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Journal Name

ARTICLE

Synthesis of water-soluble silicon-porphyrin: Protolytic behaviour of axially coordinated hydroxy groups

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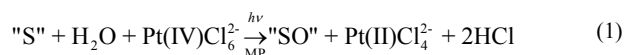
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A new water-soluble silicon (IV)-tetra(4-carboxyphenyl)porphyrin (SiTCPP) with silicon (IV) in the center of porphyrin as the second most abundant element on Earth was synthesized. Fundamental properties including protolytic behaviour of axially coordinating hydroxy groups, electrochemical behaviour were characterized. The properties were compared with those of silicon(IV)-tetra(2, 4, 6-trimethylphenyl)porphyrin (SiTMP) and silicon(IV)-tetra(4-trifluoromethylphenyl)porphyrin (SiTFMPP) and discussed in respect to electron donating/withdrawing effect of the substituents. Two axially coordinating hydroxy groups of SiTCPP exhibit a four-step protolytic behaviour in the acidic condition along with a single step protolysis of peripheral carboxyl groups. Though SiTCPP and SiTFMPP did not show any reactivity for the photochemical oxygenation of substrate with K_2PtCl_6 as a sacrificial electron acceptor, the first oxidation wave in electrochemical process of SiTCPP and SiTFMPP showed catalytic behaviour in aqueous acetonitrile solution at any pH conditions, contrasting to SiTMP which has only a reversible oxidation wave under the neutral and weakly acidic conditions. The criteria of the electrochemical oxidative activation of water and the photooxygenation of substrate were obtained. The higher oxidation wave of Si-porphyrins than ~ 0.86 Volt vs SHE is required for the electrochemical oxidation of water, while proper protecting group such as methyl substituent is requisite for the photochemical oxygenation with K_2PtCl_6 as sacrificial electron acceptor.

Introduction

Porphyrins are unique compounds which can incorporate almost all kinds of element within their ring as the central atom.^{1, 2} Silicon (IV) ion is also able to be the central ion species within porphyrins. Silicon (IV)-porphyrins have attracted much attention, since silicon is the second most abundant and easily available element on the Earth.³⁻¹⁰ Synthesis of several neutral silicon-porphyrins have been reported,³⁻⁸ while photochemical behaviour of them has been rarely reported.^{9, 10} Recently we have found an unique 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-trimethylphenyl)porphyrinosilicon (SiTMP) as the first example of a photocatalytic reaction with water induced by silicon porphyrins.¹¹ The visible light induced oxygenation of substrate by water would be most interesting for the viewpoint of artificial photosynthesis. Artificial photosynthesis by visible light is one of the most desirable chemical systems at present as well as other probable renewable energy methodologies. Among the problems to be

resolved for the realization of artificial photosynthesis, one of the most crucial issues should be on how could water molecules be utilized as an electron source in the redox system.^{12, 13} 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.¹³⁻²³ (eq. 1)



, where “S”, “SO”, MP denote substrate, oxygenated substrate, and metalloporphyrins, respectively. Two-electron conversion was involved in the net chemistry of equation (1), which was actually demonstrated to be induced by one-photon by a laser flash photolysis study.²³ After the first electron transfer from the excited triplet state of Ru-porphyrin, in the delayed time region the second electron transfer to electron acceptor from an adduct intermediate between the one-electron oxidized Ru-porphyrin and cyclohexene as the substrate was clearly observed.²³ In applying an actual sunlight radiation as the light source for artificial photosynthetic system, the photo-system should solve and get through the “photon-flux-density problem” of sunlight radiation with rather weak light intensity.¹³ As a half reaction of artificial photosynthesis in the oxidation side, the two-electron oxidative activation of water by one-photon excitation (eq. 1) thus would be the more plausible alternative than a four-electron oxidation by stepwise four-photon excitation. The former, which can

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Electronic Supplementary Information (ESI) available: fluorescence spectral changes of SiTCPP, visible absorption spectral changes of SiTCPP in water under various pH condition, fluorescence decay profiles of SiTCPP in aqueous acetonitrile, phosphorescence spectra of SiTCPP and SiTFMPP, visible absorption spectra of SiTFMPP in aqueous acetonitrile under various pH conditions, contact molecular surface area of carbon atoms in meso-position. See DOI: 10.1039/x0xx00000x

proceed with only one-photon and does not need to wait for the next photon, can avoid the “photo-flux-density problem,” while the latter requires stepwise four-photon excitation and faces directly with the problem.¹³ Another crucial issue, furthermore, to be resolved would be to explore ways to utilize major elements for the artificial photosynthetic system rather than rare elements.^{11, 24-26} From both viewpoints, Si-porphyrins with the second most abundant element, which can exert a two-electron oxidation of water, are very attractive compounds. Here we will report synthesis of new water-soluble Si-porphyrin viewing over a possible approach for the purpose. In designing an artificial photosynthesis system, fundamental characteristics of sensitizer/catalyst such as protolytic equilibria, excited energy and redox nature are very crucial, because the characterization in the actual aqueous solution under various pH conditions affords the information on which species is excited and which form is serving as a catalyst. Here the fundamental properties of the water soluble Si-porphyrins will be also reported.

Experimental

Materials and Methods

Synthesis of trans-dihydroxo [5, 10, 15, 20-tetra(4-carboxyphenyl)porphyrinato] silicon (IV) : Si(IV)TCPP(OH)₂

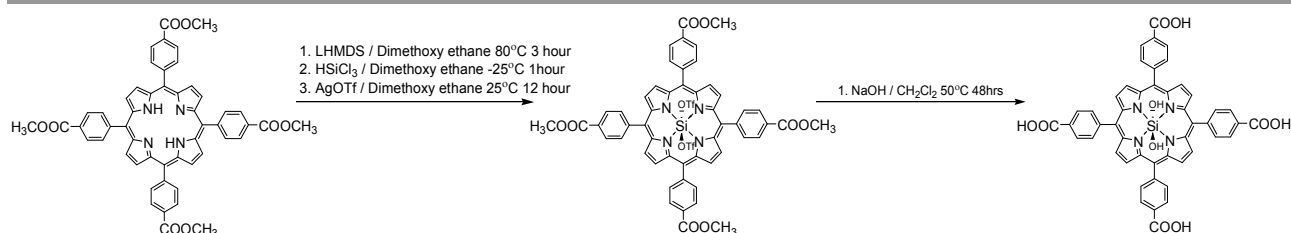
SiTCP was synthesized by a method similar to that reported by Kane and coworkers.⁶ In a typical method 50ml of dimethoxyethane (DME) was added to 150mg of free base 5, 10, 15, 20-tetra(4-methoxycarbonylphenyl)porphyrin (H₂TCPP MeESTER) and stirred at 50 °C for 30 minutes. To the solution a little excess of lithium bis(trimethylsilyl)amide (LHMDS) was added and stirred at 80 °C for 3 hours. After 3 hours UV visible spectrum of the reaction mixture was measured, a red shift of Soret band to 442nm from 416nm indicated the completion of reaction to form the lithium salt of pophyrin dianion (Li₂(TCPPMeESTER)). The reaction mixture was then cooled to -25 °C and kept at that temperature for 1 hour. To the reaction mixture, 20 μL of trichlorosilane (HSiCl₃) was added and stirred at -25 °C for 30 minutes. The reaction pot was then slowly warmed up to room temperature and stirred for 1 hour. Then UV-Vis spectrum was measured to confirm a blue shift of Soret band to 434nm from 442 nm, indicating the completion of reaction to form silicon inserted porphyrins, SiCl₂TCPPMeESTER. The reaction mixture was then slowly warmed up to 80 °C and excess amount of silver(I) trifluoromethanesulfonate (AgOTf) was added. The reaction mixture was kept for one overnight and UV visible spectrum

was recorded to confirm a blue shift of Soret band to 418 nm from 434 nm, indicating the substitution of chloride ions with trifluoromethanesulfonate ions (OTf) as the two axial ligands on silicon atom to form SiTCPMeESTER(OTf)₂. The reaction mixture was then filtered through polytetrafluoroethylene membrane (0.1 μm, PTFE). After the red-purple filtrate was dried, it was then stirred for 3 days in a 1:1 mixture of dichloromethane (DCM) and aqueous NaOH(1M) solution. The aqueous layer was separated and acidified to get pink colored precipitate of SiTCP(OH)₂. The precipitate was then collected by filtration through 0.1 μm PTFE and washed with hot HCl aqueous solution and water several times to get pure SiTCP(OH)₂.

EA: Obsd. C 65.99%, H 3.91%, N 6.22 %, Calcd. for [Si(IV)TCPP(OH)₂](H₂O), C 66.35%, H 3.71 %, N 6.45 %. ¹H-NMR (D₂O, pH=12) : δ = 9.06 (s, 8H), 8.24 (d, J = 6.36Hz, 8H), 8.21 (d, J = 6.36Hz, 8H). ¹³C-NMR (D₂O, pH=12): δ = 115.17(s), 127.50(s), 131.86(s), 134.10(s), 143.59(s), 161.73(s), 175.65(s). ²⁹Si-NMR (D₂O, pH=12): δ = -204.92(s). UV-viz: ε = 5.07 × 10⁵ M⁻¹dm⁻³ (λ_{max} = 417.5 nm in H₂O, pH=11), 1.76 × 10⁴ M⁻¹dm⁻³ (λ = 550nm in H₂O, pH=11). ESI-MS (positive mode): m/z = 847.32.

Synthesis of trans-dihydroxo [5, 10, 15, 20-tetra(4-trifluoromethylphenyl)porphyrinato] silicon (IV) : Si(IV)TFMPP(OH)₂

Fifty ml of DME was added to 100mg of free base 5, 10, 15, 20-tetra(4-trifluoromethylphenyl)porphyrin (H₂TFMPP) and stirred at 80 °C for 30 minute. To the solution 40 mg of LHMDS was added and stirred at 80 °C for 3 hours. After 3 hours UV visible spectrum of the reaction mixture was measured to confirm a red shift of Soret band to 436 nm from 414 nm, indicating the completion of reaction to form the lithium salt of pophyrin dianion (Li₂TFMPP). The reaction mixture was then cooled down to -25 °C and kept at that temperature for 1 hour. To the reaction mixture 0.2ml of HSiCl₃ was added and stirred at -25 °C for 30 minutes. The reaction pot was then slowly warmed up to room temperature and stirred for 1 hour. An UV-Vis spectrum was measured to confirm a blue shift of Soret band to 431 nm from 436nm indicating the completion of reaction to form SiTFMPP(Cl₂). The reaction mixture is then slowly warmed to 25 °C and excess amount (144 mg) of AgOTf was added. The reaction mixture was kept for one overnight and UV visible spectrum measured. A blue shift of Soret band to 418.4 nm from 431 nm indicated the formation of SiTFMPP(OTf)₂. The reaction mixture was then filtered



Scheme 1 Synthesis of trans-dihydroxo [5, 10, 15, 20-tetra(4-carboxyphenyl)porphyrinato] silicon (IV) : Si(IV)TCPP(OH)₂

through 0.1 μm PTFE to collect red-purple solid and subsequently be dried. The crude crystal was further stirred for 48 hours in a 1:1 mixture of DCM: aqueous solution of NaOH(1M). The aqueous layer was separated and purified by silica gel column chromatography using DCM as an eluent.

¹H-NMR (CDCl₃): δ = 8.88 (s, 8H), 8.26 (d, J = 5.0Hz, 8H), 8.03 (d, J = 5.0Hz, 8H). ¹³C-NMR (CDCl₃): δ = 116.53(s), 124.21(s), 128.82(s), 134.19(s), 134.89(s), 143.28(s), 167.75(s). ¹⁹F-NMR (D₂O): δ = -62.23(s). ²⁹Si-NMR (D₂O): δ = -200.83(s). UV-viz: ϵ = $4.57 \times 10^5 \text{ M}^{-1}\text{dm}^{-3}$ (λ_{max} = 420 nm in acetone), $1.77 \times 10^4 \text{ M}^{-1}\text{dm}^{-3}$ (λ_{max} = 552 nm in acetone). ESI-MS (negative mode): m/z = 946.17.

Other materials

trans-Dihydroxo [5, 10, 15, 20-tetra(2, 4, 6-methylphenyl)porphyrinato] silicon (IV) (Si(IV)TMP(OH)₂) was synthesized as reported elsewhere.¹¹ Dimethoxyethane (DME) purchased from TCI chemicals was stored over molecular sieves (4A), dried over Na, and was vacuum transferred prior to use. Lithium bis(trimethylsilyl)amide (LHMDS) solid was purchased from Aldrich and stored in dry condition. Trichlorosilane (HSiCl₃) was purchased from TCI chemicals. Silver trifluoromethanesulfonate (AgOTf) was purchased from TCI chemicals. Cyclohexene (Tokyo Kasei) was distilled under nitrogen before use and was stored under nitrogen. Acetonitrile (HPLC grade) was used as received from Nakarai Tesque. K₂Pt^{IV}Cl₆ 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 $\mu\text{S}/\text{cm}$.

Measurements

UV-visible spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer. Fluorescence quantum yield of each species of SiTCPP in protolytic equilibria was determined in CH₃CN/H₂O (8/2 v/v; refractive index = 1.3473²⁷ by excitation at 540 nm under the condition with absorbance at 540 nm being smaller than 0.02. Free base tetraphenylporphyrin (H₂TPP) was taken as the reference molecule (fluorescence quantum yield = 0.110 in toluene.²⁸ Oxidation peak potentials of Si-porphyrins were measured by cyclic voltammetry with an electrochemical analyzer (Model 611DST, BAS), with a boron doped diamond as a working electrode, Ag/AgCl or Ag/AgNO₃ as a reference one, and Pt wire as a counter one in dimethylformamide (DMF), acetonitrile/aqueous acetonitrile, or water containing 0.1 M supporting electrolyte, (C₄H₉)₄N⁺PF₆⁻. An Nd³⁺YAG laser-pumped OPG (EKSPLA, PL2210JE + PG432-JE; FWHM 26 ps, 1

kHz) as the excitation source for measuring the fluorescence lifetime of Si-porphyrins. The fluorescence was monitored by a streak camera (Hamamatsu, C4334) equipped with a polychromator (CHROMEX, 250IS).

Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a TC-17 column (GL Sciences Inc. 30m, 60-250C), and a mass spectrograph (Shimadzu GCMS-2010SE) 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.

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 × 1 × 4.5cm quartz cell (EIKO-SHA) were irradiated with monochromatic light (420nm/430nm) through an interference filter MX0420/a sharp cut-off filter L-39 for 420 nm, MX0430/L-39 for 430 nm, and VY54/MZ0560 for 560 nm from a 500W Xe arc lamp (USHIO 500-DKO). The photoreaction was monitored with UV-visible 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.

Results and discussion

Protolytic behaviour of axial ligands of tetra(4-carboxyphenyl)porphyrinatosilicon(IV) (Si(IV)TCPP(OH)₂)

The new water soluble Si-porphyrin, SiTCPP(OH)₂, synthesized here has two hydroxyl group as the axial ligands to the central Si atom as revealed by the characterization described in the experimental part. The two axially ligating hydroxyl groups exhibit protolytic equilibria as observed in other metalloporphyrins.²⁵ Visible absorption spectra of SiTCPP under various pH conditions in aqueous acetonitrile solution (CH₃CN/H₂O (8/2 v/v)) are shown in Figure 1.

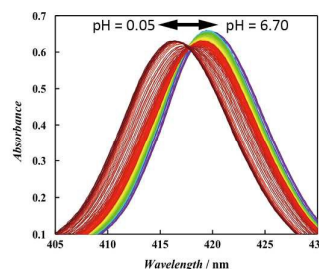


Figure 1. Visible absorption spectra of SiTCPP under the various pH conditions: [SiTCPP] = $1.2 \times 10^{-6} \text{ M}$ in CH₃CN/H₂O (8/2 v/v), pH (= 6.8~0.1) value was adjusted by the addition of HCl aqueous solution.

Table 1. Fundamental properties of SiTCPP in CH₃CN/H₂O (8/2 v/v).

λ_{max} Of Absorption /	417	419	419	420	420	420
λ_{max} Of Emission / nm	601, 645	602, 656	601, 653	601, 652	602, 654	602, 655
pKa		0.71	1.96	3.56	5.32	5.83
E_{00} / eV ^{a)}	2.08	2.07	2.08	2.08	2.08	2.07
τ_{flu} / ns ^{b)}	5.42	6.40	6.08	5.67	5.90	5.87
Q_{flu} ^{c)}	0.12	0.12	0.12	0.13	0.14	0.14
E_{oxp}^1 ^{d)} , E_{oxp}^2 ^{e)} / Volt	1.00, 1.40	0.95, 1.24	0.90, 1.17	0.88, 1.14	0.88, 1.14	0.88, 1.11
E_{redp}^f / Volt	-1.45	-1.45	-1.48	-1.48	-1.48	-1.48

a) Energy of the lowest singlet state estimated from the crossing point between absorption and fluorescence spectra.

b) Fluorescence lifetime of each species in protolytic equilibria.

c) Fluorescence quantum yield of each species in protolytic equilibria.

d) The first oxidation peak potential.

e) The second oxidation peak potential.

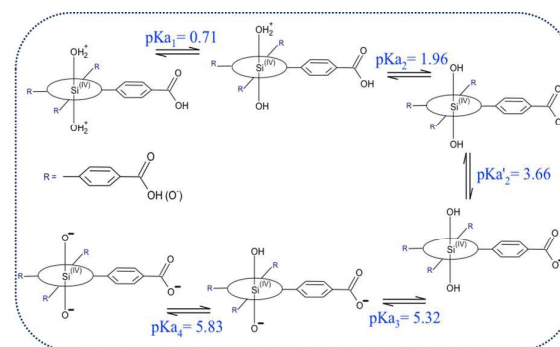
f) The reduction peak potential.

The λ_{max} of Soret band under the neutral condition ($\lambda = 420$ nm) gradually shifted to the blue down to 417 nm under the more acidic condition with pH below 0.7. They have clear changes in five-step with five isosbestic points. The spectral changes were completely reversible when the pH conditions were reversibly varied. From the inflection points of the absorbance at the fixed wavelength, five pKa values were deduced (Figure 2, Scheme 2, Table 1). Fluorescence spectra also reversibly changed in five-step and the corresponding five pKa values were also estimated (Table 1, Electronic Supplementary Information 1 (ESI-1)). Systematic peak shifts of ¹H-NMR spectra of SiTCPP in CD₃CN/D₂O (8/2 v/v) were observed under the various pH conditions as shown in Figure 3

The peaks of both phenyl and pyrrole protons shifted to the lower magnetic field by decreasing the pH of the solution. (Figure 3) Among them the peak shifts were the most obvious between pH = 4.5 ~ 3.0 (Figure 3) along with sudden decrease of the solubility in water as shown in ESI-2. Since the λ_{max} of SiTCPP in the visible absorption spectrum in water under the pH region (4.5~3.0) did not change even with the sudden change of the solubility, the change was thus assigned as the

values were estimated from the inflection point in the plot. (pKa₁ = 0.71, pKa₂ = 1.96, pKa'₂ = 3.56, pKa₃ = 5.32, pKa₄ = 5.83).

protolysis of peripheral carboxylic group (pKa₃ = 3.66). Similar sudden change of solubility in water was also observed in the case of Al(III)TCPP.²⁵ All these results indicate that SiTCPP has the protolytic equilibria among the two axial ligands, hydroxy groups, along with the peripheral carboxyl group as shown in Scheme 2.



Scheme 2 Protolytic equilibria among axial ligands and peripheral carboxylic substituents of SiTCPP.

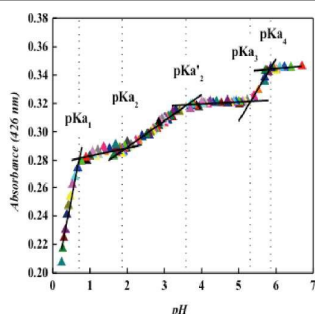


Figure 2. Change of absorbance in the visible absorption spectra of SiTCPP (1.2×10^{-6} M in CH₃CN/H₂O (8/2 v/v) observed at $\lambda = 426$ nm under various pH conditions: The pKa

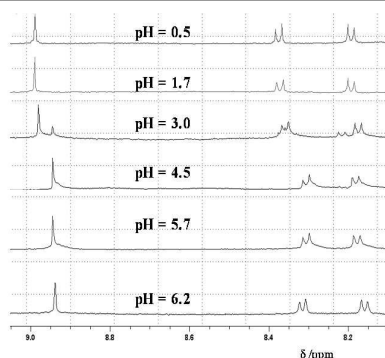


Figure 3. ^1H -NMR spectra of SiTCPP in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$ (8/2 v/v) under the various pH conditions.

Table 2. Effect of substituent on the pKa value of the axial ligand and electrochemical oxidation behavior of Si-porphyrins in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8/2 v/v).

SiTMP	pKa		0.4	1.2	3.7	4.7	
	E^1_{oxp} vs. SHE	0.95 ^{a)}	0.95 ^{a)}	0.86 ^{a)}	0.76 ^{b)}	0.74 ^{b)}	
SiTCPP	pKa		0.71	1.96	5.32	5.83	
	E^1_{oxp} vs. SHE	1.00 ^{a)}	0.95 ^{a)}	0.90 ^{a)}	0.88 ^{a)}	0.88 ^{a)}	
SITFMPP	pKa		0.04	0.5	1.7	3.5	
	E^1_{oxp} vs. SHE	1.06 ^{a)}	1.03 ^{a)}	1.02 ^{a)}	0.94 ^{a)}	0.87 ^{a)}	

a) Catalytic wave

b) Reversible wave

As already observed in the case of SiTMP(OH)₂ (*trans*-dihydroxo [5, 10, 15, 20-tetra(2, 4, 6-methylphenyl)porphyrinato] silicon (IV)), the protolytic equilibria of SiTCPP are all in acidic region. This is very crucial characteristic of Si-porphyrins as described later. Since the fluorescence spectra showed similar five-step changes, the fluorescence lifetime of each species with different axial ligands in protolytic equilibria was measured by a single photon counting condition. One of the curious points should be whether or not the excited states of SiTCPP are also in protolytic equilibria (dynamically allowed equilibria) as observed in the ground states. Their lifetimes were compared in Table 1. Very interestingly, the time resolved fluorescence intensities had all single exponential decay profiles as shown in ESI-3. These indicate that each species in protolytic equilibria in the ground state among the axial hydroxy groups decays independently in the excited singlet state without mutual interconversion.

These suggest that the rates of interconversion in their singlet excited states are much slower than their decay rates in the order of several nano seconds. Among the crucial fundamental photophysical properties, the excited singlet state energy of each SiTCPP ($^1E_{00}$) with different axial ligands in protolytic equilibria under the neutral condition was determined to situate at around 2.07~2.08 eV by the estimation from the crossing point between the normalized absorption and fluorescence spectra, while the phosphorescence spectrum of SiTCPP in ethanol at 77 K (λ_{max} =

762 nm) indicates that the excited triplet state has its energy at ~1.63 eV. (ESI-4)

To get deeper insight into the protolytic equilibria, another Si-porphyrins, *trans*-dihydroxo [5, 10, 15, 20-tetra(4-trifluoromethylphenyl)porphyrinato]silicon (IV) (SiTFMPP(OH)₂), was further prepared for comparison by hydrolysis of Si(IV)TFMPP(OTf)₂ with two trifluoromethanesulfonate groups as the axial ligands.^{4, 6} SiTFMPP(OH)₂ exhibited also similar protolytic four-step equilibria with four isosbestic points in its visible absorption spectrum under various pH conditions. (ESI-5) The pKa values of SiTFMPP were also estimated similarly with SiTCPP and tabulated in Table 2. The pKa values of SiTFMPP indicate that the protolytic equilibria is also all in acidic region. The pKa values of the three Si-porphyrins (SiTMP, SiTCPP, and SiTFMPP) for their protolytic equilibria of axial ligands are compared in Table 2. As shown in Figure 4, each pKa value is basically understood to reflect the difference of electronic character of substituents on the peripheral phenyl group. The pKa value in each step is the smallest in SiTFMPP with strongly electron withdrawing $-\text{CF}_3$ group (with Hammett constant, $\sigma = 0.53$), becomes larger in SiTCPP with moderately electron withdrawing $-\text{COOH}$ ($\sigma = 0.44$), and does the largest for SiTMP with modestly electron donating $-\text{COO}^-$ ($\sigma = -0.05$). These clearly indicate that electronic effect of *meso*-substituted phenyl group is actually operating on the axial hydroxy group through the central silicon atom. On the other hand, SiTMP with the most electron donating $-\text{CH}_3$ group in *para*-position ($\sigma = -0.14$) among the group showed a bit smaller pKa value

than SiTCPP with COO^- ($\sigma = -0.05$). This looks rather irregular for a simple anticipation of the order of electron donating and withdrawing properties. Since Si-TMP has two CH_3 groups in the *ortho*-position of the *meso*-substituted phenyl group, some steric effect against the adjacent pyrrole hydrogen atoms may induce other factor than the simple electronic effect. Even the *meso*-substituted phenyl groups without substituents on them

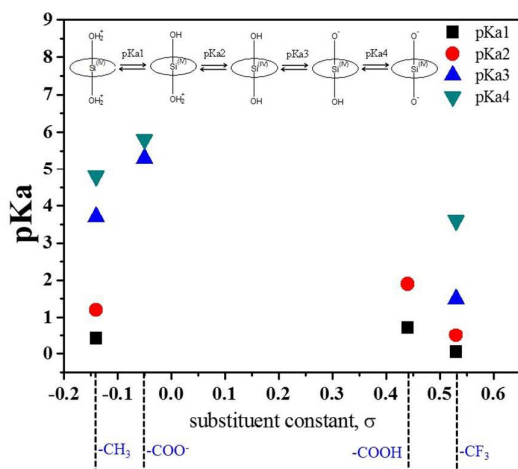


Figure 4. Effect of substituents in para- position of the *meso*-substituted phenyl group of Si-porphyrins on the pKa of axial ligands.

have already some steric strain between the *ortho*-hydrogen atoms of the phenyl groups and pyrrole hydrogen atoms to avoid coplanar conformation between the porphyrin ring and phenyl groups. The introduction of bulky methyl groups, thus, would induce more steric strain between them. To check this possibility, structural analyses of the three Si-porphyrins were carried out by DFT calculation (Gaussian09, B3LYP/6-31G*). The structurally optimized dihedral angles between the porphyrin and the *meso*-substituted phenyl rings were compared among the fully deprotonated species, SiTMP(O)₂, SiTCPP(O)₂, and SiTFMPP(O)₂. Interestingly, the dihedral angle of bulky SiTMP(O)₂ was calculated to be almost perpendicular (89.8°), while SiTCPP(O)₂, and SiTFMPP(O)₂ had 64.2° and 66.1°, respectively. The optimized structure well rationalize the irregular deviation of the pKa values for SiTMP. The perpendicular dihedral angle in SiTMP(O)₂ indicates that there should be almost no π -conjugation between the porphyrin ring and the *meso*-substituted phenyl π -electron, while SiTCPP(O)₂, and SiTFMPP(O)₂ should have moderate conjugation as reported in tetraphenylporphyrin derivatives.²⁹ In SiTMP only inductive effect would be operating, while SiTCPP and SiTFMPP would have both moderate resonance and inductive effects. The plots in Figure 4 well reflect the relation. Actually DFT calculation clearly indicates that there is almost no interaction between π -bonding molecular orbitals on porphyrin ring and the *meso*-substituted phenyl rings in the case of SiTMP(O)₂, while many π -bonding molecular orbitals delocalize both over the porphyrin ring and the *meso*-substituted phenyl rings in the cases of SiTCPP(O)₂, and SiTFMPP(O)₂.

All three Si-porphyrins (SiTMP, SiTCPP, SiTFMPP) have been revealed to have their pKa's of the axial ligand hydroxy groups in the acidic region. These are very contrasting to the case of aluminum-porphyrins that have their pKa's in basic region.²⁵ The remarkable contrast between Si-porphyrins and Al-porphyrins could be rationalized by the large difference of their electro-negativities ($E_a(\text{Si}) = 1.74$, $E_a(\text{Al}) = 1.47$) in addition to the higher valence state of Si(IV) than Al(III).

Electrochemical characterization of SiTCPP with various axial ligands in protolytic equilibria

One of the most crucial properties in designing reaction center for artificial photosynthesis should be redox potentials of the potential sensitizer. Oxidation and reduction properties of SiTCPP were measured by cyclic voltammetry (CV) with an electrochemical analyzer (Model 611DST, BAS), equipped with a boron-doped diamond with wide electrochemical window³⁰ or a glassy carbon as a working electrode, Ag/AgCl or AgNO₃ as reference ones, and Pt wire as a counter one in dimethylformamide (DMF), water, aqueous acetonitrile (CH₃CN) containing 0.1 M supporting electrolyte, (C₄H₉)₄N⁺PF₆⁻. SiTCPP exhibits oxidation waves ($E^1_{\text{oxp}} = 0.497$ Volt vs Ag/Ag⁺, $E^2_{\text{oxp}} = 0.741$ Volt vs Ag/Ag⁺) and reduction wave ($E^1_{\text{redp}} = -1.10$ Volt vs Ag/Ag⁺) in CV cycles in DMF (Fig. 5a)). The oxidation wave does not look to be a beautiful reversible one, but it definitely show re-reduction peaks for E¹ at 0.441 Volt vs Ag/Ag⁺ ($\Delta E = 56$ mV) and for E² at 0.684 Volt vs Ag/Ag⁺ ($\Delta E = 57$ mV). It can thus

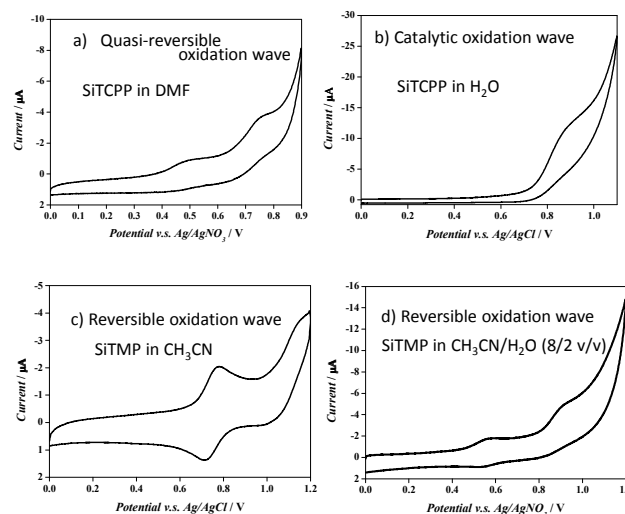


Figure 5. Cyclic voltammogram of Si-porphyrins: a) Quasi-reversible oxidation wave of SiTCPP in DMF, b) Catalytic oxidation wave of SiTCPP in H₂O at neutral condition, c) Reversible oxidation wave of SiTMP in CH₃CN, d) Reversible oxidation wave of SiTMP in CH₃CN/H₂O (8/2 v/v). Scan rate: 100mV•s⁻¹.

be treated as a quasi-reversible one. From the viewpoint of applying water molecule as electron source for artificial photosynthesis, the information of the electrochemical oxidation properties in aqueous solution is of course requisite for the study. As described above, attention has been focused on how to activate water molecule by only one-photon process. For the purpose the first oxidation wave of Si-

porphyrins in the electrochemical behavior should be the most curious one. In this context the oxidation waves of the three Si-porphyrins were carefully examined. Very interestingly, in the case of SiTCPP the quasi-reversible oxidation waves in DMF (Figure 5 a)) changed into characteristic catalytic waves in water (pH = 10) as typically shown in Figure 5 b). The anodic current was much higher in water as compared with in DMF and the CV showed a typical irreversible catalytic wave. (Figure 5 a), b)) The catalytic current observed in the first oxidation wave indicates that water obviously participates in the oxidation processes of SiTCPP.

To get deeper insight into the catalytic phenomena by comparing the three Si-porphyrins, aqueous acetonitrile ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8/2 v/v)) solution was used to assure the enough solubility of the neutral SiTMP and SiTFMPP. The catalytic current in the oxidation waves were measured by differential pulse voltammetry to correctly detect the peak potential. Under the various pH conditions, the peak potential of oxidation wave (E_{oxp}) for each species in protolytic equilibria of each Si-porphyrins was carefully determined as listed in Table 2. Each species of SiTCPP in protolytic equilibria among the axial hydroxy groups systematically changes its redox peak according to the electron donating and withdrawing characters of the axial ligands in the order of $(\text{O}^-)_2 \sim (\text{O})(\text{OH}) > (\text{OH})_2 > (\text{OH})(\text{OH}_2) > (\text{OH}_2)_2$. (Table 2) E_{oxp} 's were the most negative in the case of $(\text{O}^-)_2 / (\text{O})(\text{OH})$ and the most positive in $(\text{OH}_2)_2$. (Table 2) Pourbaix diagram between the oxidation peak potential (E_{oxp}) for each species versus the pH condition is

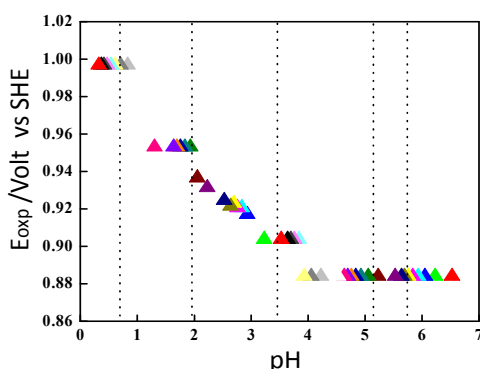


Figure 6. Pourbaix diagram of SiTCPP in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (8/2 v/v).

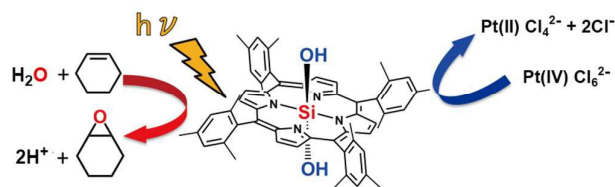
shown in Figure 6. When oxidation process is coupled with proton transfer, the oxidation peak potential should be dependent upon pH being correlated with Nernst Equation. The Pourbaix diagram indicates that only SiTCPP(OH)₂ species, which can exist under the condition $\text{pH} = 1.96 \sim 3.66$, exhibit a proton-coupled oxidation, while one-electron oxidation of all four other protolytic species are independent on pH conditions. When they are further compared with the redox peaks of SiTMP and SiTFMPP, each species among the different five kinds of axial ligand also exhibits systematic shift according to the electron donating and withdrawing characters of the peripheral substituents on the *meso*-phenyl group. The E_{oxp} 's were again well reflecting electronic properties of substituents

on the *meso*-phenyl group in the order of $-\text{CH}_3$ (SiTMP) < $-\text{COO}^-$ (SiTCPP) < $-\text{COOH}$ (SiTCPP) < $-\text{CF}_3$ (SiTFMPP). (Table 2) When the electrochemical oxidation behaviour was compared among the three Si-porphyrins, there exist very interesting differences among each species. Among the five species of SiTMP, only SiTMP(O^-)₂ and SiTMP(OH)(O^-) having the most negative E_{oxp} 's have reversible oxidation waves even in aqueous acetonitrile (Table 2, Figure 5 c), d)), while other species such as SiTMP(OH)₂, SiTMP(OH)(OH_2), SiTMP(OH)₂ with the higher E_{oxp} 's showed catalytic waves. SiTCPP's and SiTFMPP's having the higher E_{oxp} 's also exhibited catalytic waves in all the protolytic species as described above.

These could be understood that the oxidation of water is substantially dependent on the oxidation ability of the catalyst. The criteria became obvious here that Si-porphyrins with the higher E_{oxp} than ~ 0.86 Volt vs SHE exhibit catalytic oxidation waves in aqueous solution. The critical E_{oxp} may be correlated with thermodynamic requirement for oxygen evolution from water ($E_0 = 1.23$ Volt and $E = 0.82$ Volt at $\text{pH} = 7$). Tuning the E_{oxp} of Si-porphyrins would thus be requisite for oxidation of water.

Photochemical Oxygenation of Cyclohexene with Water Sensitized by Silicon (IV) Porphyrins with Visible Light

The catalytic oxidation waves of Si-porphyrins observed in electrochemistry prompted us to further examine whether or not the photochemical oxygenation of substrates such as alkenes with water would be induced. We have already reported the photochemical oxygenation of substrate by



Scheme 3. Photochemical epoxydation of cyclohexene with water catalysed by SiTMP.¹¹

Water as oxygen atom donor catalysed by various metalloporphyrins.^{13-24, 31} The reaction mechanism in the case of Ru-porphyrins was experimentally clarified²³ and theoretically rationalized.^{22, 31}

The interesting photochemical oxygenation of alkenes with water molecule both as electron and oxygen atom donor was also observed in the case of SiTMP.¹¹ When SiTMP (1×10^{-5} M) in aqueous acetonitrile ($\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9/1 v/v)) was irradiated with monochromatic visible light of $\lambda = 420$ 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, K_2PtCl_6 (5×10^{-4} M) as an electron acceptor, and KOH ($0 \sim 5 \times 10^{-3}$ M) under the degassed condition, formation of oxygenated products of cyclohexene were observed (Scheme 3). The detail of the photoreaction was reported elsewhere.¹¹

SiTCPP and SiTFMPP were thus examined for the photochemical oxygenation of cyclohexene under the exactly

the same conditions with those for SiTMP. Very interestingly, striking differences were observed among the three Si-porphyrins. When either SiTCPP or SiTFMPP was irradiated with visible light of $\lambda = 420$ nm under the conditions described above, very rapid decrease of the Soret band of Si-porphyrins was observed within several minutes of the visible light irradiation without any formation of the oxygenated products of cyclohexene, indicating efficient decomposition of SiTCPP or SiTFMPP being predominating. (Figure 6) On the other hand, SiTMP was rather stable upon visible light irradiation; the absorbance of Soret band slightly decreased, but exhibited the photochemical oxygenation. (Figure 7) Since the fundamental physical properties of the three Si-porphyrins clearly indicate

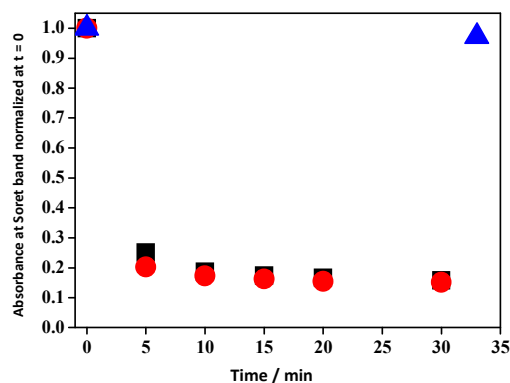


Figure 7. Change of absorbance of Soret band normalized at $t = 0$ during the photoreaction of Si-porphyrins (1×10^{-5} M) with K_2PtCl_6 (5×10^{-4} M) in the presence of cyclohexene (1×10^{-2} M) and KOH (1×10^{-3} M) in the degassed CH_3CN/H_2O (9/1 v/v) upon steady state irradiation with the light of $\lambda = 420$ nm.; \circ : SiTCPP, \blacksquare : SiTFMPP, \blacktriangle : SiTMP.

that electron transfers from both the excited singlet and triplet states of Si-porphyrins are all thermodynamically very feasible. The excited singlet state of each SiTMP ($^1E_{00} = 2.08$ eV),¹¹ SiTCPP (2.07 eV), SiTFMPP (2.08 eV) and the excited triplet states have their energies for SiTMP ($^3E_{00} = 1.64$ eV),¹¹ SiTCPP (1.63 eV (ESI-4)), SiTFMPP (1.66 eV (ESI-4)). The electron transfer to K_2PtCl_6 ($E_{redp} = +0.76$ Volt vs SHE) should be sufficiently exo-ergonic either from the excited singlet or triplet state. Upon visible light irradiation, at least one electron oxidized species, radical cations, of the Si-porphyrins should be formed, but the striking difference of the photo-stability among them thus could be ascribable to the difference of chemical behaviour of the one electron oxidized species.

As we had already observed in the case of Ru-porphyrins, the *ortho*-substituted methyl groups on the *meso*-substituted phenyl group have very crucial roles to prevent the carbon atom in *meso*-position of the porphyrin ring from the attack of nucleophile such as chloride ion in the reaction system. The electrochemical one-electron oxidation of metalloporphyrin in the presence of chloride ion in solution actually induces an efficient chlorination of porphyrin ring. Another possible mechanism may be a coupled reaction of electron transfer and chlorination within a solvent cage, since K_2PtCl_6 should liberate chloride ion upon receiving electron. (eq 1) Though the detail of the chlorination is not yet clear, the difference of the chemical behaviour among the three Si-porphyrins is obvious. Without the bulky methyl groups, the carbon atoms in the *meso*-position would be exposed outside to allow the access of chloride ion. To check whether or not the methyl groups provide the protective effect, the contact molecular surface area of the carbon atom in the *meso*-position was calculated by ARVOMOL program.³² It enables the estimation of the exposed surface area defined as "contact molecular surface area" when the counter atom in a van der Waals radius (chloride ion in this case) is rolling over the corresponding atom (the carbon atom in *meso*-position in this case).^{33,34}

As shown in ESI-6, SiTCPP(O^-)₂ (21.74 Å²) and SiTFMPP(O^-)₂ (21.63 Å²) have larger contact molecular surface area of the four carbon atoms in *meso*-position by a factor of two than

that of SiTMP(O^-)₂ (13.39 Å²), demonstrating the restricted accessibility to the *meso*-carbon atom by methyl group in the *ortho*-position to exhibit the protective effect. Though the protection of the *meso*-carbon atoms was revealed to be requisite for the photochemical oxygenation with sacrificial electron acceptor such as K_2PtCl_6 which supply chloride ion as the attacking nucleophile (eq.1), it should be noted here that the Si-porphyrins (SiTCPP, SiTFMPP) even without such protective substituents on the *ortho*-position are rather stable enough for the electrochemical oxidation of water when such reactive nucleophile is absent in the system. Is there any difference between the photochemical oxygenation and electrochemical oxidation of water? What is the role of water molecule and what is the reaction mechanism of the electrochemical catalytic oxidation processes? These should be the most curious points to be studied further. As we have revealed in the photochemical oxygenation of substrate by water as an oxygen atom donor sensitized by AITMP and

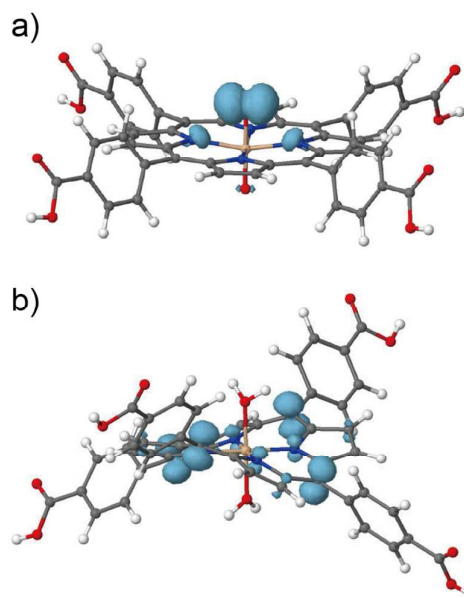


Figure 8. Electronic Spin density of one-electron oxidized forms of a) SiTCPP(O[•])₂ and b) SiTCPP(OH₂)₂ estimated by DFT calculation.

SiTMP, the difference of electronic structure such as spin densities in the one-electron oxidized forms of the catalysts, metalloporphyrins, would cause the difference of their chemical behaviour.^{11, 24} DFT calculation on the one electron oxidized form of SiTCPP clearly indicates the followings. In the deprotonated species of axial ligand (-O[•]), the one-electron oxidized form of the catalyst has exclusive spin density on the axial ligand oxygen atom to exhibit almost oxygen radical type electronic structure such as -O[•], while the fully protonated species of axial ligand (-OH₂) of the one-electron oxidized form has its spin delocalized over the porphyrin ring as shown in Figure 8. The former is understood as a direct oxidative activation of hydroxy group as the axial ligand, leading to oxygenation of substrate, while the latter would cause the attack of nucleophile such as chloride ion to the porphyrin ring, leading to a transformation of porphyrin such as chlorination of the ring or a decomposition. In the photochemical oxygenation reaction with K₂PtCl₆ as sacrificial electron acceptor, the reaction system becomes rapidly acidified during the reaction as indicated by eq. 1. Si-porphyrins are thus supposed to change into the fully protonated form in the case and to have spin densities on the porphyrin ring. Though SiTCPP and SiTFMPP have such drawback for photoreaction in the presence of chloride ion, they have promising reactivity against water. Since we have already found that the sacrificial electron acceptor, K₂PtCl₆, can be replaced by semiconductor such as SnO₂ and TiO₂ as non-sacrificial electron acceptor/transporting media,²⁶ Si-porphyrins would be very much expected to serve as sensitizer/catalyst in the real artificial photosynthetic system without sacrificial reagents. On the basis of understanding the different chemical behaviour of each species of Si-porphyrins in the protolytic equilibria, bulk electrolyses of water by Si-porphyrins as promising catalysts are now in progress. The fundamental properties of Si-porphyrins, especially the water soluble SiTCPP, obtained here would provide crucial guide in this context.

Conclusion

Novel water soluble Si-porphyrins, SiTCPP, was synthesized and its fundamental properties such as photophysical, electrochemical, and photochemical ones were investigated. All three Si-porphyrins (SiTMP, SiTCPP, SiTFMPP) examined here have their pK_a's of the axial ligand hydroxyl groups in the acidic region, contrasting to the case of aluminum-porphyrins²⁵ that have their pK_a's in basic region. These are very crucial for designing a system of artificial photosynthesis which would prefer an optimized pH condition for each system, especially for each half reaction of the oxidation and reduction side. For the half reaction in the oxidation side, Si-porphyrins thus can provide option for the acidic condition and Al-porphyrin for the basic condition. Crucial criteria of the oxidation of water and the photooxygenation of substrate were obtained. The higher oxidation wave of Si-porphyrins

than ~0.86 Volt vs SHE is required for the electrochemical oxidation of water, while proper protecting group such as methyl substituent is requisite for the photochemical oxygenation with K₂PtCl₆ as sacrificial electron acceptor.

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Graphical abstract

