

論文の内容の要旨

論文題目 Construction of Photochemical Water Oxidation System Catalyzed by Ruthenium Complexes in Vesicles (ルテニウム錯体を触媒とするベシクル中における水の光酸化反応系の構築)

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Introduction

In natural photosynthetic systems, a redox reaction having a positive free-energy change, in which H_2O is oxidized to O_2 and NADP^+ is reduced to NADPH, proceeds with the aid of light energy using the phospholipid bilayer membranes as a reaction field (Figure 1). The photosynthetic membranes play an essential role, which not only support molecules that participate in light absorption and charge separation, but also act as a barrier to inhibit the charge recombination reaction between photogenerated oxidized and reduced species. Therefore, bilayer membranes such as vesicle membranes are thought to be a fascinating reaction field to construct artificial systems mimicking natural photosynthetic system, in which light energy can be converted into chemical potential with high efficiency.

Vesicles are approximately spherical bilayer membranes formed by self-organization of amphiphiles such as phospholipids. Although vesicular systems for photochemical reductions such as hydrogen production and CO_2 reduction have been reported, those for photochemical water oxidation have been scarce and not completely explored due to the difficulty of 4-electron oxidation to generate O_2 from H_2O . Recently, water oxidation catalysts such as Ru, Ir, Mn, Fe, Co and other metal complexes have been reported. Among them, a ruthenium complex

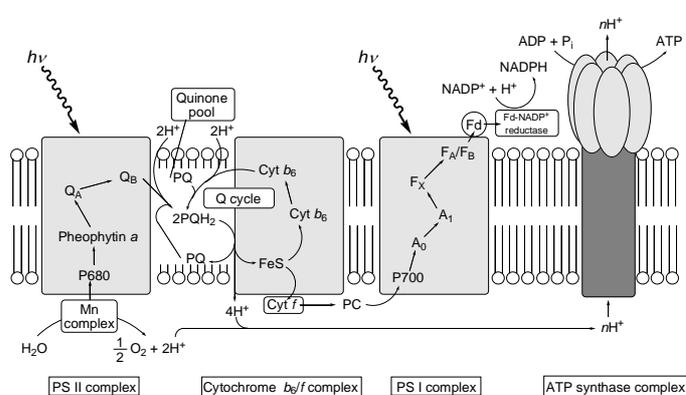


Figure 1. Schematic diagram of photosynthetic system in green plants.

Ru(bda)(pic)₂ (H₂bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, pic = 4-picoline) reported by Sun *et al.* has high catalytic activity toward chemical and photochemical water oxidation.^[1] I decided to employ this type of Ru complex for photochemical water oxidation in vesicular systems because of not only its high catalytic efficiency but also facile chemical modifications including introduction of substituent groups such as alkyl chains to increase the affinity to the vesicle membranes. With the aim of constructing whole water splitting system in vesicles, which is capable of producing H₂ and O₂ simultaneously, I studied photochemical water oxidation using the above Ru complex embedded in vesicles.

Substituent effects on water oxidation in homogeneous system

Prior to the incorporation of the Ru catalyst into vesicles, I investigated the substituent effects at the 4-position of the axial pyridine ligand on electrochemical properties and catalytic activity toward water oxidation in a homogeneous solution. Ru complexes **1–6** were synthesized in 21–58% yields by the reaction of Ru(bda)(DMSO)₂, which was generated in situ from Ru(DMSO)₄Cl₂ and H₂bda in the presence of excess triethylamine, and the corresponding 4-substituted pyridine in MeOH. In cyclic voltammetric measurement, each Ru complex gave a reversible oxidation wave that is assigned to the Ru^{III/II} couple. The electrochemical data shown in Table 1 indicate that the electron-donating ability of the substituent on the pyridine ligand was reasonably reflected in HOMO energy level of the complex.

Chemical water oxidation experiments were carried out as follows: UV-Vis absorption change of the solution containing complex **1–6** (1.0 μM) and Ce(NH₄)₂(NO₃)₆ (1.5 mM) as an oxidant in aqueous nitric acid (0.1 M) with 3% acetonitrile was measured at 360 nm, where the absorption intensity corresponds to the concentration of Ce(IV). From the initial rate of the Ce(IV) consumption, the chemical water oxidation rate was estimated using first-order exponential fitting. As shown in Table 1, it was found that Ru complexes **4–6**, which have electron-withdrawing groups at the 4-position of pyridine ligands, exhibit notably high catalytic activity. Noteworthy, complex **1** having the most electron-donating group in the series of substituents, OMe, showed relatively high catalytic performance rather than **2** and **3**.

Next, photochemical water oxidation experiments were carried out as follows: a solution containing [Ru(bpy)₃]²⁺ (0.85 mM), S₂O₈²⁻ (5.0 mM), and complex **1–6** (17 μM) in 1:1 acetonitrile/aqueous borate buffer (40 mM, pH 8.0) was irradiated by a xenon arc lamp equipped with a cut-off filter

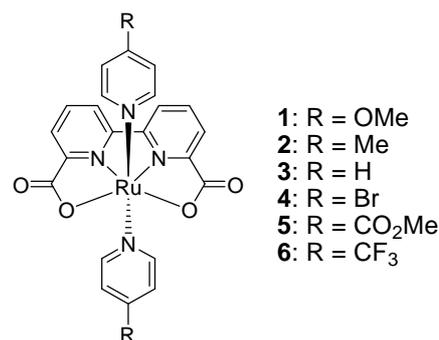


Figure 2. Chemical structure of ruthenium complexes **1–6**.

Table 1. Electrochemical properties of the complexes **1–6** and kinetic data of chemical and photochemical water oxidation catalyzed by **1–6**.

R	$E_{1/2(\text{oxdn})} / \text{V}$ (vs. Fc^+/Fc) ^a	Chemical $v_i / \mu\text{M s}^{-1}$	Photochemical TOF / h^{-1}
OMe (1)	-0.09	0.829	80.5
Me (2)	-0.06	0.381	33.4
H (3)	-0.03	0.449	56.8
Br (4)	0.01	4.62	85.2
CO ₂ Me (5)	0.05	4.87	114
CF ₃ (6)	0.08	5.98	111

^aFc = ferrocene

(>390 nm). The amounts of O₂ evolved were determined by GC analysis. The O₂ formation started immediately on the irradiation and ceased after 120 min. The catalytic activity of complexes **1–6** was evaluated with the initial turnover frequency (TOF) for O₂ generation. The TOF values for **1–6** are collected in Table 1. Complexes **5** and **6**

with the electron-withdrawing groups showed especially high catalytic activity. In addition, complex **1** catalyzed the reaction more efficiently than **2** and **3**. These results qualitatively parallel to those from chemical water oxidation described in the above paragraph, indicating that a step accelerated by the electron-donating groups also contributes to the overall rate of both chemical and photochemical water oxidation.

Photochemical water oxidation in vesicular system

Taking into account the fact that electron-withdrawing groups such as CO₂Me and CF₃ largely enhance the catalytic activity, I designed amphiphilic Ru complex **5R** (Figure 3), which has a long alkyl chain connected by an ester bond at the 4-position of the pyridine ligand. Complex **5R** was synthesized by a modified procedure for preparation of **5**. The intermediate complex Ru(bda)(DMSO)₂ prepared from Ru(DMSO)₄Cl₂ and H₂bda in MeOH was isolated, and the complex was treated with an equimolar mixture of methyl isonicotinate and octadecyl isonicotinate in THF to give **5R** in 27% yield.

Vesicle solution containing **5R** was prepared by the following procedure. In a typical experiment, the solution of **5R** (0.520 μmol) and phospholipid DPPC (12.0 μmol) in CHCl₃ was evaporated to form a thin film, and the film was treated in borate buffer (40 mM, pH 8.0) with ultrasonic process to give small unilamellar vesicle solution. Complex **5R** outside the vesicles was removed by gel filtration column chromatography to obtain 11.4 mL of the vesicle solution, which was used in photochemical reactions. In a typical vesicle preparation, 43.4% of **5R** used in the preparation was incorporated into the vesicles while complex **5** was not incorporated almost at all. The concentration of **5R** in vesicles was roughly controlled by the amount of **5R** used in the thin film formation.

In the presence of [Ru(bpy)₃]²⁺ (0.85 mM) and S₂O₈²⁻ (5.0 mM) in the outer aqueous phase, the vesicle solution containing **5R** was irradiated (>390 nm), and the generation of O₂ was observed by GC. Comparing with the experiment under the identical condition using **5** in a homogeneous solution, the turnover number of O₂ production with respect to the Ru catalyst in the vesicular system is more than twice as much as that in the homogeneous solution (Figure 4). The dependence of the initial rate of O₂ production on the catalyst concentration was examined both in the vesicle solution and in the homogeneous solution (Figure 5). The initial rate in the vesicle solution increased with an increase in [**5R**] up to ~30 μM. The rate in the homogeneous solution also linearly increased with an increase of [**5**]. The TOF in the homogeneous system is only a half of that in the vesicular system up to ~30 μM, but the efficiencies of both systems are comparable in the higher concentration range due to an unexpected decrease in the vesicle solution.

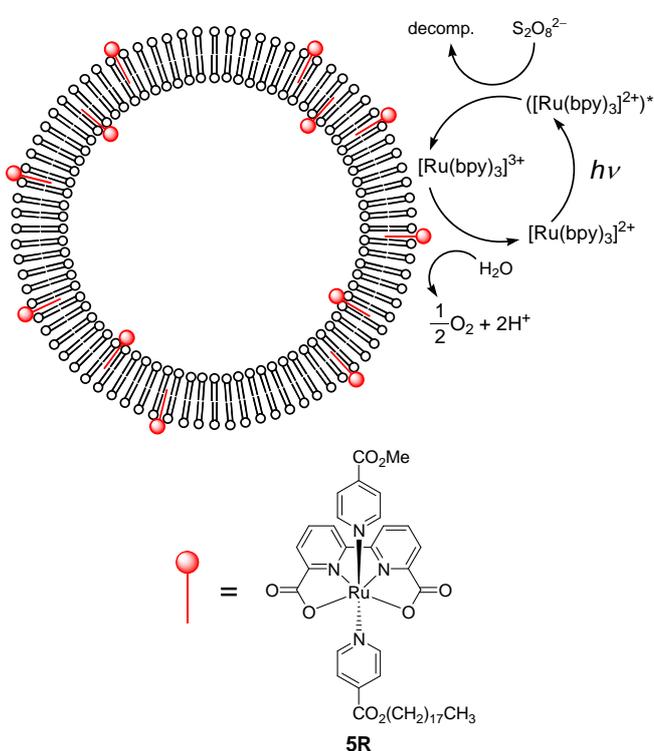


Figure 3. Schematic diagram of the photochemical water oxidation catalyzed by amphiphilic ruthenium complex **5R** embedded into the vesicle membrane and chemical structure of **5R**.

Moreover, the fact that the initial rate of O₂ production is linear to the catalyst concentration indicates that the

rate-determining step of water oxidation is the oxidation of Ru(IV)-OH species of the catalyst by $[\text{Ru}(\text{bpy})_3]^{3+}$ to form Ru(V)=O.

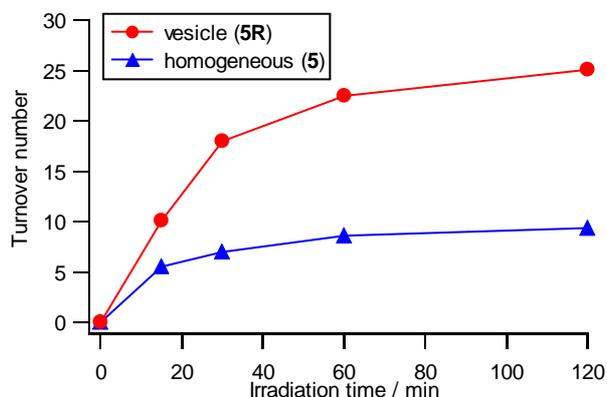


Figure 4. Turnover number of O₂ production in the vesicular system or in the homogeneous solution.

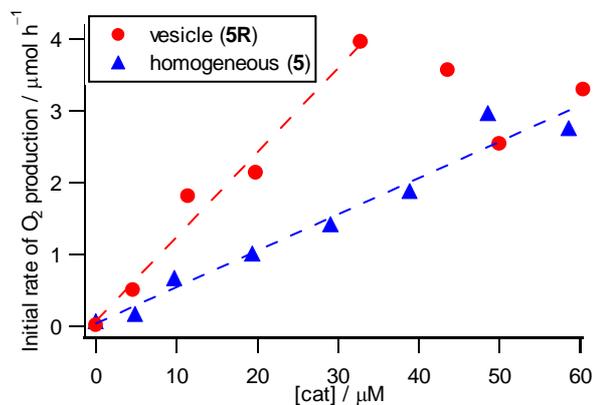


Figure 5. Dependence of the initial rate of O₂ production on the concentration of the catalyst in photochemical water oxidation in the vesicular system or in the homogeneous solution.

Conclusions

Ru complexes **1–6** with different substituents were successfully synthesized. The electron-donating ability of the substituent group at the 4-position of the axial pyridine ligand influences the electrochemical property and catalytic activity toward chemical and photochemical water oxidation. The electron-withdrawing groups fairly enhanced the catalytic activity, whereas OMe group exhibits a small positive effect on the catalytic activity.

Ru complex **5R** embedded into vesicle membranes catalyzed the photochemical water oxidation in the presence of a sensitizer and a sacrificial electron acceptor in the outer aqueous solution. It is also important to note that incorporation of the Ru complex into vesicle membranes enhanced its catalytic activity. The TOF of O₂ production in the vesicular system is larger than that in the homogeneous solution by a factor of more than two in the concentration range up to [cat] ~ 30 μM. These studies will contribute to reaching the final goal, the construction of vesicular systems which can split H₂O into H₂ and O₂ using solar energy.

Reference

[1] L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **2010**, *49*, 209-215.