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COMMUNICATION

A Nonheme Manganese(IV)-Oxo Species Generated in Photocatalytic Reaction Using Water as an Oxygen Source

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A nonheme manganese(IV)-oxo complex, $[\text{Mn}^{\text{IV}}(\text{O})(\text{BQCN})]^{2+}$, was generated in photochemical and chemical oxidations of $[\text{Mn}^{\text{II}}(\text{BQCN})]^{2+}$ with water as an oxygen source, respectively. The photocatalytic oxidation of organic substrates, such as alcohol and sulfide, by $[\text{Mn}^{\text{II}}(\text{BQCN})]^{2+}$ has been demonstrated in both neutral and acidic media.

A typical artificial photosynthesis system consists of two half reactions, water oxidation and hydrogen production, which attracts a great interest due to the utilization of the solar energy and production of renewable clean energy.¹ The oxidation of water by the oxygen evolving complex (OEC) in Photosystem II (PS II) induces the generation of high-valent manganese-oxo (Mn-oxo) species via a proton-coupled electron transfer (PCET) mechanism, in which the oxygen atom in the Mn-oxo intermediates derives from water.^{2,3} In biomimetic studies, a number of water oxidation catalysts (WOCs) using transition metals (e.g., Ru, Ir, Fe, Co, Ni, and Cu) were synthesized and used in the investigation of water oxidation. One of the key investigations in water oxidation using the synthetic metal catalysts is to generate high-valent metal-oxo intermediates to investigate their chemical properties.⁴⁻¹⁰ For example, a number of high-valent Mn^{IV} -oxo and Mn^{V} -oxo complexes have been synthesized using various chemical oxidants, such as peroxy acids, iodosylbenzene (PhIO), and cerium(IV) ammonium nitrate (CAN), and the reactivities of the Mn-oxo intermediates have been investigated in various oxidation reactions.¹¹⁻¹³ However, there has yet to be much investigation of high-valent Mn-oxo species in photocatalytic system, which is extremely important for developing efficient photocatalysts based on low-cost and earth-abundant metals and improving mechanistic insights into water splitting system.^{14,15}

Recently, Fukuzumi, Nam, and co-workers have shown the generation of a mononuclear nonheme $[\text{Fe}^{\text{IV}}(\text{O})(\text{N4Py})]^{2+}$ complex (N4Py = *N,N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) in a reaction of $[\text{Fe}^{\text{II}}(\text{N4Py})]^{2+}$, $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine), and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ under the photoirradiation in an acidic aqueous

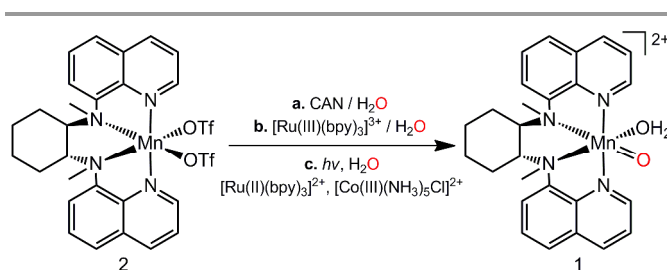
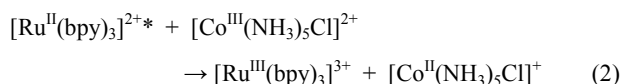
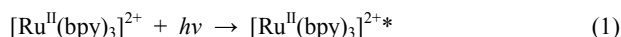


Fig. 1 Chemical and photocatalytic generation of $[\text{Mn}^{\text{IV}}(\text{O})(\text{H}_2\text{O})(\text{BQCN})]^{2+}$ (**1**) from the corresponding $\text{Mn}^{\text{II}}(\text{BQCN})(\text{CF}_3\text{SO}_3)_2$ complex (**2**) in the presence of water.¹⁸

solution.¹⁶ More recently, Costas, Pérez-Prieto, Lloret-Fillol, and co-workers reported mechanistic studies on the photocatalytic generation of a nonheme Fe^{IV} -oxo complex and its reactivity towards oxygen-atom transfer reactions.¹⁷ However, to the best of our knowledge, there has been no report on the photocatalytic generation of nonheme Mn-oxo species with water as an oxygen source. We therefore attempted to generate high-valent Mn-oxo species with the use of visible light irradiation ($\lambda > 420$ nm) at 273 K. Herein, we report the photocatalytic generation of a mononuclear nonheme $[\text{Mn}^{\text{IV}}(\text{O})(\text{BQCN})]^{2+}$ complex (**1**; BQCN = *N,N'*-dimethyl-*N,N'*-bis(8-quinolyl)cyclohexanediamine; Fig. 1) from the starting complex $\text{Mn}^{\text{II}}(\text{BQCN})(\text{CF}_3\text{SO}_3)_2$ (**2**),¹⁸ using $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ as a photosensitizer, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ as a sacrificial electron acceptor, and water as an oxygen source (Fig. 1). We also report the chemical generation and spectroscopic characterization of the Mn^{IV} -oxo complex **1** in the reaction of **2** with one-electron oxidant $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ in an acidic aqueous solution. The photocatalytic oxidation of organic substrates in alcohol oxidation and sulfoxidation reactions has been discussed as well.

Photoirradiation ($\lambda > 420$ nm) of a deaerated acetate buffer (pH 4.0, 50 mM) and MeCN (*v/v* 1:6) mixed solution containing **2** (1.0×10^{-3} M), $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (5.0×10^{-4} M), and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ (5.0×10^{-3} M) at 273 K afforded the

formation of an intermediate with a broad absorption band at 640 nm within 10 min (Fig. S1 and Experimental Section for the detail of the photocatalytic generation of **1**, ESI†), which is assigned as $[\text{Mn}^{\text{IV}}(\text{O})(\text{BQCN})]^{2+}$ (**1**) (*vide infra*).¹⁸ The formation of **1** was not observed in the absence of **2**, photosensitizer, sacrificial electron acceptor or visible-light irradiation (Fig. S2, ESI†), suggesting all these components are necessary for the photocatalytic generation of **1**.



According to the literature,^{15a,19} $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ could be produced by photoinduced oxidative quenching of the excited state of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$, $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+*}$ (where * denotes the excited state), by one-electron oxidant $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ under the photoirradiation ($\lambda > 420$ nm) [eqns (1) and (2)], and it is usually used as a one-electron oxidant in water oxidation to generate high-valent metal-oxo species. Therefore, we attempted to generate **1** by $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ under the same condition of light-driven oxidation, to confirm the formation of Mn^{IV} -oxo species in the three components system (*vide supra*).









Addition of 1 equiv. of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ (1.0×10^{-3} M) to a deaerated acetate buffer (pH 4.0, 50 mM) and MeCN (*v/v* 1:6) mixed solution containing **2** (1.0×10^{-3} M) did not afford the formation of **1**, but Mn^{III} -hydroxo species ($\text{Mn}^{\text{III}}\text{-OH}$) was formed via the one-electron oxidation reaction (Fig. S3, ESI†).^{17,20} However, an absorption band at 640 nm increased immediately upon addition of the second aliquot of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ (Fig. S1, ESI†; $t_{1/2} \approx 3$ h), which is consistent with the UV-vis spectrum of **1** formed in light-driven oxidation and chemical oxidation by CAN under the same reaction conditions (Figs. S1 and S4, ESI†). The yield of **1** was determined to be ~80% based on the absorbance at 640 nm. Similarly, addition of 2 equiv. of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ to a solution containing **2** resulted in the formation of **1** with a broad absorption band at 640 nm (*vide supra*), accompanied by the solution color changed from deep green to bright orange, indicating the conversion of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ to $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ species. Finally, the intermediate **1** was also generated in the reaction of **2** with a strong one-electron oxidant (e.g., CAN, 4 equiv.), as reported previously (Fig. S4, ESI†).¹⁸

The formation of **1** by $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ in the presence of H_2O was further confirmed by electrospray ionization mass (ESI-MS) and electron paramagnetic resonance (EPR) spectroscopic methods. The ESI-MS spectrum of **1** shows prominent ion peaks at m/z 484.3, 669.2, and 719.2 (Fig. S5a, ESI†), the mass and isotope distribution patterns of peaks correspond to $[\text{Mn}^{\text{IV}}(\text{O})(\text{OH})(\text{BQCN})]^+$ (calc. m/z 484.2), $[\text{Ru}^{\text{II}}(\text{bpy})_3(\text{ClO}_4)]^+$ (calc. m/z 669.1), and $[\text{Ru}^{\text{II}}(\text{bpy})_3(\text{CF}_3\text{SO}_3)]^+$ (calc. m/z 719.1).¹⁸ When the reaction was carried out in the presence of isotopically labeled H_2^{18}O , the mass peak shifts from m/z 484.3 to 488.3, indicating that **1** contains two oxygen atoms originated from water. The X-band EPR spectrum of **1** shows a broad signal at $g \approx 4.1$ (Fig. S5b, ESI†), which is characteristic of high-spin $S = 3/2$ Mn^{IV} species and consistent with

the reported EPR spectrum of the same Mn^{IV} -oxo intermediate generated in the reaction by CAN.¹⁸

To investigate the photocatalytic activity of **2** in the oxidation of organic substrates in a wide pH range, we performed reactions in a deaerated phosphate buffer (pH 6.8, 50 mM) and MeCN (*v/v* 19:1) mixed solvent and a deaerated acetate buffer (pH 4.0, 50 mM) and MeCN (*v/v* 19:1) mixed solvent. The reaction solution containing **2** (4.0×10^{-5} M), substrates (2.0×10^{-2} M), $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (4.0×10^{-4} M), and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ (2.0×10^{-2} M) has been stirring continuously under photoirradiation ($\lambda > 420$ nm) for 2 h. The analysis of products and the determination of turnover numbers (TONs) and initial turnover frequencies (TOFs) were conducted by ^1H NMR spectroscopy, Gas Chromatography (GC), and Gas chromatography-mass spectrometry (GC-MS).^{21,22} The oxidation of benzyl alcohol was found to give the $2e^-$ -oxidation product (i.e., benzaldehyde) through hydrogen-atom transfer (HAT) reaction with a TON of 22 and an initial TOF of 49 h^{-1} in a neutral aqueous solution at pH 6.8, but a TON of 75 and an initial TOF of 93 h^{-1} were obtained in an acidic aqueous solution at pH 4.0 (Table 1; Figs. S6 – S8, ESI†). For the oxygen-atom transfer (OAT) reaction using thioanisole as a substrate, methyl phenyl sulfoxide was obtained as a sole product with a TON of 90 and an initial TOF of $3.6 \times 10^2 \text{ h}^{-1}$ at pH 6.8, and both the TON and an initial TOF value increased to 2.1×10^2 and $7.1 \times 10^2 \text{ h}^{-1}$ at pH 4.0 (Table 1; Figs. S9 – S11, ESI†). When the photocatalytic oxidation of thioanisole was carried out using H_2^{18}O instead of H_2^{16}O , ^{18}O -incorporated methyl phenyl sulfoxide was obtained as the sole product (Fig. S12, ESI†), indicating that the oxygen source in the product is water. It should be noted that, in the absence of the catalyst **2**, only trace amounts of benzaldehyde and methyl phenyl sulfoxide were obtained in the photocatalytic reactions. Furthermore, essentially no product was produced in the absence of photosensitizer, ($[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$), or visible-light irradiation. These results indicate that the photocatalytic oxidation of organic substrates by **2** occurs via the formation of a

Table 1 Photocatalytic oxidation of organic substrates by catalyst **2**

Entry	Substrate	Product	TON ^[c]	TOF ^[c]
1 ^[a]			22	49
2 ^[b]			75	93
3 ^[a]			90	360
4 ^[b]			210	710

Reaction conditions: [catalyst] = 4.0×10^{-5} M, [substrate] = 2.0×10^{-2} M, $[[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}] = 4.0 \times 10^{-4}$ M, $[[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}] = 2.0 \times 10^{-2}$ M, at room temperature, under light illumination by Xe lamp (300 W, $\lambda > 420$ nm). [a] Deaerated phosphate buffer (pH 6.8, 50 mM) and MeCN (*v/v* 19:1) mixed solvent. [b] Deaerated acetate buffer (pH 4.0, 50 mM) and MeCN (*v/v* 19:1) mixed solvent. [c] TON = $\text{TON}_{(\text{with catalyst})} - \text{TON}_{(\text{without catalyst})}$, where TON defined as moles of per produced product per mole of catalyst, $n_{\text{product}} / n_{\text{catalyst}}$. TOF = $(\text{TON} / \text{Reaction Time})_{\text{initial}}$, h^{-1} , where TOF defined as moles of per produced product per mole of catalyst per unit of time.

Mn-oxo species. Finally, the quantum yields (Φ) of the photocatalytic oxidation of alcohol and sulfide by **2** were determined according to the literature method.²³ The maximum Φ of 0.26 was obtained in a 10 min oxidation reaction of thioanisole by **2** under irradiation with monochromatic light ($\lambda = 450$ nm) at pH 4.0 (see ESI†, Experimental Section for the detail of the quantum yield measurement), which is a promising result compared with previously reports.²²

By analyzing UV-vis, ESI-MS, and EPR spectroscopic data, Mn^{II} and Ru^{II} species were formed in the photocatalytic oxidation of thioanisole by **2**, as we have shown previously the formation of **2** as a product in the OAT reaction by **1** (Fig. S13, ESI†).²⁴ In contrast to the OAT reaction, Mn^{III} -OH species was formed as the major product in the photocatalytic oxidation of benzyl alcohol by **2**, which is consistent with the previous observation in the C-H bond activation reactions by high-valent manganese-oxo and iron-oxo complexes via the HAT pathway (Fig. S14, ESI†).^{24,25}

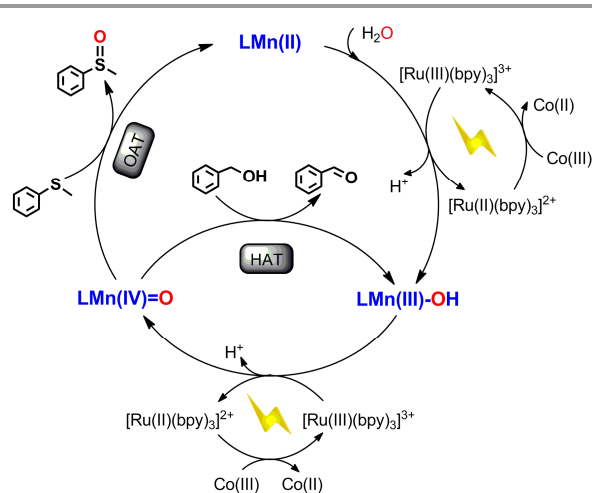
On the basis of the experimental results, a proposed mechanism for the photocatalytic oxidation of organic substrates by **2** is depicted in Scheme 1. Photoinduced electron transfer from excited photosensitizer ($[Ru^{II}(bpy)_3]^{2+*}$) to a sacrificial electron acceptor $[Co^{III}(NH_3)_5Cl]^{2+}$ occurs to produce $[Ru^{III}(bpy)_3]^{3+}$, which then oxidizes $[Mn^{II}(BQCN)]^{2+}$ to give the high-valent Mn^{III} -hydroxo and Mn^{IV} -oxo species via stepwise one-electron oxidation processes. The reactive Mn^{IV} -oxo intermediate then reacts with organic substrates to afford the corresponding oxidized products with the generation of Mn^{II} species in the sulfoxidation reaction (i.e., OAT) and Mn^{III} -OH species in the alcohol oxidation reaction (i.e., HAT) (Scheme 1).

Conclusions

We have demonstrated the generation of a mononuclear nonheme Mn^{IV} -oxo complex, $[Mn^{IV}(O)(BQCN)]^{2+}$ (**1**), via a photocatalytic reaction of a manganese(II) complex, $[Mn^{II}(BQCN)]^{2+}$ (**2**), with $[Ru^{II}(bpy)_3]Cl_2$ as a photosensitizer, $[Co^{III}(NH_3)_5Cl]Cl_2$ as a low-cost sacrificial electron acceptor, and water as an oxygen source. We have also presented an efficient homogeneous photocatalytic system for the oxidation of alcohol and sulfide by the earth-abundant Mn^{II} and Co^{III} complexes. This work provides valuable insights into the development of new efficient manganese-based molecular catalysts in photocatalytic oxidation of organic substrates and the effective utilization of solar energy using water as an oxygen source. Future work will focus on the design of more advanced manganese-based molecular catalysts for water oxidation as well as the construction of functional devices for applications in artificial photosynthesis systems.

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Scheme 1 Proposed reaction mechanisms of light-driven oxidation of organic substrates by $[Mn^{II}(BQCN)]^{2+}$ (**2**) as a catalyst, $[Ru^{II}(bpy)_3]^{2+}$ as a photosensitizer, and $[Co^{III}(NH_3)_5Cl]^{2+}$ as a low-cost sacrificial electron acceptor in the presence of water.

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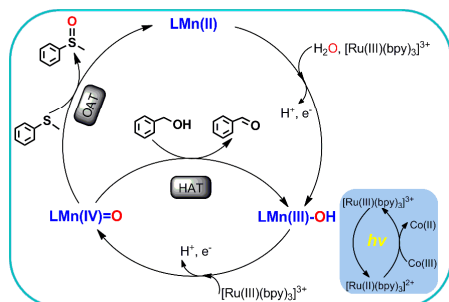
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- † Electronic Supplementary Information (ESI) available: Experimental details of photocatalytic oxidation, mass spectrum of ^{18}O -labeling experiment and the data of control experiments. See DOI: 10.1039/c000000x/

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A nonheme manganese(IV)-oxo complex was generated in photocatalytic reaction of $[\text{Mn}^{\text{II}}(\text{BQCN})]^{2+}$ with $[\text{Ru}^{\text{II}}(\text{bpy})_3]\text{Cl}_2$, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, and water as an oxygen source.