



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



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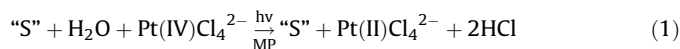
## ABSTRACT

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  $H_2^{18}O$ . 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 reaction.

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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)).



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-flux-density 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.

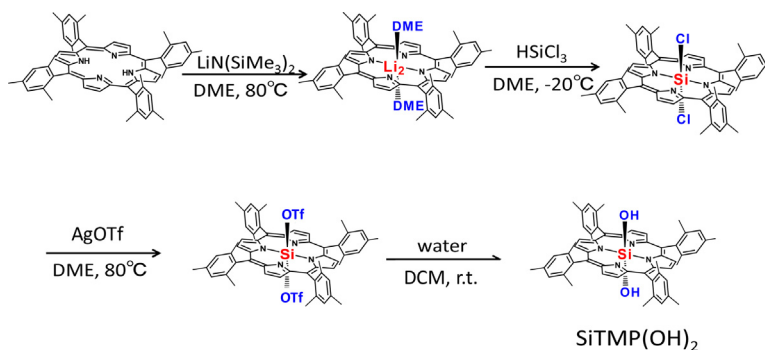
## 2. Experimental

### 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)<sub>2</sub>

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)<sub>2</sub>.

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 tetramesitylporphyrin (H<sub>2</sub>TMP: 399 mg, 0.51 mmoles) was taken in a reaction pot and cooled 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 HSiCl<sub>3</sub> (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 SiO<sub>2</sub> 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)<sub>2</sub> 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)<sub>2</sub>](<sup>1</sup>/<sub>2</sub> H<sub>2</sub>O·C<sub>6</sub>H<sub>14</sub>·<sup>1</sup>/<sub>4</sub> CH<sub>2</sub>Cl<sub>2</sub>), C 77.92%, H 7.30%, N 5.84%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 8.63 (s, 8H), 7.18 (s, 8H), 2.54 (s, 12H), 1.85 (s, 24H), –3.04 (s, 1.4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 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). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ = –202.77 (s). UV–vis: ε = 5.06 × 10<sup>5</sup> M<sup>–1</sup> dm<sup>–3</sup> (λ<sub>max</sub> = 422.5 nm in CHCl<sub>3</sub>). 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 (HSiCl<sub>3</sub>) 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<sub>2</sub>Pt<sup>IV</sup>Cl<sub>6</sub> 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 μS/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, (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>–</sup>. An Nd<sup>3+</sup>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 dye-laser (LUMONICS H-300D, coumarin 540A dye, 590 nm, 8-ns 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<sup>–7</sup> 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<sup>–5</sup> torr. The degassed samples in a 1 × 1 × 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

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