

Preparation of copper complexes coordinated by N^{21} , N^{22} -etheno bridged porphyrin and the application to photooxidation of phenol derivatives

Yuko Takao^{*a}⁰, Fukashi Matsumoto^a, Kazuyuki Moriwaki^a, Takumi Mizuno^a, Toshinobu Ohno^a and Jun-Ichiro Setsune^{*b}

^a Osaka Municipal Technical Research Institute, Joto-ku, Osaka 536-8553, Japan ^b Department of Chemistry, Graduate School of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan

Received 2 May 2014 Accepted 19 March 2015

ABSTRACT: Copper(I) complexes coordinated with a N^{21} , N^{22} -etheno bridged porphyrin ligand were synthesized as a unique coordination structure. The copper porphyrin complexes promoted photooxidations of a phenol derivative in organic solution under aerobic condition with visible photoirradiation. The complexes could be immobilized on silica gel as a support and the obtained copper porphyrin composites showed high ability as photocatalysts for heterogeneous photooxidation of a phenol derivative in aqueous solution. The composites could be easily recovered and re-used after the reaction. The structural study found that the active species contributing to the photooxidation reaction was the di(μ -hydroxo)dicopper(II) complex of N^{21} , N^{22} -etheno bridged porphyrin generated by oxidation of corresponding copper(I) complex in the reaction system under homogeneous and heterogeneous condition.

KEYWORDS: bridged porphyrin, copper complex, photooxidation, phenol derivative, heterogeneous reaction.

INTRODUCTION

Oxidation of phenol derivatives is of special interest because the oxidized products of phenol derivatives have various industrial applications. For example, benzoquinone derivatives are known to be precursors of Vitamin E and other medicines, and they are important specialty chemicals in the pharmaceutical and dye industries [1, 2]. On the other hand, some phenol derivatives such as chlorinated or *p*-alkylated phenols are known to resist from biodegradation and accumulate in the environment, so sustainable methods of oxidative decomposition for the wastewater treatment are needed [3, 4]. Among several methods for oxidation of phenol derivatives, photooxidation method using a singlet oxygen photosensitizer is regarded as a friendly process for environment compared with other chemical oxidation. It uses minimum harmful chemicals, and utilizes oxygen from air and visible light having the largest energy density in solar radiation as unlimited natural resources [1, 5, 6c]. Further, immobilizations of photosensitizers on solid supports have been attempted to increase utility of the photosensitizers [2]. Heterogeneous reaction allows for easy separation of products and sensitizers, which is an advantage from the viewpoint of easier isolation of the products in the case of photochemical synthesis. In the situation of the wastewater treatment, immobilization means that insoluble photosensitizers provide the reaction sites in aqueous solution, and the recovery and re-use of photocatalysts become more convenient. Immobilization also has an advantage to decrease quenching of photosensitizers by singlet oxygen. Although a number of examples about the photooxidations have been reported

⁶SPP full member in good standing

^{*}Correspondence to: Yuko Takao, email: yuktakao@omtri.or.jp, fax: +81 6-6963-8049; Jun-ichiro Setsune, email: setsunej@ kobe-u.ac.jp, fax: +81 78-803-5770

in which the photosensitizers are classic dyes such as Methylene Blue and Rose Bengal, it is a problem for the sensitizers to be photodegraded upon long irradiation. Thus it is important to develop efficient and stable photosensitizers.

Porphyrin derivatives are candidates of excellent photosensitizer for the photooxidation of various substrates, while several catalytic oxidations using porphyrinoid complexes have been studied also including usage of strong oxidants [3, 5, 7]. Burrows and co-workers have investigated photooxidations of phenolic derivatives and reported that porphyrin derivatives well photosensitized such reactions leading to formation of the corresponding quinones [1a, 6]. They proposed the reaction process involving formation of singlet oxygen as one of the dominant mechanisms and suggested the contribution of also photostability of the photosensitizers. Then much effort has been made to develop effective photooxidations of phenols using photochemical characteristics of porphyrins [4, 5, 8]. We have investigated the coordination chemistry and organometallic chemistry of palladium complexes of N^{21} , N^{22} -etheno bridged porphyrin [9], which played a role of bidentate ligand, strongly coordinated to metal, and influenced the dynamic behavior of the coexisting ligand [10]. Then, we have already reported the properties and application of unique μ -(dihydroxo) dipalladium(II) complex with N^{21} , N^{22} -etheno porphyrin ligand that can be used as a photosensitizer in oxidation of phenol derivatives [11]. The reaction proceeded under mild conditions in neutral solution at room temperature,

probably because the OH ligand of the $Pd_2(OH)_2$ core of the bidentate porphyrin complex acted as a base.

This time, we prepared copper complexes coordinated by the N^{21} , N^{22} -etheno bridged porphyrins as unique bidentate ligands. Copper is not so expensive metal, and its complexes have been known as practical catalysts for hydrolysis or a variety of carbon–carbon bond forming reactions [12]. While copper complexes of porphyrins have been studied variously from structural, and physicochemical points of view [13], recently applications of the complexes have been reported as photocatalysts [14]. Then here we describe the preparation and structure of the copper complexes with the N^{21} , N^{22} -etheno bridged porphyrin ligands, application of the complex as a photosensitizer in oxidation of phenol derivatives, and further the behavior and effect of the complex as a photocatalyst in heterogeneous reaction.

RESULTS AND DISCUSSION

Copper complexes with N^{21},N^{22} -etheno bridged porphyrin ligand were prepared by reactions of N^{21},N^{22} etheno bridged porphyrin monoprotonated form with excess amount of Cu(I) reagent at room temperature (Scheme 1). Monoprotonated N^{21},N^{22} -(diphenyletheno) octaethylporphyrin (**2**) was allowed to react with [Cu(I) (CH₃CN)₄]PF₆ (5 equiv.) in CH₂Cl₂ at room temperature under argon for one day to afford N^{21},N^{22} -(PhC=CPh)(OEP) Cu(I)PF₆ (**3a**). N^{21},N^{22} -(PhC=CPh)(OEP)Cu(I)ClO₄ (**3b**) was prepared by the reaction of **2** with [Cu(I)(CH₃CN)₄]

HN ٠N Ν ii) iii) . Ph Ph Ph Ph Cu N: NΗ Ν ΗŅ CIO₄ X **3a**: X = PF₆ OEP 2 **3b**: X = ClO₄ i) Ph Ph N Cu(MeCN)₄PF₆ Ph Ph Ph Ph Ph ,Cu HN PF_6 CIO₄ Ρh Ph 3c 1 2c

Reagent: i) $Cu(OAc)_2$, ii) $Co(OAc)_2$, $FeCl_3$, $Ph \equiv Ph$, $HClO_4$, iii) $Cu(MeCN)_4X$

Scheme 1. Preparation of copper(I) complexes with porphyrin or N^{21} , N^{22} -(diphenyletheno) bridged porphyrin derivatives



Fig. 1. UV-vis spectra of 2 and 3a in acetonitrile



Fig. 2. Ortep drawings with 50% level thermal ellipsoids of **3b** (a) and **4b** (b). Counter ions (ClO_4^{-}) , solvent molecules, and all hydrogen atoms are omitted for clarity

ClO₄. A TPP analog, N^{21} , N^{22} -(PhC=CPh)(TPP)Cu(I)PF₆ (**3c**) was prepared similarly. Figure 1 shows the UV-vis spectra of **2** and **3a** in acetonitrile. The intense Soret band in the UV-vis spectrum of **3a** showed bathochromic shift from 401 nm for **2** to 412 nm, and three weak absorptions at 535, 569 and 615 nm in the Q-band region for **2** were split into four absorptions at 536, 569, 578 and 612 nm for **3a**. The MALDI TOF-MS spectrometry of **3a** showed a peak at 773.3584 that is in good agreement with the theory (773.3644 for [M–PF₆]⁺).

Recrystallization of Cu(I) complex of N^{21}, N^{22} -etheno bridged porphyrin **3b** from a mixture of Et₂O and CH₂Cl₂ with a small amount of MeOH in a refrigerator gave flaky single crystals. X-ray crystallography of **3b** showed that a copper atom was placed out of the porphyrin plane and existed between the double bond of the N^{21}, N^{22} -(PhC=CPh) bridge moiety and two imine nitrogen atoms, N²³ and N²⁴, with the Cu–C(bridge) distance of 1.934(3) and 1.937(3) Å, and the Cu–N(imine) distance of 1.858(3) and 1.859(3) Å (Fig. 2a) [15]. The length of the double bond of the etheno bridge was 1.409(5) Å and longer than that of N^{21}, N^{22} -diphenyletheno bridged tetraphenylporphyrin monoprotonated form $[N^{21}, N^{22}-$ (PhC=CPh)(TPP)HCIO₄] (1.333 Å) reported by Callot and co-workers [16]. This elongation suggests π -back donation from a d-orbital of Cu to the anti-bonding molecular orbital of the ethylene moiety. On the other hand, recrystallization of **3b** in a mixture of CH₂Cl₂ and MeOH at ambient temperature promoted air-oxidation to generate crystals of di(μ -hydroxo)dicopper(II) diporphyrin **4b** in 64% yield. The X-ray crystallography of **4b** revealed a Cu₂(OH)₂ diamond core where Cu(II) is ligated by two pyrrolenine nitrogens and two hydroxyl oxygens with the Cu–N distances of 1.974(2) and 1.988(2) Å and the Cu–O distances of 1.927(2) and 1.916(3) Å (Fig. 2b) [15]. 3

The efficiencies of the Cu(I) complexes of N^{21} , N^{22} etheno bridged porphyrins (3) as photosensitizers were evaluated in the photooxidation of 2,6-di-tert-butylphenol (DBP). When the acetonitrile solution of DBP (3 mM) containing 3a (0.3 mM) was irradiated with visible light by a xenon lamp (350 nm $< \lambda < 800$ nm) under air, only 2,6-di-tert-butyl-1,4-benzoquinone (DBQ) was formed selectively as an initial oxidized product, which has been proven by ¹H NMR chemical shifts of the product in comparison with those of the authentic sample [11b]. Table 1 shows the activity of photosensitizers as estimated by the DBQ yields, determined by ¹H NMR spectra. Then 80% conversion from DBP to DBQ was observed after 90 min photoirradiation with addition of 3a. The photooxidation never proceeded in the absence of porphyrins, and addition of 3a to deaerated solution resulted in no conversion of DBP after 90 min photoirradiation. And 50 min photoirradiation in the presence of 3b afforded 64% conversion of DBP, while only 7% of DBP changed without photoirradiation. While the efficiency of TPP derivative (3c) was not very

Table 1. Efficiency in photooxidation of DBP with photosensitizers under visible light irradiation^a

Dye	[DBP], mM	Time, min	Conv., %
	3	40	0
3a	3	90	80
3a	3	90	0^{b}
3a	2	50	58
3b	2	50	7°
3b	2	50	64
4b	2	50	61
3c	2	50	55
2	2	50	86
OEP	2^{d}	50	52
1	2 ^e	50	22

^a Photoirradiation (350 nm $< \lambda < 800$ nm) of DBP in acetonitrile in the presence of 10 mol% of dye. ^bO₂ was removed by Ar bubbling. ^cNot irradiated. ^d Solvent contains 10% CH₂Cl₂. ^cIn CH₂Cl₂.



Fig. 3. Change in visible spectrum at Q-band of **3a** $(2.2 \times 10^{-4} \text{ M})$ in acetonitrile with time through the visible light irradiation with a 500-W xenon lamp



Scheme 2. Generation of active species from bidentate porphyrin Cu complex in photooxidation system

different from those of OEP derivatives under the same condition, N^{21} , N^{22} -etheno bridged porphyrin structure seemed to afford higher conversion than ordinary tetradentate Cu(II) porphyrin (1) and free base OEP. This would be partly because of the photostability, since it was confirmed that Pd complex of N^{21} , N^{22} -etheno bridged porphyrin was more photostable than the free base porphyrin and Pd complex of normal porphyrin [11]. In this reaction N^{21} , N^{22} -etheno bridged porphyrin monocation (2) afforded higher conversion than Cu(I) complex of the bridged porphyrin. Although the oxidation activity of 2 and OEP may be ascribed to the photosensitized formation of singlet oxygen, the Cu(I) complexes seem to act in a different manner.

To elucidate the mechanism of these photooxidation catalyzed by the Cu(I) complex of N^{21} , N^{22} -etheno bridged porphyrin, the UV-vis spectral change of 3a through photoirradiation in the absence of phenol derivatives was monitored in acetonitrile under the standard reaction condition. Four peaks at 536, 566, 577 and 610 nm in the Q-band region of **3a** were red-shifted to 543, 568, 585 and 614 nm with time (Fig. 3). The resulting spectral pattern with the second lowest energy band in the Q-band region specifically decreased is in accord with the UV-vis spectral pattern of 4b. So it is considered that Cu(I) porphyrin complex of N^{21} , N^{22} -bridged porphyrin was photooxidized to di(u-hydroxo)dicopper(II) complex in acetonitrile solution under aerobic condition (Scheme 2). Then in this case, it is presumed that the photooxidation of phenol derivative using **3b** was promoted by $di(\mu$ hydroxo)dicopper(II) complex of N²¹, N²²-bridged porphyrin as an active species formed in the photoreaction system. In fact, 4b showed very similar reactivity for the photooxidation of DBP (61%) to that of 3b under the same reaction conditions. The catalytic activity of some di(µ-hydroxo)dicopper(II) complexes in the oxidation of phenols and catechols has been reported in the literature [17], and also we have previously reported that the $di(\mu$ hydroxo)dipalladium(II) complex of N^{21} , N^{22} -etheno

bridged porphyrin in 5 mol% catalyzes photooxidation of DBP to DBQ in 96% yield when irradiated for 60 min [11b]. This Pd complex shows the higher photocatalytic activity than **3a**.

The photocatalytic activity of the Cu complexes in heterogeneous reaction was also studied in photooxidation of *p-n*-propylphenol (PNPP) in aqueous solution for the purpose of application to wastewater treatment. The photosensitizers were simply adsorbed on silica gel as support to make composite photocatalysts employed in aqueous solution. It is expected that the composite gives active sites for photooxidation of the phenol substrate and then allows easy recovery. In this way, 0.1 g of a support was merely immersed in a chloroform solution of a regular amount of photosensitizer (4×10^{-6} mol), and after adsorption the solution was evaporated and subjected directly to the heterogeneous photooxidation in water. So the composite may include also some amount of free solid photosensitizer unadsorbed on support depending on their adsorptive ability. The amount of immobilized sensitizers on support without desorption is estimated as shown in Table 2. The adsorptive abilities $(4 \times 10^{-5} \text{ mol.g}^{-1})$ of **3a** and 3c on support were higher than those of OEP, (S-Pc)Cu and the monoprotonated porphyrin 2c. The most part of the added copper complex of N^{21} , N^{22} -bridged porphyrin was immobilized on support without desorption in the abovementioned protocol for the preparation of photocatalyst from 3a and 3c. Their adsorptive ability was also higher than that of di(µ-hydroxo)dipalladium(II) bisporphyrin $(2 \times 10^{-5} \text{ mol.g}^{-1})$ evaluated similarly. It was confirmed that the photosensitizers were not desorbed with water from the composite by absorption-spectral measurement of that water.

The aqueous solution of PNPP (1.5 mM) containing the composite of **3a** was irradiated with visible light, and the photodegradation of PNPP was monitored by ¹H NMR spectra. Under the condition the concentration of PNPP was decreased fast, and the most part was degraded in 60 min photoirradiation. Figure 4 shows

Photo-sensitizer	Added amount, mol	$\lambda_{max}^{\ b}$, nm	Absorbance in filtrate ^c	Immobilized amount, mol.g ⁻¹
3a	4.07×10^{-6}	414	0.235	4.0×10^{-5}
3c	4.01×10^{-6}	440	0.356	4.0×10^{-5}
2c	4.04×10^{-6}	433	0.550	1.2×10^{-5}
OEP	4.01×10^{-6}	401	0.651	2.3×10^{-6}
(S-Pc)Cu	4.07×10^{-6}	630 ^d	0.142	3.3×10^{-5}

Table 2. Evaluation of amount of immobilized sensitizers on support^a by UV-vis spectrophotometry

^a0.04 g of silica gel. ^bIn CHCl₃. ^cCHCl₃ solution diluted to 1 L. ^dAqueous solution.



Fig. 4. Heterogeneous photodegradation of PNPP in aqueous solution with porphyrin complexes on silica gel under visible light irradiation with a 500-W xenon lamp

the heterogeneous photodegradation of PNPP in aqueous solution containing the composite made from various photosensitizers. The results might reflect the photocatalytic activity of the sensitizers well. It is considered that 3a is immediately oxidized to di(μ -hydroxo)dicopper(II) complex of N^{21} , N^{22} -etheno bridged porphyrin when immobilizing on support and it played a role of active species from the beginning in the heterogeneous photoreaction process. The plausible mechanism in the heterogeneous photooxidation is shown in Scheme 3. It is considered that the oxidized Cu(II) complex 4a forms a strong coordination bond with deprotonated silanol group of silica gel in one site of Cu(II) with disaggregating. The silica-supported complex (A) can afford the reaction site for phenol by ligand exchange to form the phenolate Cu(II) complex (B). The attack of dioxygen to the aromatic ring of (B) may generate the alkylperoxide complex (C) by the process of one-step two-electron transfer to dioxygen or that of two-step one-electron transfer to dioxygen. Then radical cleavage of this active intermediate (C) liberates p-benzoquinone as a main oxidation product with forming the alkoxide complex (D), from which silica-supported Cu(II) complex of N^{21} , N^{22} -etheno bridged porphyrin (A) is regenerated



Scheme 3. Plausible mechanism for the heterogeneous photooxidation reaction

by hydrolysis and also the phenolate complex (B) can be formed by ligand exchange. Besides the catalytic process, singlet oxygen formed by the sensitizing effect of the bidentate porphyrin ligand coordinating to the copper may also contribute to the photooxidation, since there have been studies on the generation of singlet oxygen by sensitizers adsorbed on silicagel [2c–2f]. But it is considered that this heterogeneous reaction depends on the catalytic mechanism mainly and the adsorptive ability is an important factor to influence the result. Thus, in contrast to the homogeneous reaction, the photooxidation of PNPP with **3a** proceeded faster than that with **2** in the heterogeneous one. Moreover, the photostability of N^{21},N^{22} -etheno bridged porphyrin structure seems to contribute to the efficiency of the photooxidation.

In this system the used photocatalyst can be recovered through filtration and re-used after washing and drying. The composite of **3a** was little inactivated after three recycles in the photooxidation of PNPP under the same condition. So it is important that the copper complex of N^{21} , N^{22} -etheno bridged porphyrin can be applied in the heterogeneous photoreaction system with high adsorptive ability from a viewpoint of practical utilization, and is therefore significant that the complex can be easily activated in the preparation process of composite photocatalyst.

EXPERIMENTAL

General

(Octaethylpophyrinato)Cu(II) (1) and N^{21} , N^{22} -etheno bridged porphyrin (2) were prepared by the modified literature methods [18, 19]. $[Cu(I)(CH_3CN)_4]ClO_4$ was prepared in the usual way [20]. Solvents were purified prior to use by conventional methods. Deuterated solvents, [Cu(I)(CH₃CN)₄]PF₆, copper(II) phthalocyanine-3,4',4"',4"''-tetrasulfonic acid tetrasodium salt [(S-Pc) Cu(II)] and other chemicals were of reagent grade. ¹H-NMR spectra were recorded using a JEOL AL-300 spectrometer (300 MHz) at room temperature. Chemical shifts were reported in ppm with respect to the reference frequency of TMS (in CDCl₃ and CD₃CN) and TSP (in D₂O). MALDI-TOF-MS measurements were performed on a Shimadzu AXIMA Confidence mass spectrometer. The UV-visible spectra were measured on a Shimadzu UV-3100B instrument.

Synthesis

Preparation of copper(I) N^{21} , N^{22} -(diphenyletheno) octaethylporphyrin hexafluorophosphate (3a). Monoprotonated N^{21} , N^{22} -etheno bridged octaethylporphyrin 2 (10 mg, 0.012 mmol) was allowed to react with [Cu(I) (CH₃CN)₄]PF₆ (18 mg, 0.05 mmol) in CH₂Cl₂ (5 mL) at room temperature under argon in the dark for one day,

and then the solution was evaporated. Flush column chromatography of the residue on silica gel with CH₂Cl₂-acetone (20:1), followed by recrystallization of the main fraction from CH₂Cl₂ with *n*-hexane gave **3a** (4.2 mg) in 37% yield. ¹H NMR (300 MHz, CDCl₃): δ , ppm 11.07, 10.34, (s × 2, 1H × 2, *meso-H*); 10.47 (s, 2H, *meso-H*); 6.19 (t, 2H, bridge Ph-*p-H*); 5.86 (t, 4H, bridge Ph-*m-H*); 3.33 (br, 4H, bridge Ph-*o-H*); 4.41–3.99 (m, 16H, CH₂CH₃); 1.94, 1.79, 1.72, 1.48 (t × 4, 6H × 4, CH₂CH₃). HRMS (MALDI-TOF): *m/z* 773.3584 (calcd. for [C₅₀H₅₄N₄Cu]⁺ 773.3644). MS (MALDI-TOF): *m/z* 144.81 (calcd. for [PF₆]⁻ 144.96). UV-vis (MeCN): λ_{max} , nm (log ε) 612 (3.82), 578 (4.01), 569 (3.99), 536 (3.95), 412 (5.06).

Preparation of copper(I) N^{21} , N^{22} -(diphenyletheno) octaethylporphyrin perchlorate (3b). Monoprotonated form 2 (25 mg, 0.031 mmol) was allowed to react with [Cu(I)(CH₃CN)₄]ClO₄ (98 mg, 0.31 mmol) in CH₂Cl₂ (10 mL), and the reaction mixture was worked up in a similar manner as the case of 3a. Recrystallization from CH_2Cl_2 with diethyl ether gave **3b** (25 mg) in 94% yield. ¹H NMR (300 MHz, CDCl₃): δ, ppm 11.17, 10.34, (s \times 2, 1H \times 2, meso-H); 10.47 (s, 2H, meso-H); 6.19 (t, 2H, bridge Ph-p-H); 5.86 (t, 4H, bridge Ph-m-H); 3.31 (br, 4H, bridge Ph-o-H); 4.47–3.94 (m, 16H, CH₂CH₃); 1.93, 1.78, 1.73, 1.47 (t \times 4, 6H \times 4, CH₂CH₃). HRMS (MALDI-TOF): *m/z* 773.3666 (calcd. for [C₅₀H₅₄N₄Cu]⁺ 773.3644). MS (MALDI-TOF): m/z 98.93 (calcd. for $[ClO_4]^-$ 98.95). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 612 (3.87), 577 (4.07), 567 (4.06), 537 (4.01), 413 (5.18).

Preparation of copper(I) N²¹, N²²-(diphenyletheno) tetraphenylporphyrin hexafluorophosphate (3c). Monoprotonated N^{21} , N^{22} -(diphenyletheno)tetraphenylporphyrin 2c (10 mg, 0.011 mmol) was allowed to react with $[Cu(I)(CH_3CN)_4]PF_6$ (14 mg, 0.04 mmol) in CH_2Cl_2 (10 mL), and reaction mixture was treated in a manner analogous to that described above. Recrystallization from CH_2Cl_2 with *n*-hexane gave **3c** (3.0 mg) in 27% yield. ¹H NMR (300 MHz; CDCl₃): δ, ppm 9.04, 9.00, 8.70, 8.54 (d × 2, 2H × 4, pyrrole-β-H); 8.79–7.62 (m, 20H, *meso*-Ph-*H*); 6.38 (t, 2H, bridge Ph-*p*-*H*); 6.05 (t, 4H, bridge Ph-m-H); 3.42 (br, 4H, bridge Ph-o-H). HRMS (MALDI-TOF): *m/z* 853.2441 (calcd. for [C₅₈H₃₈N₄Cu]⁺ 853.2392). MS (MALDI-TOF): m/z 144.81 (calcd. for $[PF_6]$ ⁻ 144.96). UV-vis (CH₂Cl₂): λ_{max} , nm (log ϵ) 635 (3.71), 596 (4.13), 556 (4.03), 441 (5.14).

Oxidation of 3b to di(μ -hydroxo)dicopper(II) bis[N^{21} , N^{22} -(diphenyletheno)octaethylporphyrin] bis(perchlorate) (4b). Copper(I) N^{21} , N^{22} -(diphenyletheno) octaethylporphyrin perchlorate 3b (9.8 mg, 0.011 mmol) was recrystallized from CH₂Cl₂ and MeOH overnight to give the Cu^{II} complex 4b (6.0 mg) in 60% yield. ¹H NMR (300 MHz; CDCl₃): δ , ppm 11.43, (br, 2H, *meso-H*); 7.83 (br, 6H, *meso-H*); 6.38, 5.61 (br × 2, 4H × 2, Ph-*m-H*); 5.72 (t, 4H, Ph-*p-H*); 5.17, 4.87 (br × 2, 4H × 2); 5.02 (s, 2H); 4.34, 3.66 (br × 2, 8H × 2); 4.13, 3.10 (br × 2, 4H × 2); 2.03, 1.53, 1.26, 0.71 (br × 4, 12H × 4, CH₂CH₃). MS (MALDI-TOF): m/z 790.06 (calcd. for $[C_{50}H_{55}N_4OCu]^+$ 790.37). UV-vis (CH₂Cl₂): λ_{max} , nm (log ε) 618 (3.96), 588 (4.15), 573 (4.17), 547 (4.15), 419 (5.19).

Homogeneous photooxidation

DBP (2 mM) and a sensitizer (0.2 mM) were dissolved in an aerated acetonitrile- d_3 solution and irradiated with visible light (350 nm < λ < 800 nm) by a 500 W xenon lamp passed through cut filters with stirring in a flask at room temperature. A 0.5 mL of sample solution was withdrawn and analyzed by ¹H NMR spectroscopy before and after photoirradiation. The conversions were evaluated from a ratio of the integral values of a doublet signal at 7.16 ppm for DBP before the photoreaction and a singlet signal at 6.48 ppm for photooxidatively produced DBQ assigned to *m*-phenyl protons using a singlet signal at 7.37 ppm for *p*-dichlorobenzene as an internal standard.

Heterogeneous photooxidation

0.1 g of silica gel was suspended in a 2 mL of chloroform solution containing a porphyrin derivative $(4 \times 10^{-6} \text{ mol})$ or aqueous solution of (S-Pc)Cu. The suspension was stirred for 10 min, evaporated and dried under vacuum. Thus prepared composite (10 mg) was added to an aerated deuterium oxide solution (2.2 mL) containing PNPP (1.5 mM) and the mixture was photoirradiated in a similar manner as above. The content of PNPP was monitored by the ¹H NMR measurement after centrifugation and filtration of the sample solution. The integral values of two doublet signals at 7.17 and 6.85 ppm for PNPP assigned to *o*- and *m*-phenyl protons were used in comparison with a TSP signal at 0 ppm as an internal standard.

Evaluation of amount of immobilized sensitizer

0.04 g of silica gel was suspended in a 2 mL chloroform solution of a porphyrin derivative (*ca.* 4×10^{-6} mol) or aqueous solution of (S-Pc)Cu. The suspension was evaporated, washed with a 4 mL of solvent and then filtered. The volume of the washing filtrate was made exactly to 50 mL. This filtrate was further diluted 5 times for **3a**, 12.5 times for **3c**, and 10 times for OEP. The concentration of the desorbed sensitizer in washing filtrate was calculated on the basis of the UV-vis absorbance. Then the amount of immobilized sensitizer was evaluated.

UV-vis monitoring of photooxidation of Cu(I) porphyrin (3a)

A 0.3 mL of acetonitrile solution containing **3a** (0.2 mM) was placed in 1 mm optical cell. The cell was set in a holder with external water-cooling, and irradiated with visible light in a similar manner as the photocatalysis study. In the course of photoreaction process in 120 min UV-vis spectrum was recorded.

CONCLUSION

 N^{21} , N^{22} -etheno bridged porphyrins were metallated by Cu(I) reagent owing to the formation of the Cu(I)-alkene π -bonding in addition to the ligation of two pyrrole nitrogens. X-ray crystallography of the Cu(I) porphyrin demonstrated unusually short Cu-C and Cu-N distances and very long C-C double bond. Aerial oxidation of the Cu(I) porphyrin was promoted in MeOH to give $di(\mu$ hydroxo)dicopper(II) complex. The copper porphyrin complexes promoted photooxidation of a phenol derivative in acetonitrile solution under aerobic condition with visible light irradiation. It is considered that the active species in the photooxidations were di(µ-hydroxo)dicopper(II) porphyrin complexes produced by oxidation of Cu(I) complexes of N^{21} , N^{22} -etheno bridged porphyrins, though di(μ -hydroxo)dipalladium(II) complex of N^{21} , N^{22} -etheno bridged porphyrin has shown the higher photocatalytic activity than the copper complexes. In the homogeneous photoreaction system, it seems a merit that the active $di(\mu$ hydroxo)dicopper(II) porphyrin complex is generated spontaneously in aerated solution. Further, the copper porphyrin complexes were utilized to heterogeneous photoreaction in aqueous solution by immobilization on support. It seems that on immobilization the $di(\mu$ hydroxo)dicopper(II) porphyrin complex is effectively formed from Cu(I) complex resulting in composite photocatalyst. The copper complex with N^{21} , N^{22} -etheno bridged porphyrin has a high adsorptive ability and the composite contains much amount of immobilized active sensitizer for the photooxidation of target compounds. The high photostability of the complex with N^{21} , N^{22} -etheno bridged porphyrin is also considered to contribute the efficiency as the photocatalyst. It seems that the activity of homogeneous reaction is due to the formation of singlet oxygen more and the efficiency in the heterogeneous one is predominated by the catalytic pathway. Thus the photooxidation of phenol derivative with the composite photocatalyst of the copper complex with N^{21} , N^{22} -etheno bridged porphyrin proceeded faster than that of the monoprotonated derivative in spite of the higher efficiency of the latter than the former in the homogeneous reaction. Another advantage in heterogeneous system is that the composite photocatalyst can be easily recovered and re-used by filtration, washing and drying. Thus the copper complexes described here contributed to photooxidation of phenol derivative under aerobic condition with visible irradiation as photosensitizer in both of homogeneous and heterogeneous system in which the (hydroxo)Cu(II) complexes to be formed from the Cu(I) complexes with N^{21} , N^{22} -etheno bridged porphyrin played a role of the key species.

7

REFERENCES

 (a) Murtinho D, Pineiro M, Pereira MM, Rocha Gonsalves AMd'AR, Arnaut LG, Miguel MG and Burrows HD. *J. Chem. Soc.*, *Perkin Trans.* 2 2000: 2441–2447. (b) Suchard O, Kane R, Roe BJ, Zimmermann E, Jung C, Waske PA, Mattay J and Oelgemöller M. *Tetrahedron* 2006; **62**: 1467–1473.

- (a) Gerdes R, Bartels O, Schneider G, Wöhrle D and S-Ékloff G. *Polym. Adv. Technol.* 2001; **12**: 152–160.
 (b) Ribeiro SM, Serra AC and Rocha Gonsalves AMd'AR. *Tetrahedron* 2007; **63**: 7885–7891.
 (c) Kasuga K. Imai M, Irie H, Tanaka H, Ikeue T, Handa M, Wada S and Sugimori T. *J. Porphyrins Phthalocyanines* 2006; **10**: 1212–1218. (d) Giaimuccio J, Zamadar M, Aebisher D, Meyer GJ and Greer A. *J. Phys. Chem.* 2008; **112**: 15646–15650.
 (e) Kasuga K, Irie H, Tanaka H, Ikeue T, Sugimori T and Handa M. *J. Porphyrins Phthalocyanines* 2011; **15**: 1078–1084. (f) Kuznetsova NA, Yuzhakova OA, Strakhovskaya MG, Shumarina AO, Kozlov AS, Krasnovsky AA and Kaliya OL. *J. Porphyrins Phthalocyanines* 2011; **15**: 718–726.
- (a) Kasuga K, Mori K, Sugimori T and Handa M. *Bull. Chem. Soc. Jpn.* 2000; **73**: 939–940. (b) Sanchez M, Hadash A, Fell RT and Meunier B. *J. Catal.* 2001; **202**: 177–186.
- 4. (a) Kasuga K, Miyazako T, Sugimori T and Handa M. *Inorg. Chem. Commun.* 2003; 6: 807–809.
 (b) Kluson P, Drobek M, Krejcikova S, Krysa J, Kalaji A, Cajthaml T and Rakusan J. *Applied Catalysis B: Environmental* 2008; 80: 321–326.
- (a) Wöhrle D, Suvorova O, Gerdes R, Bartels R, Lapok L, Baziakina N, Makarov S and Slodek A. J. Porphyrins Phthalocyanines 2004; 8: 1020–1041.
 (b) Hassanein MT, Gerges SS, Abdo MA and Elkhalafy SH. J. Porphyrins Phthalocyanines 2005; 9: 621–625.
- (a) Silva E, Pereira MM, Burrows HD, Azenha ME, Sarakha M and Bolte M. *Photochem. Photobiol. Sci.* 2004; **3**: 200–204. (b) Sarakha M, Bolte M and Burrows HD. *J. Photochem. Photobiol. A: Chem.* 1997; **97**: 101–106. (c) Sarakha M, Burrows H and Bolte M. *J. Photochem. Photobiol. A: Chem.* 1996; **97**: 81–86.
- (a) Wiehe A, Stollberg H, Runge S, Paul A, Senge MO and Röder B. J. Porphyrins Phthalocyanines 2001;
 5: 853–860. (b) Mosinger J, Kliment Jr. V, Sejbal J, Kubát P and Lang K. J. Porphyrins Phthalocyanines 2002; 6: 514–526. (c) Tsaryova O, Semioshkin A, Wöhrle D and Bregadze VI. J. Porphyrins Phthalocyanines 2005; 9: 268–274.
- (a) Gerdes R, Wöhrle D, Spiller W, Schneider G, Schnurpfeil G and Schulz-Ekloff G. J. Photochem. Photobiol. A: Chem. 1997; **111**: 65–74. (b) Ilive V. J. Photochem. Photobiol. A: Chem. 2002; **151**: 195–199. (c) Hu M, Xu Y and Xiong Z. Chem. Lett. 2004; **33**: 1092–1093. (d) Inoue N, Ishioka T and Harata A. Chem. Lett. 2009; **38**: 358–359.
- 9. (a) Takao Y, Takeda T, Watanabe J and Setsune J. *Organometallics* 1999; **18**: 2936–2938. (b) Takao Y,

Takeda T, Watanabe J and Setsune J. *Organometallics* 2003; **22**: 233–241.

- (a) Takao Y, Takeda T, Miyashita K and Setsune J. *Chem. Lett.* 1996; **25**: 761–762. (b) Takao Y, Takeda T, Miyashita K and Setsune J. *Bull. Chem. Soc. Jpn.* 1998; **71**: 1327–1335. (c) Takao Y, Takeda T and Setsune J. *Bull. Chem. Soc. Jpn.* 2003; **76**: 1549–1553.
- (a) Takao Y, Takeda T, Tanikawa S and Setsune J. J. Porphyrins Phthalocyanines 2003; 7: 521–525.
 (b) Takao Y, Ohno T, Moriwaki K, Matsumoto F and Setsune J. J. Porphyrins Phthalocyanines 2010; 14: 64–68.
- (a) Deal KA, Park G, Shao J, Chasteen ND, Brechbiel MW and Planalp RP. *Inorg. Chem.* 2001; **40**: 4176– 4182. (b) Evans DA, Scheidt KA, Johnston JN and Willis MC. *J. Am. Chem. Soc.* 2001; **123**: 4480–4491. (c) Yang H, HongY-T and Kim S. *Org. Lett.* 2007; **9**: 2281–2284.
- (a) Arabei SM, Solovyov KN and Egorova GD. J. Porphyrins Phthalocyanines 2000; 4: 605–610. (b) Inamo M, Kamiya N, Inada Y, Nomura M and Funahashi S. Inorg. Chem. 2001; 40: 5636–5644. (c) Inamo M, Kumagai H, Harada U, Itoh S, Iwatsuki S, Ishihara K and Takagi HD. Dalton Trans. 2004: 1703–1707. (d) Turowska-Tyrk I, Kang S-J and Scheidt WR. J. Porphyrins Phthalocyanines 2011; 15: 1–9.
- (a) Wang C, Li J, Mele G, Yang G-M, Zhang F-X, Palmisano L and Vasapollo G. *Applied Catalysis B: Environmental* 2007; **76**: 218–226. (b) Silva M, Azenha ME, Pereira MM, Burrows HD, Sarakha M, Forano C, Ribeiro MF and Fernandes A. *Applied Catalysis B: Environmental* 2010; **100**: 1–9.
- Setsune J, Su CL and Takao Y. *Chem. Lett.* 2014;
 43: 1113–1115 (CCDC-990301 for 3b and CCDC-990302 for 4b).
- Callot HJ, Fischer J and Weiss RJ. J. Am. Chem. Soc. 1982; 104: 1272–1276.
- (a) Gao J and Zhong S-H. J. Mol. Catal. A: Chem. 2000; 164: 1–7. (b) Garozzo MS, Marsich N and Camus A. Gazz. Chim. Ital. 1993; 123: 697–701.
 (c) Srinivas B, Prakash PS and Zacharias PS. Transition Met. Chem. (Dordrecht, Neth.) 1993; 18: 567–569. (d) Jallabert C, Lapinte C and Riviere H. J. Mol. Catal. 1982; 14: 75–86.
- (a) Sanders JKM, Bampos N, Clyde-Watson Z, Darling SL, Hawley JC, Kim H-J, Mak CC and Webb SJ. *The Porphyrin Handbook*, Vol. 3, Elsevier Science: San Diego, 2003; pp 27–30. (b) Ogata H, Fukuda T, Nakai K, Fujimura Y, Neya S, Stuzhin PA and Kobayashi N. *Eur. J. Inorg. Chem.* 2004: 1621–1629.
- Setsune J, Ikeda M, Kishimoto Y, Ishimaru Y, Fukuhara K and Kitao T. Organometallics 1991; 10: 1099–1107.
- Kitagawa S and Munakata M. *Inorg. Chem.* 1981;
 20: 2261–2267.