

# Catalytic activity of $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}-\text{O}-\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$ for four-electron water oxidation

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## Abstract

Water oxidation catalysis by  $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}-\text{O}-\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$  ( $\text{Ru}^{\text{III}}(\text{OH}_2)-\text{O}-\text{Ru}^{\text{III}}(\text{OH}_2)$ ) complex was studied in a homogeneous aqueous solution (AS) as well as heterogeneous Nafion membrane (HM) using Ce(IV) oxidant. The initial  $\text{O}_2$  evolution rate,  $V_{\text{O}_2}$  ( $\text{mol s}^{-1}$ ) increased linearly at low complex concentrations under the excess Ce(IV) oxidant, showing that 4-electron water oxidation is catalyzed by one molecule of the complex. The intrinsic catalytic activities,  $k_{\text{O}_2}$  ( $\text{s}^{-1}$ ), in the AS and HM were  $4.2 \times 10^{-3} \text{ s}^{-1}$  and  $2.4 \times 10^{-3} \text{ s}^{-1}$ , respectively. These values are much higher than those of well-known metal and metal oxide catalysts. Comparison of catalytic activity for various metal complexes and oxides is presented. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Water oxidation; Ruthenium complex; Nafion

## 1. Introduction

Water oxidation catalyst is attracting much attention not only as a synthetic model to understand the mechanism of photosynthetic oxygen evolving center (OEC) but also as an important part of an artificial photosynthetic system which aims at a solar energy conversion to obtain a renewable energy resource [1–3]. Some synthetic ruthenium and manganese complexes such as  $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}-\text{O}-\text{Ru}(\text{H}_2\text{O})(\text{bpy})_2]^{4+}$  ( $\text{Ru}^{\text{III}}(\text{OH}_2)-\text{O}-\text{Ru}^{\text{III}}(\text{OH}_2)$ ) [4], *o*-phenylene-bridged porphyrin manganese dimer [5], trinuclear ruthenium complex ( $[(\text{NH}_3)_5\text{Ru}-\text{O}-$

$\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$ ; Ru-red) [6] and  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$  [7] have been hitherto reported.

The  $\text{Ru}^{\text{III}}(\text{OH}_2)-\text{O}-\text{Ru}^{\text{III}}(\text{OH}_2)$  complex has been extensively investigated from the view points of redox and structural chemistry for understanding mechanism of water oxidation [4,8–13]. Hust et al. showed that one of the intermediates possesses terminal ruthenyl oxo group ( $\text{Ru}=\text{O}$ ) [12]. Recently, Meyer et al. proposed the mechanism of water oxidation by the complex using global kinetic analysis of the absorption spectral change [13]. In various studies,  $\text{Ru}^{\text{IV}}-\text{O}-\text{Ru}^{\text{IV}}$ ,  $\text{Ru}^{\text{IV}}-\text{O}-\text{Ru}^{\text{V}}$  and  $\text{Ru}^{\text{V}}-\text{O}-\text{Ru}^{\text{V}}$  species have been considered as catalytically active forms [4,8,9]. Although such studies on the water oxidation mechanism is important,

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the problem whether water oxidation catalysis is a unimolecular or a bimolecular process with respect to the  $\text{Ru}^{\text{III}}(\text{OH}_2)\text{--O--Ru}^{\text{III}}(\text{OH}_2)$  complex remains open.

The catalyst activity for water oxidation is also crucial for its application to an artificial photosynthetic system in addition to the mechanism. However, there has been no report on the catalytic activity of  $\text{Ru}^{\text{III}}(\text{OH}_2)\text{--O--Ru}^{\text{III}}(\text{OH}_2)$  complex for water oxidation. Since it is important in our research direction that the catalyst works in a heterogeneous system in view of its application, we have investigated catalysis in a heterogeneous system [14,15]. In the present paper, water oxidation catalysis by the  $\text{Ru}^{\text{III}}(\text{OH}_2)\text{--O--Ru}^{\text{III}}(\text{OH}_2)$  complex is studied in a homogeneous aqueous solution as well as in a heterogeneous Nafion membrane using  $\text{Ce}(\text{IV})$  oxidant. The catalytic activity of the complex will be shown and discussed compared with other catalysts.

## 2. Experimental section

### 2.1. Materials

$[(\text{bpy})_2(\text{OH}_2)\text{Ru--O--Ru}(\text{OH}_2)(\text{bpy})_2](\text{ClO}_4)_4$  was prepared as described elsewhere [4]. Cerium (IV) diammonium nitrate and Nafion 117 membrane (thickness 180  $\mu\text{m}$ ) were purchased from Wako and Aldrich Chemical, respectively.

### 2.2. Preparation of a Nafion membrane incorporating $\text{Ru}^{\text{III}}(\text{OH}_2)\text{--O--Ru}^{\text{III}}(\text{OH}_2)$

Nafion membrane was sufficiently swollen by soaking in distilled water for ca. 24 h. The swollen membrane was immersed in an aqueous solution (3 ml) containing  $1 \times 10^{-7}$ – $1.3 \times 10^{-5}$  mol of  $\text{Ru}^{\text{III}}(\text{OH}_2)\text{--O--Ru}^{\text{III}}(\text{OH}_2)$  for ca. 5 h to incorporate the complex into the membrane by cation exchange. The complex amount in the membrane was estimated from the absorbance change (at 650 nm) of the aqueous solution before and after adsorption of the complex. The

complex concentration in the membrane was calculated from the complex amount and the membrane volume.

### 2.3. Measurements

For  $\text{O}_2$  evolution experiments in a homogeneous aqueous solution (AS) system, excess  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  oxidant ( $3.1 \times 10^{-3}$  mol) was added quickly to  $3.0 \times 10^{-5}$ – $1.1 \times 10^{-3}$  M complex aqueous solution (5.0 ml) in a reaction vessel. In a heterogeneous Nafion membrane (HM) system, the membrane (volume:  $1.8 \times 10^{-4}$   $\text{dm}^3$ ) that incorporated  $5.0 \times 10^{-8}$ – $2.0 \times 10^{-6}$  mol complex was put into pure water in a reaction vessel, and excess  $\text{Ce}^{\text{IV}}$  oxidant ( $3.1 \times 10^{-3}$  mol) was added quickly. In both the systems, the atmosphere in the reaction vessel was replaced with argon gas before adding the  $\text{Ce}^{\text{IV}}$  oxidant. For all the experiments, the vessel was kept at 25°C. The  $\text{O}_2$  evolved was analyzed on a gas chromatograph equipped with a 5 Å molecular sieve column using argon carrier gas (flow rate is 40  $\text{ml min}^{-1}$ ) at 50°C.

## 3. Results and discussion

The plots of the amount of  $\text{O}_2$  evolved vs. reaction time in HM are shown in Fig. 1. The

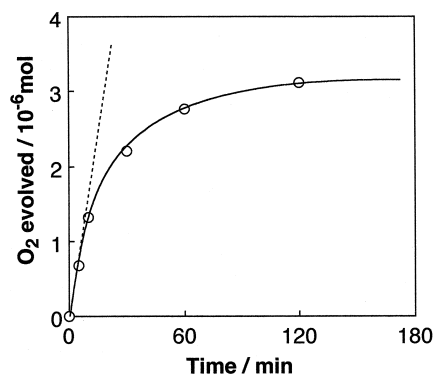
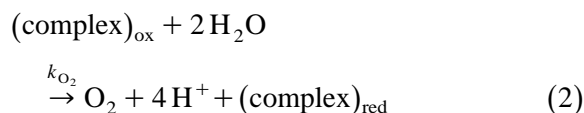
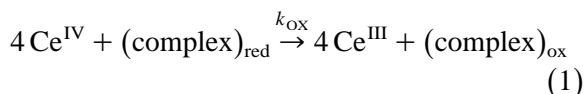


Fig. 1. Time dependence of the amount of  $\text{O}_2$  evolved in a HM using  $\text{Ce}(\text{IV})$  oxidant. The amounts of the complex and  $\text{Ce}(\text{IV})$  oxidant are  $1 \times 10^{-6}$  mol and  $3.1 \times 10^{-3}$  mol, respectively, in 10  $\text{cm}^3$  water. Membrane volume,  $3.6 \times 10^{-4}$   $\text{dm}^3$ .

amount of O<sub>2</sub> evolved increased with time and saturated after 2 h. The amount of O<sub>2</sub> evolved and the turnover number of the complex after the saturation were  $3.1 \times 10^{-6}$  mol and 3.1, respectively. The initial O<sub>2</sub> evolution rate ( $V_{O_2}/\text{mol s}^{-1}$ ) was obtained from the slope of the plots at time zero in Fig. 1.

We analyzed  $V_{O_2}$  as follows to study the mechanism of catalysis and the catalytic activity. In the present water oxidation, it is impossible that water oxidation takes place by a 2-step mechanism of 2-electron oxidation process via hydrogen peroxide formation as well as by a 4-steps mechanism of 1-electron oxidation process because these standard redox potentials of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1.77 V vs. NHE) and OH<sup>·</sup>/H<sub>2</sub>O (2.74 V vs. NHE) are higher than that (1.71 V vs. NHE) of Ce<sup>III</sup>/Ce<sup>IV</sup>. Therefore, the present water oxidation mechanism should be a 4-electron oxidation process (redox potential of O<sub>2</sub>/H<sub>2</sub>O is 1.23 V vs. NHE). When 4-electron water oxidation is catalyzed by one molecule of the complex which has 4-electron oxidation ability, the overall O<sub>2</sub> evolution consists of oxidation of the (catalyst)<sub>red</sub> (the reduced complex) by the 1-electron Ce<sup>IV</sup> oxidant (Eq. (1)) and 4-electron water oxidation by one (catalyst)<sub>ox</sub> (the oxidized complex) (Eq. (2)).



The rate equation for O<sub>2</sub> evolution was derived as follows using a steady-state method;

$$k_{\text{OX}}[\text{Ce}(\text{IV})]^4[(\text{complex})_{\text{red}}] - k_{\text{O}_2}[(\text{complex})_{\text{ox}}] = 0 \quad (3)$$

$$[(\text{complex})_{\text{red}}] + [(\text{complex})_{\text{ox}}] = m_{\text{Ru}}/v \quad (4)$$

$$[(\text{complex})_{\text{ox}}] = \frac{k_{\text{OX}}[\text{Ce}(\text{IV})]^4(m_{\text{Ru}}/v)}{k_{\text{OX}}[\text{Ce}(\text{IV})]^4 + k_{\text{O}_2}} \quad (5)$$

where  $k_{\text{OX}}$  (M<sup>-4</sup> s<sup>-1</sup>) and  $k_{\text{O}_2}$  (s<sup>-1</sup>) are the rate constant for the reaction in Eqs. (1) and (2), respectively, [Ce(IV)], [(complex)<sub>red</sub>] and [(complex)<sub>ox</sub>] are the concentrations (mol dm<sup>-3</sup>) of the respective species in steady state,  $v$  (dm<sup>3</sup>) is the aqueous solution volume in AS and membrane volume in HM, and  $m_{\text{Ru}}$  (mol) is the amount of the complex. Such concentration expression (i.e.,  $(m_{\text{Ru}}/v)$ ) was adopted in order to compare the catalyses in AS and HM. Accordingly, the O<sub>2</sub> evolution rate is given by Eq. (6)

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= (V_{\text{O}_2}/v) \\ &= k_{\text{O}_2}[(\text{complex})_{\text{ox}}] \\ &\quad \times \frac{k_{\text{O}_2}k_{\text{OX}}[\text{Ce}(\text{IV})]^4(m_{\text{Ru}}/v)}{k_{\text{OX}}[\text{Ce}(\text{IV})]^4 + k_{\text{O}_2}} \\ &= \frac{k_{\text{O}_2}(m_{\text{Ru}}/v)}{1 + k_{\text{O}_2}/\{k_{\text{OX}}[\text{Ce}(\text{IV})]^4\}} \quad (6) \end{aligned}$$

The dependency of  $V_{O_2}$  on the Ce(IV) oxidant concentration in the AS is shown in Fig. 2. The  $V_{O_2}$  increased with the Ce(IV) concentration and then was saturated beyond 100 molar ratio of Ce(IV)/Ru<sup>III</sup>(OH<sub>2</sub>)–O–Ru<sup>III</sup>(OH<sub>2</sub>) (at  $3.0 \times 10^{-2}$  M Ce<sup>IV</sup>). The saturated almost constant  $V_{O_2}$  value beyond this molar ratio of

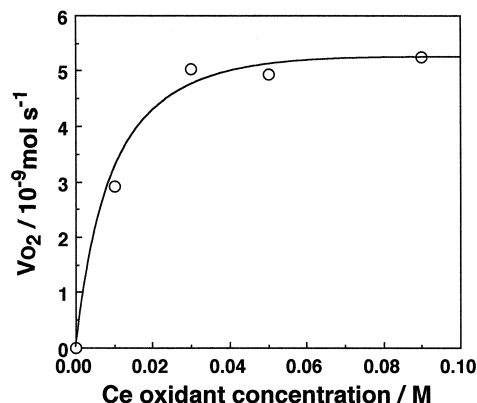


Fig. 2. Dependence of O<sub>2</sub> evolution rate ( $V_{O_2}$ ) on the concentration of Ce<sup>IV</sup> oxidant for the AS. The complex concentration is  $3.0 \times 10^{-4}$  M, and the volume of the solution 5 cm<sup>3</sup>.

$\text{Ce}^{\text{IV}}/\text{complex}$  shows that the term  $k_{\text{O}_2}/\{k_{\text{OX}}[\text{Ce}(\text{IV})]^4\}$  is negligible in the Eq. (6), i.e., the value of  $k_{\text{OX}}[\text{Ce}(\text{IV})]^4$  is large enough in comparison with the  $k_{\text{O}_2}$  value, so that the reaction in Eq. (2) is the rate determining-step for the overall  $\text{O}_2$  evolution under the large excess  $\text{Ce}^{\text{IV}}$  conditions. Therefore,  $V_{\text{O}_2}$  at a large excess  $\text{Ce}^{\text{IV}}$  oxidant (beyond ca. 100 of the molar ratio of  $\text{Ce}^{\text{IV}}/\text{Ru}^{\text{III}}(\text{OH}_2)\text{-O-Ru}^{\text{III}}(\text{OH}_2)$ ) is given as;

$$\frac{d[\text{O}_2]}{dt} = (V_{\text{O}_2}/v) = k_{\text{O}_2}(m_{\text{Ru}}/v) \quad (7)$$

When 4-electron water oxidation is catalyzed by one (complex)<sub>ox</sub>, the  $V_{\text{O}_2}$  is first order with respect to the complex concentration according to Eq. (7) under the large excess  $\text{Ce}^{\text{IV}}$  conditions. All the  $\text{O}_2$  evolution experiments was carried out under the conditions of a large excess  $\text{Ce}^{\text{IV}}$  oxidant (at least 560 of the molar ratio of  $\text{Ce}^{\text{IV}}/\text{Ru}^{\text{III}}(\text{OH}_2)\text{-O-Ru}^{\text{III}}(\text{OH}_2)$ ).

The plots of the  $V_{\text{O}_2}$  vs. the complex concentration in the AS is shown in Fig. 3. The plots gave a straight line at low concentrations and a slightly downward deviation curve at high concentrations. The linear plots at low concentrations show that  $\text{O}_2$  evolution can be treated as first order with respect to the complex concentration according to Eq. (7). This result supports that 4-electron water oxidation is catalyzed by

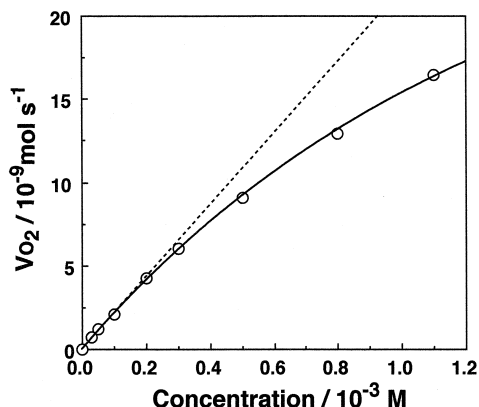


Fig. 3. Dependence of  $\text{O}_2$  evolution rate ( $V_{\text{O}_2}/\text{mol s}^{-1}$ ) on the complex concentration in an AS. The amount of  $\text{Ce}(\text{IV})$  is  $3.1 \times 10^{-3}$  mol in  $5 \text{ cm}^3$  water.

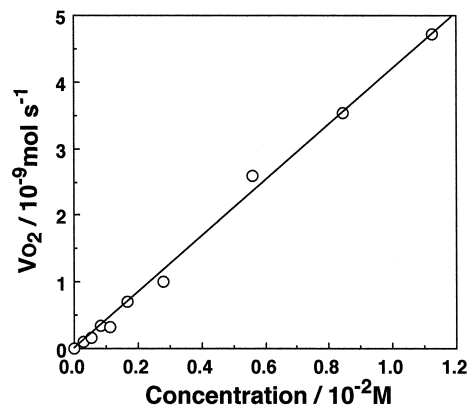


Fig. 4. Dependence of  $\text{O}_2$  evolution rate ( $V_{\text{O}_2}/\text{mol s}^{-1}$ ) on the catalyst concentration in a HM. Membrane volume,  $1.8 \times 10^{-4} \text{ dm}^3$ ;  $\text{Ce}(\text{IV})$ ,  $3.1 \times 10^{-3}$  mol in  $5 \text{ cm}^3$  water.

one molecule of the complex. The catalytic activity,  $k_{\text{O}_2}$  ( $\text{s}^{-1}$ ), in the AS was obtained from the slope of the straight line to be  $4.2 \times 10^{-3} \text{ s}^{-1}$ . The downward deviated curve at high concentrations shows the deactivation of the complex, which would be ascribed to an intermolecular decomposition, probably, to produce mononuclear species, e.g.,  $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]$ . Such decomposition has been supported by an experimental result that the maximum turnover number of the complex is 4 to 5, and  $\text{O}_2$  evolution stops afterwards.

The relationship between the  $V_{\text{O}_2}$  and the complex in the HM exhibited a straight line at a whole concentration range as shown in Fig. 4, supporting that the complex works as a 4-electron oxidation catalyst in the membrane. The  $k_{\text{O}_2}$  in the HM was obtained as  $2.4 \times 10^{-3} \text{ s}^{-1}$  from the slope of the straight line. The complex did not deactivate in the membrane even at the higher complex concentrations than those in the AS by one order of magnitude. This can be explained by the inhibition of the intermolecular decomposition by the suppressed diffusion of the complex in the membrane.

It has been known that metal oxides such as  $\text{RuO}_2$ ,  $\text{IrO}_2$ , and  $\text{MnO}_2$  possess a catalytic activity for water oxidation. We carried out water oxidation catalysis by inorganic compounds such as  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{MnO}_2$  and Pt black in an aque-

Table 1  
Comparison of the intrinsic activities ( $k_{O_2}$ ) of various catalysts for water oxidation

Catalyst	$k_{O_2}$ ( $s^{-1}$ )	
	Homogeneous aqueous solution system	Heterogeneous system
$[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$ <sup>c</sup>	$5.1 \times 10^{-2}$	$4.4 \times 10^{-2}$ <sup>a</sup>
$[(NH_3)_5Ru-O-Ru(NH_3)_5]^{4+}$ <sup>d</sup>	$1.3 \times 10^{-2}$	$1.3 \times 10^{-2}$ <sup>a</sup>
$[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$	$4.2 \times 10^{-3}$	$2.4 \times 10^{-3}$ <sup>a</sup>
$[Ru(NH_3)_5Cl]^{2+}$ <sup>e</sup>	$3.1 \times 10^{-4}$	$2.7 \times 10^{-3}$ <sup>a</sup>
$[Ru(bpy)_3]^{2+}$	$\sim 0$	$\sim 0^a$
$Ru(bpy)_2Cl_2$	$\sim 0$	$\sim 0^a$
$IrO_2$	–	$1.4 \times 10^{-3}$ <sup>b</sup>
$RuO_2$	–	$7.5 \times 10^{-4}$ <sup>b</sup>
$MnO_2$	–	$\sim 0^b$
Pt-black	–	$2.5 \times 10^{-4}$ <sup>b</sup>

<sup>a</sup>Nafion membrane system.

<sup>b</sup>Suspension system.

<sup>c</sup>Ref. [14].

<sup>d</sup>Ref. [16].

<sup>e</sup>Ref. [15].

ous suspension system using a Ce(IV) oxidant to compare their catalytic activities with that of the complex. The plots of  $V_{O_2}$  vs. the amount of the compounds gave a linearity, and the  $k_{O_2}$  values of the inorganic compounds were obtained from the slope of the plots. Intrinsic catalytic activities of various compounds in a homogeneous aqueous solution and heterogeneous systems were summarized in Table 1 together with the results reported earlier by our group [14–16].  $IrO_2$  was the most active metal oxide catalyst reported hitherto by Harriman et al. [17]. The  $k_{O_2}$  of the  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$  in the membrane is higher than those of metal oxide and metal used, showing that a molecular catalyst is much more effective for an artificial photosynthetic OEC model than the metal and metal oxide catalysts.

The comparison of the activity of  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$  with those of other complex catalysts provides important information on the structure for an active catalyst. The  $k_{O_2}$  of  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$  in a homogeneous system is higher than that of  $[Ru(NH_3)_5Cl]^{2+}$  by one order of magnitude. Since  $[Ru(NH_3)_5Cl]^{2+}$  is two-electron oxidation catalysts, two molecules of  $[Ru(NH_3)_5Cl]^{2+}$  catalyze co-

operatively four-electron water oxidation [15]. The higher  $k_{O_2}$  of  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$  than  $[Ru(NH_3)_5Cl]^{2+}$  is ascribable to a four-electron oxidation catalysis by one molecule of  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$ . Multinuclear structure is an important factor for the design of a synthetic molecular water oxidation catalyst. The ammine-coordinated complexes such as  $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$  and  $[(NH_3)_5Ru-O-Ru(NH_3)_5]^{4+}$  are much more active than  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$ , showing that it is effective to design an artificial photosynthetic OEC model by ammine-coordinated complexes. In Table 1, it is also to be noted that the catalytic activity of the molecular catalyst is maintained in the heterogeneous system in comparison with the homogeneous one.

#### 4. Conclusion

Water oxidation catalysis by  $[(bpy)_2(H_2O)Ru-O-Ru(H_2O)(bpy)_2]^{4+}$  ( $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$ ) complex was studied in a homogeneous AS as well as HM using Ce(IV) oxidant. The initial  $O_2$  evolution rate,  $V_{O_2}$

(mol s<sup>-1</sup>) increased linearly at low complex concentrations under the excess Ce(IV) oxidant, showing that 4-electron water oxidation is catalyzed by one molecule of the complex. The intrinsic catalytic activities,  $k_{O_2}$  (s<sup>-1</sup>), in the AS and HM were  $4.2 \times 10^{-3}$  s<sup>-1</sup> and  $2.4 \times 10^{-3}$  s<sup>-1</sup>, respectively. These values are much higher than those of well-known metal and metal oxide catalysts. The  $k_{O_2}$  values of the complex catalysts in a heterogeneous system is higher than those of metal oxides and metal, showing that a molecular catalyst are much more effective for an artificial photosynthetic OEC model. The ammine-coordinated complexes such as  $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$  and  $[(NH_3)_5Ru-O-Ru(NH_3)_5]^{4+}$  are much more active than  $Ru^{III}(OH_2)-O-Ru^{III}(OH_2)$ , showing that it is effective to design an artificial photosynthetic OEC model by ammine-coordinated complexes.

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