Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx-xxx



Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry



journal homepage: www.elsevier.com/locate/jphotochem

Photochemical oxygenation of cyclohexene with water sensitized by aluminium(III) porphyrins with visible light

Siby Mathew, Fazalurahman Kuttassery, Yuki Gomi, Daisuke Yamamoto, Ryuichi Kiyooka, Satomi Onuki, Yu Nabetani, Hiroshi Tachibana, Haruo Inoue*

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Center for Artificial Photosynthesis, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

ARTICLE INFO

Article history: Received 14 April 2015 Received in revised form 28 May 2015 Accepted 1 June 2015 Available online xxx

Keywords: Artificial photosynthesis Water oxidation Oxygenation Aluminium ion Visible light Porphyrin

ABSTRACT

Aluminium(III)-tetramesitylporphyrin, with the Earth's the most abundant metal and the third most abundant element as the Al(III) ion, induces the photochemical oxygenation of cyclohexene in deaerated aqueous acetonitrile to form the corresponding epoxide and alcohol with water as both electron and oxygen atom donor upon visible light irradiation. The Al(III) should be the most available and meaningful element to be utilized in the artificial photosynthetic unit. The excited triplet state of the water-coordinated porphyrin is responsible for the photochemical oxygenation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Artificial photosynthesis by visible light is one of the most sought-after chemical systems at present. Among the problems to be resolved for the realization of artificial photosynthesis, the way in which water molecules could be incorporated at the oxidation terminus of the system is one of the most crucial issues [1–7]. Among various approaches for the oxidation of water upon light irradiation, i.e., by (1) a one-electron process, (2) a two-electron one, (3) or a four-electron one, 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 [7–17]. Eq. (1)

$$"S" + H_2O + Pt(IV)Cl_6^{2-\frac{h\nu}{MP}}"SO" + Pt(II)Cl_4^{2-} + 2HCl$$
(1)

where "S", MP, and "SO" denote substrate, metalloporphyrins, and oxygenated reaction product of substrate, respectively. For example, we have found that the visible light irradiation of a reaction mixture

* Corresponding author. Tel.: +81 42 677 2840; fax: +81 42 653 3416. *E-mail address:* inoue-haruo@tmu.ac.jp (H. Inoue).

 $\label{eq:http://dx.doi.org/10.1016/j.jphotochem.2015.06.001 \\ 1010-6030 / @ 2015 Elsevier B.V. All rights reserved.$

of CO-coordinated tetra(2,4,6-trimethyl) phenylporphyrinatoruthenium(II)(Ru^{II}TMP(CO)) as a sensitizer, hexachloroplatinate (IV) as an electron acceptor, and an alkene as the substrate in alkaline aqueous acetonitrile induces the highly selective epoxidation of the alkene, with a high quantum yield (~60%) under deaerated conditions [14,15]. Detailed mechanistic study mainly by means of laser flash photolysis has revealed that the water molecule is activated through axial ligation to the one-electron-oxidized Ru-porphyrin to induce an oxygen atom transfer to the substrate with two-electron conversion followed by the second one-electron transfer to the electron acceptor [16,17]. 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 induces the "photon-flux-density problem." [7] Another crucial problem to be resolved would be to devise ways to utilize major elements for the artificial photosynthetic system rather than Ru, Re, Ir, etc. To this end, we report here our finding that the aluminium (III) ion can be utilized as the central metal ion in the metalloporphyrin. Aluminum is the most abundant metal and the third most abundant element on Earth. It is the most available and meaningful element to be utilized in the artificial photosynthetic unit from the practical viewpoint.

S. Mathew et al./Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx-xxx

2. Materials and methods

2.1. Synthesis of tetra(2,4, 6-trimethyl) phenylporphyrinatoaluminum (III) (Al(III)TMP(OH)(H₂O))

Free-base tetramesitylporhyrin in bezonitrile was treated by AlCl₃ for two hours under reflux conditions. After confirming the peak shift of the Soret band, the reaction mixture was cooled to ambient temperature and the solvent was further evaporated. The precipitate was dissolved in chloroform and was washed well with 3 M HCl aqueous solution, and further washed with water. The chloroform solution was dried up to give a crude Al(III)TMP, which was purified by passing through a silica-gel column with dichloromethane/methanol (8/2) as eluent. The obtained crystals were further dissolved in chloroform and were washed well with 0.1% AgNO₃ aqueous solution until no white precipitate (AgCl) was observed. The solution was further washed with 0.5 M aqueous solution of ammonia and was dried. Yield: 85%. EA: Obsd. C 80.24%, H 6.82%, N 6.56%, Calcd. for [Al(III)TMP(OH)(H₂O)], C 79.78%, H 6.58%, N 6.65%. ¹H NMR (CDCl₃): 8.83(s, 8H), 7.30(s, 4H), 7.27(s, 4H), 2.63(s, 12H), 1.94(s, 9H), 1.94(s, 3H), 1.83(s, 9H), 1.79(s, 3H), -1.24(s, 1H), -6.53(s, 1H).

2.2. Other materials

Cyclohexene (Tokyo kasei) was distilled under nitrogen before use and was stored under nitrogen. Acetonitrile (HPLC grade) was used as received from Nakalai Tesque. K_2PtCl_6 was used as received from Aldrich. Distilled water was passed through an ion-exchange column (G-10, ORGANO Co.). The specific resistance of the water was below 0.1 μ S/cm².

2.3. Measurements

UV-visible spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer. Oxidation potential of Al (III)TMP was measured by cyclic voltammetry with a Hokuto Denko HA1010mM1A electrochemical system, with a boron doped diamond 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 (EKS-PLA, PL2143B + PG401; FWHM 25 ps, 5 Hz) as the excitation source for measuring the fluorescence lifetime of the Al(III)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, 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) used 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 (294K). Gas chromatographic analyses were performed on a Shimadzu GC-17A equipped with a TC-17 column (GL Sciences Inc., 30 m, 60-250C), 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.

2.4. 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 KL-42/a sharp cut-off filter L-39 for 420 nm and KL-43/L-39 for 430 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.

2.5. Labeling experiment with the use of $^{\rm 18}{\rm O}$

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) phenylporphyrinatoaluminium (III) (Al(III)TMP)

Metalloporphyrins are well known to have axial ligands in addition to their equatorial porphyrin ligand [18]. Water molecule is a strong candidate for the two probable axial ligands in aqueous solution. They are expected to have protolytic reactions under the given pH conditions [18]. Before examining photoreaction of Al(III) TMP, the protolytic behaviour of the two axial ligands was carefully examined by UV–vis and fluorescence spectroscopies. As shown in Fig. 1, the Soret band absorption of Al(III)TMP exhibits a systematic shift of its λ max from 418.5 nm (at pH 7.0), 422.5 nm (at pH 10.0), up to 427 nm (at pH 10.9). The spectral changes have four isosbestic points at 422.5 nm in the range of pH 7–10, 421.3 nm for pH 9.7–10.3, 424.7 nm for pH 10.3–10.9, and 424.2 nm for pH 10.9–11.1, respectively. The spectral changes are completely reversible by changing the pH conditions. From the inflection points observed in the plot between the absorbance at 422.5 nm and pH values, four



Fig. 1. Absorption spectral change of Al(III)TMP in CH₃CN/H₂O (9/1 v/v); [Al(III) TMP]= 8.5×10^{-7} M, the pH value of aqueous solution was adjusted by KOH.

Please cite this article in press as: S. Mathew, et al., Photochemical oxygenation of cyclohexene with water sensitized by aluminium(III) porphyrins with visible light, J. Photochem. Photobiol. A: Chem. (2015), http://dx.doi.org/10.1016/j.jphotochem.2015.06.001

2

 pK_a values were determined as 9.56, 10.1, 10.7, 11.0, respectively (Supplemental information SI-Fig. 1(a-d)).

The fluorescence spectra also changed their shapes and emission intensities by varying the pH of the aqueous acetonitrile as shown in the supplemental information (SI-Fig. 2a)). The pK_a values were similarly estimated from the fluorescence spectral changes to be 9.5, 10.0, 10.7, and 11.0, which coincide well with those determined by UV-vis spectroscopy (Supplemental information SI-Fig. 2b)). The observation of four pK_a 's with clear four isosbestic points in the pH range examined indicates that five species are actually existing in the pH range in equilibrium as shown in Scheme 1.

The NMR spectrum in CDCl₃ indicates that Al(III)TMP synthesized has two axial ligands of $-OH (\delta = -6.53 \text{ ppm})$ and $-OH_2$ $(\delta = -1.23 \text{ ppm})$ as shown in the supplemental information (SI-Figure 3). The observed two phenyl protons (s, 4H, 7.30 ppm, s, 4H, 7.27 ppm) well rationalize the de-symmetric axial ligand structure with one -OH and one -OH₂ axial ligation. The addition of D₂O induced symmetric phenyl protons (s, 8H, 7.31 ppm), owing to the symmetric ligation of two water molecules to Al(III)TMP. Addition of a trace amount of H₂O to a CDCl₃ solution of Al(III)TMP $(OH)(H_2O)$ exhibited the hydroxyl protons of water at the lower field $\delta = -1.13$ ppm, different from that of the axial OH (-6.5 ppm). Interestingly the NMR spectra in aqueous acetonitrile (CD₃CN/H₂O (9:1)) exhibit a systematic peak shifting under various pH conditions (supplemental information, SI-Figure 4). These strongly support the protolytic equilibria in Scheme 1. Al(III)TMP exists as a two-water-molecule-coordinated species in the neutral reaction mixture CD_3CN/H_2O (9:1) and the species. Al(III)TMP(H_2O)₂ (419 nm), undergoes four deprotonation steps to form Al(III)TMP $(OH)(H_2O)$ (422 nm), Al(III)TMP(OH)₂ (~422 nm), Al(III)TMP(OH) (O^{-}) (~427 nm), and Al(III)TMP $(O^{-})_2$ (427 nm) depending on the pH of the solution.

3.2. Photophysical and electrochemical characterization of Al(III)TMP

Since Al(III)TMP has been revealed above to have the protolytic equilibria among the axial ligands in the ground state, it should have such equilibria also in their excited state. It is, thus, very curious whether the equilibria in the excited state is dynamic enough within the lifetimes of the corresponding excited states or rather static without mutual conversion among the species. To get deeper insight into this point, the fluorescence lifetime measurement was carried out under various pH conditions. As shown in the supplemental information (SI-Figure 5), upon excitation of each species the fluorescence showed a beautiful single exponential decay with each different time constant for Al(III)TMP(H₂O)₂ $(\tau_{\rm F} = 9.5 \text{ ns}), \text{Al(III)TMP(OH)(H_2O)} (\tau_{\rm F} = 8.7 \text{ ns}), \text{Al(III)TMP(OH)_2}$ $(\tau_{\rm F}$ = 8.7 ns), Al(III)TMP(OH)(O⁻) ($\tau_{\rm F}$ = 7.3 ns), and Al(III)TMP(O⁻)₂ $(\tau_{\rm F}$ = 6.6 ns), depending on the pH of the solution. These results strongly suggest that the five species are not in dynamic equilibria within their lifetimes and the protolytic processes in the excited singlet states are much slower than the deactivation of each excited species. Furthermore, the lifetimes of the triplet excited states were also measured by observing the decay of T_n-T_1 transient absorption. Though the measurements were carried out only for Al(III)TMP(H₂O)₂ (τ _T = 1.1 ms, λ max = 452 nm), Al(III)TMP (OH)(O⁻) ($\tau_{\rm T}$ = 1.1 ms, λ max = 454 nm), and Al(III)TMP(O⁻)₂ ($\tau_{\rm T}$ = 1.0 ms, λ max = 457 nm), the single exponential decays with almost the same lifetimes but with different $\lambda_{\text{max}}\mbox{'s}$ and different shapes of spectra indicate that the dynamic equilibria are also not established in the triplet excited states and the protolytic processes in the triplet excited states are also much slower than their deactivation processes (SI-Fig. 6(a-d)). These results lead to a crucial conclusion that each species of Al(III)TMP with different axial ligands behaves independently in both the excited singlet and triplet states. Photoreaction induced by an excitation of each species under the given pH condition should be thus accepted to proceed through either singlet or triplet state within the same species.

For examining a photo-induced redox chemistry, electrochemical characterization on redox potentials provides also a crucial information. The redox potentials of each species of Al(III)TMP with different axial ligands were estimated by cyclic voltammetry with boron-doped diamond (BDD) electrode which allows the measurement in aqueous solution owing to the wide electrochemical potential window [19]. Pourbaix diagram between the oxidation potential ($E_{1/2}$) for each species versus the pH condition is shown in Fig. 2. When a one-electron oxidation process is coupled with proton transfer, the oxidation potential ($E_{1/2}$) should be linearly dependent upon pH with a slope of 59 mV according to Nernst Equation. The oxidation potentials ($E_{1/2}$) of each species of Al(III)TMP with different axial ligands changed with the pH region



Fig. 2. Pourbaix diagram for the oxidation potential of Al(III)TMP with different axial ligands in CH₃CN/H₂O (9/1 v/v); the broken line represents each pK_{a1} , pKa_2 , pKa_3 , pKa_4 .



Scheme 1. Protolytic equilibria among the axial ligands of Al(III)TMP in aqueous acetonitrile.

S. Mathew et al./Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx-xxx

as expected by each pK_a value, but is almost constant within each pH region as seen in Fig. 2. The Pourbaix diagram indicates that the oxidation of each species of Al(III)TMP in protolytic equilibria among their axial ligands is not coupled with proton transfer processes, which should be much slower than the electron transfer on the BDD electrode. The spectroscopic, photophysical, and electrochemical characteristics of each species of Al(III)TMP with different axial ligands are summarized in Table 1.

3.3. Photochemical oxygenation of cyclohexene with water sensitized by aluminium(III) porphyrins with visible light

On the basis of the spectroscopic, photophysical, and electrochemical information obtained above, photochemical oxygenation of substrate sensitized by Al(III)TMP was examined. As mentioned above, the two-electron oxidation of water by one-photon excitation Eq. (1) would be the more plausible alternative compared to the four-electron oxidation and another crucial problem to be resolved would be a possible utilization of major elements rather than rare earth ones. Aluminum is the most abundant metal and the third most abundant element on Earth. It should be thus most interesting to explore a photochemical reaction of aluminum porphyrin with water. When the Al(III)TMP as a sensitizer, having a similar but less positive redox potential (+0.71 V vs. SHE under the neutral condition) than that of Ru(II) TMP (+1.03 V vs. SHE), was irradiated with visible light, the photochemical oxygenation of cyclohexene as the substrate with water in the presence of hexachloroplatinate (IV) (0.5 mM) as an electron acceptor was found to be induced in deaerated aqueous acetonitrile ($CH_3CN/H_2O(9/1 v/v)$), (Scheme 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 photochemical oxygenation proceeds under either Q-band (560 nm) or Soret-band (420 or 430 nm) excitation. As in the case of Ru(II)TMP, a weakly alkaline condition ($[OH^{-}] < 1.5 \text{ mM}$) favoured the epoxide (1) formation [14–17], while the alcohol (**3**) was selectively formed under a stronger alkaline condition ($[OH^{-}] = 5 \text{ mM}$). (Table 2) The selectivity of the "epoxide" formation increased with decreasing [OH⁻] (Table 2). Under the neutral and the weakly alkaline conditions ([OH⁻]=0.5 mM), another product, 2-chlorocyclohexanol (2), appeared. With no addition of KOH, the pH value of the reaction mixture after the photoreaction decreased to 3.8, owing to the formation of HCl Eq. (1). The "epoxide" was actually confirmed to be slowly converted into 2-chlorocyclohexanol (2) under the low pH condition (3.8) in the presence of HCl; thus, the newly appeared (2) was thought to be derived from the reaction of the "epoxide" with HCl generated during the photoreaction Eq. (1). This suggests that the epoxide selectivity, including the formation of 2 (18.5% (1) + 20.9 % (2) = 39.4%), is the highest under an alkaline condition $([OH^{-}] = 0.5 \text{ mM})$ (Table 1).

The oxygen atom of water was confirmed to be incorporated in the oxygenated reaction products by means of experiments using ${\rm H_2}^{18}{\rm O}$: The ${\rm ^{18}O}$ uptakes (%) under the experiment in ${\rm H_2}^{16}{\rm O}$ — ${\rm H_2}^{18}{\rm O}$

Table 1

Characteristics of Al(III)TMP with different axial ligands in CH_3CN /H_2O (9/1 v/v).

Al(III)TMP	pK _a	E _{ox} vs SHE	E _{red} vs SHE	$\tau_{\rm F}/{\rm ns}$	$\tau_{\rm T}/{\rm ms}$
$\begin{array}{l} Al(III)TMP(H_2O)_2\\ Al(III)TMP(OH)(H_2O)\\ Al(III)TMP(OH)_2\\ Al(III)TMP(OH)(O^-)\\ Al(III)TMP(O^-)_2 \end{array}$	$pK_a 1 = 9.6$ $pK_a 2 = 10.1$ $pK_a 3 = 10.7$ $pK_a 4 = 11.0$	0.71 1.10 0.70 1.08 0.69 0.97 0.69 0.99 0.67 1.05	$\begin{array}{r} -1.53 & -1.83 \\ -1.53 & -1.83 \\ -1.55 & -1.83 \\ -1.56 & -1.83 \\ -1.58 & -1.83 \end{array}$	9.5 8.7 8.7 7.3 6.6	1.1 - 1.1 1.0



Scheme 2. Photochemical oxygenation of cyclohexene with water under alkaline condition sensitized by Al(III)TMP.

(87.9:12.1) at [KOH] = 1.5 mM for each reaction product were 1 (9.9%), **2** (12.4%), **3** (10.6%), **4** (11.6%), and **5** (10.1%). The λ_{max} of Al (III)TMP in each alkaline condition was different: 427 nm for $[OH^{-}] = 1-5 \text{ mM}, 422 \text{ nm for } [OH^{-}] = 0.5 \text{ mM}, \text{ and } 419 \text{ nm under the}$ neutral condition. During the photoreaction, the λ_{max} values under alkaline conditions gradually shifted to shorter wavelengths and finally reached 419 nm, which corresponds to that for neutral or acidic conditions. The λ_{max} of Al(III)TMP under each condition and its shifting during the photoreaction well coincide with the protolytic equilibria among the two axial ligands (Scheme 1) and the pH change during the reaction as anticipated by Eq. (1), while there was no induction period for the formation of oxygenated reaction products. The quantum yields were thus estimated at an early stage of the reaction, within several minutes after the start of irradiation before the shifting of the λ_{max} of Al(III)TMP. The apparent quantum yields under various conditions are summarized in Table 2. They are relatively low compared to those obtained with Ru(II)TMP [14,15]. When other substrates such as norbornene ($E_{1/2}$ = 2.17 Volt vs SHE), styrene ($E_{1/2}$ = 1.92 Volt vs SHE), and 1-hexene ($E_{1/2}$ =2.71 Volt vs SHE) were examined for the photochemical oxygenation sensitized by Al(III)TMP, very interestingly, almost no reaction was observed, indicating the sensitizer Al(III)TMP exhibited a high selectivity for cyclohexene $(E_{1/}$ $_2$ = 2.08 Volt vs SHE). The apparent lower quantum yield with high selectivity can be ascribed to the lower oxidation ability of the sensitizer Al(III)TMP (E_{ox} = +0.71 V vs. SHE under the neutral condition) than that of Ru(II)TMP (E_{ox} = +1.03 V vs. SHE). Since cyclohexene was the most reactive substrate in the case of Ru(II) TMP, the lower oxidation ability of Al(III)TMP might not sensitize the oxygenation of other less reactive substrates. In the case of styrene with similar oxidation potential with cyclohexene, steric factor of substrate might be also operating as observed in the case of RuTMP(CO) [14,15].

3.4. Excited state of Al(III)TMP responsible for the photochemical oxygenation of cyclohexene and the reaction mechanism

The excited singlet state of Al(III)TMP 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 excited triplet states of metal-loporphyrins are considered to have their energy around ~1.8 eV [20]. The oxidation potential of Al(III)TMP (E_{ox} = 0.71 Volt vs SHE), the reduction potential of K₂PtCl₆ (E_{red} = 0.76 Volt vs SHE), and the excited state energy clearly indicate that an electron transfer to K₂PtCl₆ is sufficiently exo-ergonic either from the excited singlet (ΔG = -2.12 eV) or the triplet states (ΔG = ~-1.85 eV) of Al(III)TMP. To examine which excited state is actually responsible in the reaction mixture, quenching experiments were carried out. Very interestingly fluorescence (τ_F = 9.5 ns, 1/ τ_F = 1.1 × 10⁸ s⁻¹) of Al(III)

S. Mathew et al./Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx-xxx

Table 2

Photochemical oxygenation of cyclohexene sensitized by Al(III)TMP with visible light irradiation under deareated CH₃CN/H₂O (9/1 v/v); [Cyclohexene] = 0.1 M, [K₄PtCl₆] = 5.0×10^{-4} M.

Selectivity (%)							
[KOH]/mM		CI	₽	<u>م</u>	°	CI	Φ^{a} /%
	(1)	(2)	(3)	(4)	(5)	(6)	
5.0 ^b	Trace	Trace	90.0	Trace	10.0	Trace	0.70
1.5 ^b	11.9	1.7	68.2	4.5	9.3	4.4	0.74
1.0 ^b	24.8	3.0	42.5	5.9	5.9	18.8	0.60
0.5 ^c	18.5	20.9	11.4	1.3	1.1	44.0	0.63
0 ^c	2.0	26.9	7.1	0.5	0.9	62.5	0.32

^a Quantum yield.

^b λ = 430 nm irradiation.

^c λ = 420 nm irradiation.

 $TMP(H_2O)_2$ under neutral conditions was not quenched by the addition of $Pt(IV)Cl_6^{2-}$ (0.5 mM), while the triplet excited state $(\tau_{\rm T} = 1.1 \text{ ms}, 1/\tau_{\rm T} = 9.1 \times 10^2 \text{ s}^{-1})$ was effectively quenched by Pt(IV) Cl_6^{2-} with a quenching constant $k = 9.2 \times 10^7 M^{-1} s^{-1}$. The photochemical oxygenation is thus considered to proceed through an electron transfer to K₄PtCl₆ from the triplet excited state of the Al (III)TMP. The short lifetime of the singlet state cannot allow the rather slow electron transfer rate $(k_{et} = k(=9.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}) \times$ $[K_2PtCl_6](=5 \times 10^{-4} \text{ M}) = 4.6 \times 10^6 \text{ s}^{-1}$). Intermediates similar to those detected in the case of Ru(II)TMP are presumed to have key roles in the photochemical oxygenation [16,17] Density functional theory (DFT) calculations indicate that the spin densities of the one-electron-oxidized Al(III)TMP(OH)(O⁻) (at [KOH] = 0.5 mM) and Al(III)TMP(O⁻)₂ (at [KOH] = 1-5 mM) have exclusive populations on the deprotonated axial ligand as -0° , suggesting that the hydroxyl oxygen atom coordinated to the Al metal ion is substantially suffering an oxidative activation to become oxyl-radical as shown in Fig. 3.

In the case of Ru(II)TMP, similar spin densities were obtained in the axial -OH group and the further deprotonated $-O^{-}$, respectively. The former undergoes epoxidation, while the latter undergoes alcohol formation [16,17]. The product distribution in Table 2, where the alkaline condition favours alcohol formation, while the epoxide is the major reaction product under slightly alkaline conditions, well rationalize the reaction mechanism as revealed in the photochemical oxygenation of cyclohexene with water sensitized by Ru(II)TMP (Fig. 4) [16,17]. In the photoreaction, di-chlorinated product (6) was also produced in addition to the oxygenated products, but it was only observed under the neutral and weakly alkaline condition, which converted to an acidic condition during the photoreaction, as mentioned above. Under the basic condition, however, the formation of 6 was nearly suppressed. This suggests that the di-chlorinated product (6) has a different reaction pathway than that for the other oxygenated reaction products. The di-chlorinated product, 6, could be ascribable to chloride radical possibly generated through oneelectron oxidation by the radical cation of Al(III)TMP under acidic condition, where Al(III)TMP bears two water molecules as its axial ligands and the one-electron oxidized Al(III)TMP has the electronic structure of porphyrin π -radical cation.

Though the currently found photochemical oxygenation is induced in the presence of a sacrificial electron acceptor, $Pt(IV) Cl_6^{2-}$, a similar photochemical oxygenation with water sensitized by Sn(IV)TCPP (tetra(4-carboxy) phenylporphyrinatotin(IV)) has been found to be induced on the TiO_2 semiconductor as an electron acceptor, with hydrogen evolution from Pt loaded on TiO_2 [21]. On



Fig. 3. Spin density of the one-electron oxidized Al(III)TMP calculated by Gaussian09 rev.D01 B3LYP/6-31G^{*}, (a) one-electron oxidized form of [Al(III)TMP (OH)(O⁻)], (b) one-electron oxidized form of [Al(III)TMP(O⁻)₂].

the basis of the present study, the construction of a photochemical system on TiO_2 is now in progress. The photochemical oxygenation sensitized by Al(III)-porphyrins would serve as a crucial model for the utilization of this most easily available, abundant element by means of the two-electron oxidative activation of water to induce the oxygenation of substrates. The photochemical oxygenation of substrates with water as a half reaction in the oxidation side of

6

ARTICLE IN PRESS

S. Mathew et al./Journal of Photochemistry and Photobiology A: Chemistry xxx (2015) xxx-xxx



Fig. 4. Reaction mechanism of the photochemical oxygenation of cyclohexene sensitized by [Ru(II)TMP(CO)][7].

artificial photosynthesis, which can produce useful chemicals, would be a more plausible alternative than the simple oxygen evolution.

Supplementary information

Supplemental Information (SI) available: Absorption spectral changes of Al(III)TMP upon addition of OH⁻ and their pK_a determination (SI-Fig. 1), fluorescence spectral changes of Al(III) TMP (SI-Fig. 2), ¹H NMR spectrum of Al(III)TMP (SI-Fig. 3), ¹H NMR spectra of Al)III)TMP under various pH condition (SI-Fig. 4), fluorescence lifetime measurement (SI-Fig. 5), decay profile and spectra of Tn–T₁ transient absorption of Al(III)TMP (SI-Fig. 6).

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.2015.06.001.

References

- K. Kalyanasundaram, M. Gratzel, Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993 and references therein.
- [2] A.J. Bard, M.A. Fox, Acc. Chem. Res. 28 (1995) 141 and references therein.
 [3] A. Harriman, G. Porter, M.-C. Richoux, J. Chem. Soc. Trans. 2 (1981) 833.

- [4] G.S. Nahor, S. Mosseri, P. Neta, A. Harriman, J. Phys. Chem. 92 (1988) 4499.
 [5] G.S. Nahor, P. Neta, P. Hambright, A.N. Thompson Jr., A. Harriman, J. Phys. Chem.
- 93 (1989) 6181.
- [6] POWERING THE. WORLD WITH SUNLIGHT, A White Paper Describing the Discussions and Outcomes of the 1st Annual Chemical Sciences and Society Symposium (CS3) Kloster Seeon, Germany, July 23-25, 2009: https://www3. csj.jp/news/cs3-whitepaper.pdf.
- [7] H. Inoue, T. Shimada, Y. Kou, Y. Nabetani, D. Masui, S. Takagi, H. Tachibana, Chem. Sus. Chem. 4 (2011) 173–179.
- [8] H. Inoue, M. Sumitani, A. Sekita, M. Hida, Chem. Commun. (1987) 1681.
- [9] H. Inoue, T. Okamoto, M. Hida, J. Photochem. Photobiol. A: Chem. 65 (1992) 221.
- [10] H. Inoue, T. Okamoto, Y. Kameo, M. Sumitani, A. Fujiwara, D. Ishibashi, M. Hida, J. Chem. Soc., Perkin Trans. 1 (1994) 105.
- [11] T. Shiragami, K. Kubomura, D. Ishibashi, H. Inoue, J. Am. Chem. Soc. 118 (1996) 6311.
- [12] S. Takagi, M. Suzuki, T. Shiragami, H. Inoue, J. Am. Chem. Soc. 119 (1997) 8712.
- [13] S. Takagi, H. Morimoto, T. Shiragami, H. Inoue, Res. Chem. Intermed. 26 (2000) 171.
- [14] S. Funyu, T. Isobe, S. Takagi, D.A. Tryk, H. Inoue, J. Am. Chem. Soc. 125 (2003) 5734.
- [15] H. Inoue, S. Funyu, T. Shimada, S. Takagi, Pure Appl. Chem. 77 (2005) 1019.
 [16] S. Funyu, M. Kinai, D. Masui, S. Takagi, T. Shimada, H. Tachibana, H. Inoue, Photochem. Photobiol. Sci. 9 (2010) 931.
- [17] T. Shimada, A. Kumagai, S. Funyu, S. Takagi, D. Masui, Y. Nabetani, H. Tachibana, D.A. Tryk, H. Inoue, Faraday Disc. 155 (2012) 145–163.
- [18] F. Kuttassery, S. Mathew, D. Yamamoto, S. Onuki, Y. Nabetani, H. Tachibana, H. Inoue, Electrochemistry 82 (2014) 475.
- [19] Y. Fujishima, T.N. Rao, D.A. Tryk, Diamond Electrochemistry, Elsevier B.V. Amsterdam and BKC Inc., Tokyo, 2005.
- [20] F.R. Hopf, D.G. Whitten, Porphyrins and Metallopophyrins, Elsevier Scientific Publishing Company, Amsterdam, 1975, pp. 669.
- [21] K. Kurimoto, T. Yamazaki, Y. Nabetani, D. Masui, S. Takagi, T. Shimada, H. Tachibana, H. Inoue, Photochem. Photobiol. Sci. 13 (2014) 154.