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Visible light induced oxygenation of alkenes with water sensitized by silicon-porphyrins with the second most earth-abundant element



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ABSTRACT

Silicon as the second most abundant element on Earth was effectively utilized as the central atom in the porphyrin to induce photochemical oxygenation of alkenes as the first example of photocatalytic reaction through activation of water molecule in the presence of K_2PtCl_6 as an electron acceptor. Oxygen atom of water was confirmed to be incorporated in the oxygenated product by the photoreaction with H_2 ¹⁸O. The excited triplet state of silicon porphyrin was revealed to be responsible for the photochemical oxygenation. The one-electron oxidized silicon porphyrin was predicted by DFT calculation to have its spin population mostly on the axially ligated hydroxyl oxygen atom. The oxyl radical character of the axial ligand could rationalize the oxygenation.

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1. Introduction

Porphyrins are well known to incorporate almost all kinds of element within their ring as the central atom [1]. Silicon porphyrins have attracted much attention, since silicon is the second most abundant and easily available element on Earth [2,3]. Though many reports on their synthesis have appeared [2], photochemical behavior of silicon porphyrins has been rarely reported [3]. Here we report a visible light induced oxygenation of alkenes such as cyclohexene, norbornene, and styrene with water as an oxygen atom donor sensitized by tetra(2, 4, 6-trimethyl) phenylporphyrinatosilicon (SiTMP) as the first example of a photocatalytic reaction with water induced by silicon porphyrins. One of the crucial view points to the visible light induced oxygenation of substrate with water would be on artificial photosynthesis. Artificial photosynthesis by visible light is one of the most desirable chemical systems at present. Among the problems to be resolved for the realization of artificial photosynthesis, how could water molecules be incorporated at the oxidation terminus of the system is one of the most crucial issues [4.5]. We have recently focused our attention on the two-electron oxidation of water by one-photon excitation to form oxygenated products of various substrates sensitized by metalloporphyrins [5–8] (Eq. (1)).

$$S" + H_2O + Pt(IV)C{l_4}^{2-} \xrightarrow{hv}_{MP} "S" + Pt(II)C{l_4}^{2-} + 2HCl$$
(1)

where "S", "SO", MP denote substrate, oxygenated substrate, and metalloporphyrins, respectively. As a half reaction in the oxidation side of artificial photosynthesis, the two-electron oxidation of water by one-photon excitation (Eq. (1)) would be the more plausible alternative compared to the four-electron oxidation by stepwise four-photon excitation under actual sunlight radiation with rather low light intensity, which faces with the "photon-fluxdensity problem [5]." Another crucial issue, furthermore, to be resolved would be to devise ways to utilize major elements for the artificial photosynthetic system rather than rare elements. We have already found that aluminum(III) porphyrins can induce photochemical oxygenation of substrate with water [9]. Here we will report that another promising major element, silicon, can be also utilized as Si(IV)- porphyrins to induce the photoreaction. Silicon should be the most promising element for the purpose.

2. Experimental

2.1. Materials

2.1.1. Synthesis of trans-dihydroxy[5,10, 15, 20-tetra(2,4,6-trimethyl) phenyl porphyrinato] silicon (IV): Si(IV)TMP(OH)₂

Tetra(2, 4, 6-trimethyl) phenylporphyrinatosilicon (SiTMP) as a new compound was synthesized from the free base tetramesitylporphyrin through four steps of lithiation, insertion of silicon,



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Scheme 1. Synthesis of SiTMP(OH)2.

dechlorination, and hydrolysis of axial ligands. The synthesis was carried out as a multi-step single pot synthesis till step 3 as shown in Scheme 1. The free base tetramesitylporhyrin (H₂TMP: 399 mg, 0.51 mmoles) was taken in a reaction pot and kept under vacuum for 30 min. 80 ml of dimethoxyethane (DME) was vacuum transferred to the reaction vessel and stirred at 80 °C for 1 h under nitrogen atmosphere. To the solution, lithium bis(trimethylsilyl) amide (LHMDS: 350 mg, 2.1 mmoles) was added and stirred under 80 °C for an hour. The completion of step 1 was confirmed by a red shift in UV-vis spectrum (416-436 nm) of reaction mixture measured in dry DME. The reaction mixture is then cooled to -20 °C and then HSiCl₃ (0.1 ml, 0.99 mmoles) was added carefully and stirred under the same condition for 1 h. The reaction mixture was then slowly warmed up to room temperature and stirred under room temperature for 12 h. The completion of step 2 was confirmed by a blue shift in UV-vis spectrum (436-432 nm) of the reaction mixture. Then a little excess amount of silver trifluoromethanesulfonate (AgOTf: 1800 mg, 7 mmoles) was added to the reaction mixture and stirred for one overnight at 80 °C. The completion of step 3 was confirmed by a blue shift in UV-vis spectrum (432-415 nm) of the reaction mixture. The reaction mixture was then filtered through PTFE membrane (pore size: 0.1 µm) and celite successively to remove solid inorganic impurities. The purple colored solution thus obtained was vacuum dried to get purple powder which was then dissolved in 100 ml of dichloromethane. Water (100 ml) was further added and the mixture was kept stirring for one overnight. The completion of Step 4 was confirmed by a red shift in UV-vis spectrum (415-422 nm). The organic layer was then separated and purified by passing through SiO₂ column using 1:3 ethyl acetate/ hexane as eluent to get pure SiTMP as purple crystal (295 mg, 68% yield). The Si porphyrin synthesized was identified as SiTMP(OH)₂ which have two hydroxy groups as axial ligands on the central Si atom.

EA: Obsd. C 77.97%, H 7.17%, N 5.55%, Calcd. for [Si (IV)TMP (OH)₂](${}^{1}_{/2}$ H₂O·C₆H₁₄· ${}^{1}_{/4}$ CH₂Cl₂), C 77.92%, H 7.30%, N 5.84%. ¹H NMR (CDCl₃): δ = 8.63 (s, 8H), 7.18 (s, 8H), 2.54 (s, 12H), 1.85(s, 24H), -3.04 (s, 1.4H). ¹³C NMR (CDCl₃): δ = 21.36 (s), 21.60 (s), 115.17(s), 127.77(s), 131.16(s), 136.23(s), 137.92(s), 139.30(s), 142.48(s). ²⁹Si NMR (CDCl₃): δ = -202.77(s). UV-viz: ε = 5.06 × 10⁵ M⁻¹ dm⁻³ (λmax = 422.5 nm in CHCl₃). ESI-MS: *m*/*z* = 842.29

2.1.2. Other materials

Dimethoxyethane (DME) purchased from TCI chemicals was stored over molecular sieves (4A), and dried over Na and vacuum transferred immediately prior to use.

Lithium bis(trimethylsilyl) amide (LHMDS) solid was purchased from Aldrich and stored in dry condition. Trichloro silane (HSiCl₃) was purchased from TCI chemicals. Silver trifluoromethanesulfonate (AgOTf) was purchased from TCI chemicals. Cyclohexene (TCI chemicals) was distilled under nitrogen before use and was stored under nitrogen. Acetonitrile (HPLC grade) was used as received from Nakalai Tesque. $K_2Pt^{IV}Cl_6$ was used as received from Aldrich. Distilled water was passed through an ion-exchange column (G-10, ORGANO Co.). The electrical conductivity of the water was below 0.1 μ S/cm.

2.2. Measurements

UV-vis spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer. Oxidation potential of SiTMP was measured by cyclic voltammetry with an electrochemical analyzer (Model 611DST, BAS), with a boron doped diamond/glassy carbon as a working electrode, Ag/AgCl as a reference one, and Pt wire as a counter one in acetonitrile containing 0.1 M supporting electrolyte, (C₄H₉)₄N⁺PF₆⁻. An Nd³⁺YAG laser-pumped OPG (EKSPLA, PL 2210JE + PG432JE; FWHM 26 ps, 1 kHz Hz) as the excitation source for measuring the fluorescence lifetime of the Si(IV)TMP. The fluorescence was monitored by a streak camera (Hamamatsu, C4334) equipped with a polychromator (CHROMEX, 250IS). Nanosecond laser flash photolysis was performed with a dyelaser (LUMONICS H-300D, coumarin 540A dye, 590 nm, 8ns fwhm) pumped by an XeCl excimer laser (LUMONICS Hyper EX-300, 308 nm, 12-ns fwhm) and a 500W Xe arc lamp (USHIO 500-DKO)/a light emitting diode (470 nm, Mightex systems) as a monitoring light source equipped with a monochromator (RITSU OYO KOGAKU MC-30, 1200 G/mm), and a photomultiplier tube (HAMAMATSU PHOTONICS R-636). The amplified signal was recorded on a digital storage oscilloscope (GOULD DSO4072, 100 MHz). Transient absorption spectra were obtained with a spectrometric multichannel analyzer (SMA: Princeton Instruments IRY-512) equipped with a polychromator (Jarrell-Ash Monospec-27). The timing was controlled by a digital time delay (STANFORD DG535). All spectral measurements were carried out at room temperature (294 K). Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a TC-17 column (GL Sciences Inc. 30 m, 60-250 C), and a mass spectrograph (Shimadzu QP-5000) as a detector. The practical detection limit of the GC-MS was ca. 10^{-7} M. Quantitative analysis was carried out in the selected ion monitoring (SIM) detection mode.

2.3. Photochemical oxygenation reaction

All of the samples for the photoreactions were degassed by seven repeated freeze-pump-thaw cycles under 10^{-5} torr. The degassed samples in a $1 \times 1 \times 4.5$ cm quartz cell (EIKO-SHA) were irradiated with monochromatic light (420 nm/430 nm) through an interference filter MX0420/a sharp cut-off filter L-39 for 420 nm

and MX0430/L-39 for 430 nm from a 500W Xe arc lamp (USHIO 500-DKO). The photoreaction was monitored with UV-vis spectroscopy. The reaction mixture after the photoreaction was vacuum-distilled and the products were analyzed by GC-MS spectroscopy. All of the procedures were performed at ambient temperature.

2.4. Labeling experiment with the use of ¹⁸O

The ¹⁸O content of the water, $H_2^{18}O/(H_2^{16}O + H_2^{18}O)$, was adjusted to 12.1% by mixing $H_2^{16}O$ and $H_2^{18}O$. The photoreactions were carried out under exactly the same conditions as the experiment carried out with $H_2^{16}O$. The reaction mixtures after the photoreaction were vacuum- distilled, and the content of ¹⁸O in the reaction product was determined by GC-MS (Shimadzu QP-5000).

3. Results and discussion

3.1. Protolytic behaviour of axial ligands of tetra(2,4,6-trimethyl) phenylporphyrinatosilicon(IV) (Si(IV)TMP(OH)₂)

The two hydroxy groups as axial ligands exhibit protolytic equilibria as observed in other metalloporpyrins [10]. Visible absorption spectra of SiTMP under various pH conditions in aqueous acetonitrile solution have clear changes in four-step with four isosbestic points as show in Figs. 1 and 2. From the inflection points of the absorbance at the fixed wavelength, four pKa values were deduced (Fig. 2, Table 1). Fluorescence spectra also changed in four-step and the corresponding four pKa values were also estimated (Table 1, SI-1). ¹H NMR spectra of SiTMP in CD₃CN/ D₂O (9/1 v/v) exhibited systematic peak shifts under the various pH conditions as shown in the supplemental material SI-2.

All these results indicate that SiTMP has the protolytic equilibria among the two axial ligands, hydroxy groups, as shown in Table 1. It should be noted here that the four pKa's of SiTMP are all in acidic region. This is very contrasting to the cases of aluminum-porphyrins that have their pKa's in basic region [9,10]. The large difference between SiTMP and Al-porhyrins could be rationalized by the substantial difference of their electronegativities (E_a (Si) = 1.74, E_a (Al) = 1.47) in addition to the higher valence

state of Si(IV) than Al(III). As a potential half reaction of artificial photosynthetic system, SiTMP can add an option of operating the system under the acidic conditions, while AITMP does it under basic condition.

Before examining the photoreaction of SiTMP, electrochemical characterization was carried out. By means of cyclic voltammetry using boron-doped diamond electrode with wide electrochemical window [11] or glassy carbon in CH₃CN/H₂O (9/1 v/v)), each oxidation peak potential (Eox_p) of each SiTMP species with different axial ligands in protolytic equilibria was estimated (Table 1). Pourbaix diagram between the oxidation peak potential (Eox_p) for each species versus the pH condition is shown in Fig. 3. When a one-electron oxidation process is coupled with proton transfer, the oxidation peak potential (Eox_p) should be linearly dependent upon pH with a slope of 59 mV according to Nernst Equation. The Pourbaix diagram indicates that only SiTMP(OH)₂ species exhibit a proton-coupled one-electron oxidation, while one-electron oxidation of all four other protolytic species are independent on pH conditions.

The excited singlet state of each SiTMP (E_{00}) with different axial ligands in protolytic equilibria under the neutral condition was determined to situate at 2.07 eV by the estimation from the crossing point between the normalized absorption and fluorescence spectra, while the phosphorescence spectrum of SiTMP (OH)₂ in methylcyclohexane at 77 K (λ max = 755 nm) indicates that the excited triplet state has its energy at 1.68 eV. The oxidation potential of SiTMP at around +0.7 ~ 0.9 Volt vs SHE indicates that an electron transfer to K₂PtCl₆ = (E_{red} = +0.76 Volt vs SHE) from the excited SiTMP state should be sufficiently exoergonic either from the S₁ (Δ G = -1.93 ~ -2.13 eV) or the T₁ states (Δ G = -1.54 ~ -1.74 eV).

3.2. Photochemical oxygenation of cyclohexene with water sensitized by silicon (IV) porphyrins with visible light

When SiTMP (1×10^{-5} M) in aqueous acetonitrile (CH₃CN/H₂O (9/1 v/v)) was irradiated with monochromatic visible light of λ = 420 nm (through glass filters of L39/MX0420) or 560 nm (VY54/MZ0560) from Xe lamp (500 W Ushio 500DKO) in the presence of cyclohexene (1×10^{-2} M) as a substrate, K₂PtCl₆ (5×10^{-4} M) as an



Fig. 1. Visible absorption spectra of SiTMP in CH₃CN/H₂O (9/1 v/v) under various pH conditions. Four isosbestic points (circled red) were observed during the reversible change between pH 0.1 and 7. [SiTMP] = 1×10^{-6} M.



Fig. 2. Estimation of pKa's of SiTMP in CH₃CN/H₂O (9/1 v/v) under various pH conditions. The pKa values were estimated from the inflection point of the plot between absorbance at λ = 423, 418, 415 nm, λ max in the spectral change and pH values of the solution. [SiTMP] = 1 × 10⁻⁶ M.

Protolytic equilibria of SiTMP among their axial ligands and oxidation potential of each species in CH_3CN/H_2O (9/1 v/v).

Table 1

	H`o+H Si H'o-H H'+H	$\stackrel{\circ}{} \stackrel{\circ}{\underset{H_{+}^{\circ}}{\overset{\circ}{}}} \stackrel{\bullet}{\leftarrow}$		$\stackrel{o}{\leftarrow} \stackrel{s}{\underset{H^{O}}{\overset{s}}} $	$\stackrel{o}{}_{-o}$
	SiTMP(OH ₂) ₂	SiTMP(OH ₂)(OH)	SiTMP(OH) ₂	SiTMP(OH)(O-)	SiTMP(O ⁻) ₂
$\lambda max/nm$	417.5	418	419	419.5	420.5
Isosbestic point ^{a)}	$\lambda_1 = 41$	8.2nm $\lambda_2 = 417$	7.3nm $\lambda_3 =$	420.8nm $\lambda_4 = 4$	421.5nm
pKa ^{b)}	pKa ₁ =	$= 0.4 pKa_2 = 0.4$	= 1.2	$pKa_3 = 3.7$ pH	$Xa_4 = 4.7$
pKa ^{c)}	pKa ₁ :	$= 0.4 pKa_2 :$	= 1.3	$pKa_3 = 3.6$ pH	$Xa_4 = 4.8$
Eox _p ^{d)} /Volt vs SHE	0.95	0.95	0.86	0.76	0.74

a) Isosbestic point observed in UV-vis spectral change in CH_3CN/H_2O (9/1 v/v).

b) The pKa value estimated from the inflection points in the plot between absorbance and pH value of the solution (Figure 2).

c) The pKa value estimated from the inflection points in the plot between fluorescence intensity and pH value of the solution (SI-1).

 d) First oxidation peak potential of SiTMP with different axial ligands in CH₃CN/H₂O (9/1 v/v) observed in cyclic voltammetry.



Fig. 3. Pourbaix diagram of SiTMP for the first $(Eox_p^{-1}: \triangleleft)$ and second $(Eox_p^{-2}: \square)$ oxidation peaks against pH value of the solution. $[SiTMP] = 5 \times 10^{-5}$ M, $[Bu_4N^+PF_6^-] = 0.1$ M in CH₃CN/H₂O (9/1 v/v). Working electrode: Glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgNO₃.



Scheme 2. Photochemical oxygenation of alkene with water sensitized by SiTMP.

electron acceptor, and KOH $(0 \sim 5 \times 10^{-3} \text{ M})$ under the degassed condition, formation of oxygenated products of cyclohexene were observed (Scheme 2, Table 2). The photochemical reaction products were the corresponding epoxide (cyclohexeneoxide (1), 2-chlorocyclohexanol (2), 2-cyclohexenol (3), cyclohexanone (4), 2-cyclohexenone (5), and 1, 2-dichlorocyclohexane (6), depending on the reaction conditions. (Table 2) The photoreaction proceeds under either Q-band (560 nm) or Soret-band (420 nm) excitation.

Time courses of the visible absorption spectra during the photoreaction are shown in Fig. 4. The concentration of K₂PtCl₆ $(5 \times 10^{-4} \text{ M})$, which can be monitored at around $\lambda = 300 \text{ nm}$, decreased efficiently to be consumed completely with the light irradiation, while the absorbance of SiTMP $(1 \times 10^{-5} \text{ M})$ at around λ = 420 nm gradually decreased down to ~30% under the neutral condition. (Fig. 4(a)) Under the basic condition, however, SiTMP was more stable (Fig. 4(b)-(d)) and remained unchanged at [KOH] = $3 \sim 5$ mM during the photoreaction (Fig. 4(e) and (f)). The apparent turnover number of the catalyst, SiTMP, for the total reaction products on the basis of the catalyst concentration $(1 \times 10^{-5} \text{ M})$ was larger than 30 under the neutral condition (Table 2). The di-chlorinated product (6) was predominant under the neutral and weakly alkaline condition. Under the basic condition, however, the formation of 6 was almost suppressed. It should be noted here that the time of light irradiation required for the complete consumption of K₂PtCl₆ is the longest under the neutral condition, while under basic conditions the reactivity was much enhanced with the increase of the initial concentration of KOH. (Fig. 4) The total amount of the reaction products derived from cyclohexene, on the other hand, decreased with the increase of the initial [OH⁻]. (Table 2) These obviously indicate that hydroxide ion itself is actually involved in the oxidation pathway to compete with cyclohexene, resulting in the suppression of the oxygenation of cyclohexene. Hydroxide ion should exert crucial roles in the process. Though the point is very interesting from the view point of oxidative activation of water and the further study is now in progress, attention is focused here on the oxygenated reaction products. As discussed later, the di-chlorinated product (6) might have a different reaction pathway than that for the other oxygenated reaction products. Among the reaction products, the oxygenated ones except the di-chlorinated product (6) have similar tendency of formation with that in the case of Ru(II)TMP [7,8]. The formation of epoxide (1) was favoured under a weakly alkaline condition ($[OH^-] < 1.5 \text{ mM}$). (Table 2) The formation of the "epoxide" (1) was the highest at $[OH^{-}] = 1.0 \text{ mM}$, while under the neutral and the weakly alkaline conditions ($[OH^-] < 1.0 \text{ mM}$), 2-chlorocyclohexanol (2), was the major component in place of 1 among the oxygenate products. When the photoreaction was started under the neutral condition without adding KOH, the

Table 2

Photochemical oxygenation of cyclohexene sensitized by SiTMP in CH₃CN/H₂O (9/1 v/v). Yield of each reaction product, **1–6**, with or without KOH added to the reaction mixture with visible light irradiation (λ = 420 nm) under degassed condition. [SiTMP] = 1 × 10⁻⁵ M, [K₂PtCl₆] = 5 × 10⁻⁴ M, [Cyclohexene] = 1 × 10⁻² M.

	Yield/ µM										
[KOH] /mM	\bigcirc	ССС	OH			CI	Total Yield				
	1	2	3	4	5	6					
0	1.0	16.5	6.7	0.0	0.0	312.9	337.2				
0.5	0.7	11.9	5.9	1.3	1.3	141.8	162.6				
1.0	3.4	2.8	4.2	1.8	2.1	33.4	47.7				
1.5	2.1	0.5	5.9	2.7	4.8	10.9	26.9				
3.0	0.1	0.1	1.6	0.1	4.2	0.0	6.1				
5.0	0.1	0.1	0.8	0.0	2.7	0.0	3.7				



Fig. 4. Time course of visible absorption spectra during the photochemical oxygenation of cyclohexene $(1 \times 10^{-2} \text{ M})$ sensitized by SiTMP $(1 \times 10^{-5} \text{ M})$ in the presence of K₂PtCl₆ (5 × 10⁻⁴ M) with KOH in CH₃CN/H₂O (9/1 v/v) with optical length corresponding to 2.5 mm: (a) [KOH] = 0 mM, the photoreaction for 365 min, (b) [KOH] = 0.5 mM, the photoreaction for 237 min, (c) [KOH] = 1 mM, the photoreaction for 224 min, (d) [KOH] = 1.5 mM, the photoreaction for 112 min, (e) [KOH] = 3 mM, the photoreaction for 91 min, (f) [KOH] = 5 mM, the photoreaction for 30 min.

reaction mixture became acidic after the photoreaction with the pH value to be \sim 3, due to the HCl formation as expected by Eq. (1). Under the acidic condition (pH 3) in the presence of HCl, the epoxide (1) was observed to be transformed into 2-chlorocyclohexanol (2). The formation of 2 in the photoreaction was thus considered to be derived from the epoxide (1) through the reaction with HCl generated during the photoreaction (Eq. (1)). The selectivity of epoxide formation among the oxygenated products except the dichlorinated one (6) in the photoreaction was thus suggested to be modified by adding the contribution of 2 to be 72.3% (4.2% (1)+68.1% (2)=72.3%) under the neutral condition (Table 2).

The experiments using $H_2^{18}O$ indicated that the source of oxygen atom in the oxygenated reaction products was derived from water. The degree of ¹⁸O uptakes (%) in each reaction product using $H_2^{16}O-H_2^{18}O$ (90:10) at [KOH] = 1.5 mM were **1** (14.9%), **2** (8.2%), **3** (9.7%), **4** (8.4%), and **5** (10.5%). When other substrates such as norbornene, styrene, and 1-hexene were examined for the photochemical oxygenation sensitized by SiTMP in the similar condition ([KOH] = 1.5 mM in CH₃CN/H₂O (9/1 v/v)), very interestingly, highly selective epoxidation was observed for norbornene (97.6%) and moderate one for styrene (45.9%), while almost no reaction was observed for 1-hexene (Table 3). The reactivity is

rather contrasting to the case of AITMP which showed highly selective reaction with cyclohexene, but has no reaction with other alkenes [9]. The quantum yield of the photochemical oxygenation of cyclohexene by SiTMP under the neutral condition as a typical case was measured at the early stage of the photoreaction to be 1.2%, rather low compared to those obtained with Ru(II)TMP [7,8]. The lower quantum yield might be ascribed to the lower oxidation ability of the sensitizer SiTMP (E_{ox} = +0.74 V vs. SHE under the neutral condition) than that of Ru(II)TMP (E_{ox} = +1.03 V vs. SHE).

3.3. Excited state of Si(IV)TMP responsible for the photochemical oxygenation of cyclohexene and the reaction mechanism

To get insight into the excited state of SiTMP responsible for the photoreaction and the reaction mechanism, quenching experiment for both the singlet and triplet excited state of SiTMP were carried out. As discussed above an electron transfer to K₂PtCl₆ should be sufficiently exo-ergonic either from the excited singlet (ΔG = -1.93~ -2.13 eV) or the triplet state (ΔG = -1.54~ -1.74 eV) of SiTMP. The excited states quenching experiments by K₂PtCl₆ were carried out to examine which excited state is actually responsible in the reaction mixture. The fluorescence of SiTMP(O⁻)₂ under the neutral conditions (τ_F = 5.9 ns, $1/\tau_F$ = 1.7 × 10⁸ s⁻¹) was not

Table 3

Photochemical oxygenation of alkenes sensitized by SiTMP in CH₃CN/H₂O (9/1 v/v). Yield of each reaction product, selectivity in parenthesis with addition of KOH $(1 \times 10^{-3} \text{ M})$ with visible light irradiation (λ = 420 nm) under degassed condition. [SiTMP] = 1 × 10⁻⁵ M, [K₂PtCl₆] = 5 × 10⁻³ M.



quenched by the addition of Pt(IV)Cl₆²⁻ (0.5 mM), while the triplet excited state ($\tau_{\rm T}$ = 2.2 ms, $1/\tau_{\rm T}$ = 4.5 × 10² s⁻¹) was effectively quenched by Pt(IV)Cl₆²⁻ with a quenching constant *k* = 9.6 × 10⁶ $M^{-1}s^{-1}$. The photochemical oxygenation is thus concluded to proceed through an electron transfer to K₂PtCl₆ from the excited triplet state of the SiTMP. Since the rate of electron transfer is estimated to be rather slow in the range of 5×10^6 $s^{-1}(10^{10}(diffusion controlled rate constant) \times [K_2PtCl_6](5 \times 10^{-4})$ $\begin{array}{ll} M) = 5 \times 10^{6} \, \mathrm{s}^{-1}) \sim 4.8 \times 10^{3} \, \mathrm{s}^{-1} & (k_{\mathrm{et}} = k(9.6 \times 10^{6} \, \mathrm{M}^{-1} \, \mathrm{s}^{-1}) \times [\\ \mathrm{K_2PtCl_6}](5 \times 10^{-4} \, \mathrm{M}) = 4.8 \times 10^{3} \, \mathrm{s}^{-1}), \ \text{it cannot compete with the} \end{array}$ decay of the singlet state $(1.7 \times 10^8 \text{ s}^{-1})$. As regards the reaction mechanism, four intermediates were actually detected in the case of Ru(II)TMP [7,8]. The similar ones are presumed to have key roles also in the photochemical oxygenation sensitized by SiTMP. A deeper insight can be obtained by estimating the electronic structure of the one-electron oxidized species of SiTMP generated by the electron transfer from the triplet excited SiTMP. Spin densities of the one-electron-oxidized SiTMP(OH)₂ (at pH 3), SiTMP(OH)(O⁻)(at pH 4) and SiTMP(O⁻)₂(at pH 7) were estimated by density functional theory (DFT) calculations (Gaussian09 rev. D01 B3LYP/6-31G*). The electron spin densities have been revealed to have exclusive populations localized on the deprotonated axial ligand as -O•in the latter two cases. These strongly suggest that the axially ligating hydroxy group on the central Si atom suffers an oxidative activation to become oxyl-radical through the deprotonation and one-electron oxidation as shown in Fig. 5(a) and (b).



Scheme 3. Mechanism of the visible light induced photooxygenation of cyclohexene sensitized by SiTMP in aqueous acetonitrile at pH 4.

The similar spin densities on the axial –OH group and the further deprotonated $-O^-$ were also suggested in the case of Ru(II)TMP [7,8,12] and AITMP [9] to rationalize the selective epoxide formation. The formation of the oxygenated reaction products in Tables 2 and 3 could be thus explained by the similar mechanism as revealed in the photochemical oxygenation of cyclohexene with water sensitized by Ru(II)TMP [7,8]. The one electron oxidized form of SiTMP generated through an electron transfer to $PtCl_6^{2-}$ has oxyl-radical nature of the axial ligand and thus suffers the attack of alkene to form the corresponding oxygenated compound through the subsequent second electron transfer from the intermediate to $PtCl_6^{2-}$ as shown in Scheme 3.

As regards the formation of di-chlorinated product (6) only observed under the neutral and weakly alkaline condition, the following mechanism could be operating. The electron spin in the one-electron oxidized species of SiTMP with different axial $-H_2O_1$, -OH, $-O^{-}$ group, depending on the pH condition of the reaction mixture, has different population as shown in Fig. 4. Since the nondeprotonated species, SiTMP(OH)₂, which is predominantly exist in acidic conditions (1.2 < pH < 3.7) as the pKa measurements indicate in Table 1, the electron spin is delocalized on the porphyrin ring without activating the axial hydroxy group (Fig. 5(c)). The photooxygenation is considered to proceed on the activated oxylradical form of the axial ligand of the one-electron oxidized SiTMP $(OH)O^{-}$) or SiTMP $(O^{-})_2$, but is silent for the delocalized spin on the porphyrin ring of SiTMP(OH)₂ which rather suffers electron transfer from Cl- ion in the reaction mixture to form chloride radical inducing the dichlorinated reaction product.

In the present system, the sacrificial electron acceptor, $Pt(IV) Cl_6^{2-}$, serves as a crucial role to drive the photoreaction. Since the photoreaction with most abundant Si atom within the molecule can be accepted as one of the promising candidates of the half reactions for oxidative activation of water molecule, further development to visible light induced artificial photosynthesis system coupled with TiO₂, as reported in the case of Sn(IV)TCPP (tetra(4-carboxy) phenylporphyrinatotin(IV))/TiO2 [13] to evolve



Fig. 5. Spin population of the one-electron oxidized SiTMP(O⁻)₂ (a), SiTMP (O⁻)(OH) (b), and SiTMP(OH)₂ (c) calculated by Gaussian09 rev.D01 B3LYP/6-31G*.

hydrogen in the reduction terminal end with simultaneous formation of useful oxygenated substrate in the oxidation terminal end, is now in progress. Si-porphyrins with easily available, abundant element would serve as most promising sensitizers which enable to induce the two-electron oxidative activation of water.

Supplementary information

Supplementary information (SI) available: fluorescence spectral changes of Si(IV)TMP (SI-1), ¹H NMR spectra of Si(IV)TMP under various pH condition (SI-2).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jphotochem.2015.07.016.

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