet encounter complex $^3(^3M^*\cdots O_2(^3\Sigma_g{}^-))$ to the ground-state sensitizer (M) and oxygen ($^3\Sigma_g{}^-$) takes place via the charge-transfer complex $^3(M^+\cdots O_2{}^-)$. Thus, the sensitization efficiency ($f_\Delta{}^T$) increases by the suppression of the charge-transfer process. The free energy change of the charge-transfer process is represented as $\Delta G^{CT} = F(E_{ox}{}^M - E_{red}{}^{O_2}) - E_T$,[12] where F is the Faraday constant, $E_{ox}{}^M$ is the half-wave oxidation potential of the sensitizer in the ground state, and $E_{red}{}^{O_2}$ is the half-wave reduction potential of oxygen (-0.78 V vs, SCE[13]). The values of $E_{ox}{}^M$ were measured by cyclic voltammetry and ΔG^{CT} were estimated as shown in Table 1. ΔG^{CT} increases by the silylation of TPP, indicating that the process 2 is suppressed by the silylation to induce the enhancement of the sensitization efficiency ($f_\Delta{}^T$).

$$\overset{1/9k_d}{\rightleftharpoons}\ {}^1(^3M^*\cdots O_2,\ ^3\Sigma_g{}^-)^* \xrightarrow{k_{et}} M + O_2(^1\Delta_g) \quad (1)$$

$$^3M^* + O_2(^3\Sigma_g{}^-) \overset{3/9k_d}{\rightleftharpoons}\ {}^3(^3M^*\cdots O_2,\ ^3\Sigma_g{}^-)^* \xrightarrow{k_{isc}} M + O_2(^3\Sigma_g{}^-) \quad (2)$$

$$\overset{5/9k_d}{\rightleftharpoons}\ {}^5(^3M^*\cdots O_2,\ ^3\Sigma_g{}^-)^*$$

Scheme 2. Sensitization mechanism of singlet oxygen by the triplet sensitizer proposed by Wilkinson et al.[12]

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