# Development of Functional Metal Complexes for Artificial Photosynthesis

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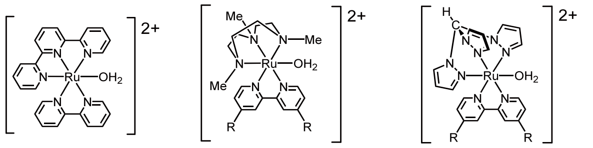
Visible light-induced water splitting ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$) has attracted considerable attention in recent years due to its potential application in artificial solar energy conversion and storage. This water-to-fuels conversion consists of the two half-cell reactions; reduction of water to $H_2$ ($2H^+ + 2e^- \rightarrow H_2$) and oxidation of water to $O_2$ ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). In this context, we have investigated oxygen evolution and photochemical hydrogen evolution from water catalyzed by metal complexes. In this report, we show (i) the mechanism of water oxidation catalyzed by mononuclear ruthenium complexes, (ii) electrocatalytic water oxidation at an ITO electrode modified with mononuclear ruthenium complexes, and (iii) photochemical hydrogen production from water catalyzed by carboxylate-bridged dirhodium(II) complexes.

## 1. Mechanism of Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes[1)]

As mentioned above, the water splitting reaction can be divided into the two half-cell reactions; reduction of water to $H_2$ and oxidation of water to $O_2$. Particularly, development of molecular catalysts for $O_2$ evolution has been targeted by many researchers, since the $O_2$ evolution requires removal of four protons and four electrons, and is therefore considered more difficult process to accelerate. Recently, several different groups, including our group, discovered that mononuclear ruthenium complexes with an aqua ligand, such as $[Ru(terpy)(bpy)(OH_2)]^{2+}$ (terpy = 2,2':6',2"-terpyridine, bpy = 2,2'-bipyridine), exhibit surprisingly high catalytic activity towards $O_2$ evolution from water in the presence of $Ce^{4+}$ as an oxidizing reagent in acidic aqueous media. These findings became a significant breakthrough in this field and various reaction mechanisms have been proposed to date.

We have investigated the mechanism of $O_2$ evolution from water catalyzed by a series of mononuclear aquaruthenium complexes, $[Ru(terpy)(bpy)(OH_2)]^{2+}$ (**1**), $[Ru(tmtacn)(R_2bpy)(OH_2)]^{2+}$ (**2** for R = H, **3** for R = Me, and **4** for R = OMe; $R_2$bpy = 4,4'-disubstituted-2,2'-bipyridines), and $[Ru(tpzm)(R_2bpy)(OH_2)]^{2+}$ (**5** for R = H, **6** for R = Me, and **7** for R = OMe), where tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, and tpzm = tris(1-pyrazolyl)methane. The kinetics of $O_2$ evolution is investigated as a function of either the catalyst concentration or the oxidant concentration by employing $Ce(NH_4)_2(NO_3)_6$ as an oxidant, revealing that these catalysts can be classified into two groups exhibiting different rate laws for $O_2$ evolution. In one class (**1**, and **5**–**7**), the rate of $O_2$ evolution is linear to both the catalyst and $Ce^{4+}$ concentrations. For the other class (**2**–**4**), the rate of $O_2$ evolution is quadratic to the catalyst concentration and independent of the $Ce^{4+}$ concentration. Moreover, the singlet biradical character of the hydroxocerium(IV) ion is realized by the experimental and DFT investigations. These results indicate that the radical coupling of the oxygen atoms of a $Ru^V{=}O$ species and a hydroxocerium(IV) ion is the key step for the catalysis of **1** and **5**–**7**, while the well-known oxo–oxo radical coupling among two $Ru^V{=}O$ species proceeds in the catalysis of **2**–**4**. This is the first report demonstrating that the radical character provided by the hydroxocerium(IV) ion plays a crucial role in the catalysis of such ruthenium complexes in $O_2$ evolution from water.



$[Ru(terpy)(bpy)(OH_2)]^{2+}$
**1**

$[Ru(tmtacn)(R_2bpy)(OH_2)]^{2+}$
**2**, R = H
**3**, R = Me
**4**, R = OMe

$[Ru(tpzm)(R_2bpy)(OH_2)]^{2+}$
**5**, R = H
**6**, R = Me
**7**, R = OMe

**Figure 1.** Structures of mononuclear aquaruthenium catalysts for water oxidation.

## 2. Electrocatalytic Water Oxidation at an ITO Electrode Modified with Mononuclear Ruthenium Complexes[2)]

An ITO (indium tin oxide) electrode modified with $[Ru(terpy)\{4,4'-(CH_2PO_3H_2)_2-2,2'-bpy\}(OH_2)]^{2+}$ (**8**) was prepared to gain insight into the mechanism of $O_2$ evolution from water catalyzed by a series of mononuclear aquaruthenium complexes. The average separation between two closest molecules can be estimated to be ca. 35 Å. This system does not allow two or more ruthenium centers to engage in the same $O_2$-evolving event, and hence the electrocatalytic $O_2$ evolution from water promoted with this system can be fully attributable to an $O_2$-evolving event at a single aquaruthenium site. Indeed, the modified ITO electrode showed a clear decrease in overpotential for $O_2$ evolution (1.35 V in an aqueous 0.1 M $Na_2SO_4/H_2SO_4$ solution, pH 4.0), indicating that the $O_2$ evolution proceeds in a unimolecular fashion without having any intermolecular associations.

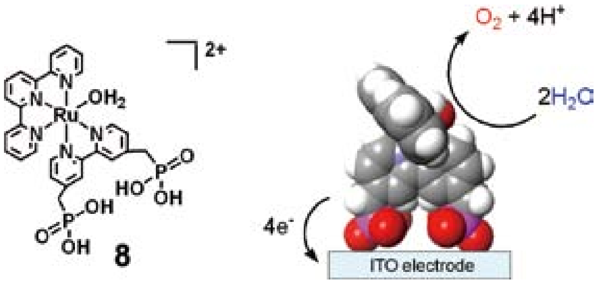
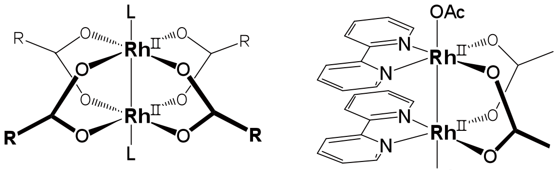


**Figure 2.** Schematic view of the electrochemical water oxidation catalyzed by a mononuculear ruthenium complex (**8**).

## 3. Photochemical Hydrogen Production from Water Catalyzed by Carboxylate-Bridged Dirhodium(II) Complexes[3)]

A series of dinuclear Rh(II) complexes, $[Rh_2(\mu\text{-}OAc)_4(H_2O)_2]$ (HOAc = acetic acid) (**9**), $[Rh_2(\mu\text{-}gly)_4(H_2O)_2]$ (Hgly = glycolic acid) (**10**), $[Rh_2(\mu\text{-}CF_3CO_2)_4(acetone)_2]$ (**11**), and $[Rh_2(bpy)_2(\mu\text{-}OAc)_2(OAc)_2]$ (**12**), were found to serve as $H_2$-evolving catalysts in a three-component system consisting of tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$), methylviologen ($MV^{2+}$), and ethylenediaminetetraacetic acid disodium salt (EDTA). It was also confirmed that thermal reduction of water into $H_2$ by $MV^{+\bullet}$, in situ generated by the bulk electrolysis of $MV^{2+}$, is effectively promoted by **9** as a $H_2$-evolving catalyst. The absorption spectra of the photolysis solution during the photocatalysis were monitored up to 6 h to reveal that the formation of photochemical or thermal byproducts of $MV^{+\bullet}$ is dramatically retarded in the presence of the $Rh(II)_2$ catalysts, for the $H_2$ formation rather than the decomposition of $MV^{+\bullet}$ becomes predominant in the presence of the $Rh(II)_2$ catalysts. The stability of the $Rh(II)_2$ dimers was confirmed by absorption spectroscopy, $^1H$ NMR, and ESI-TOF mass spectroscopy. The results indicated that neither elimination nor replacement of the equatorial ligands take place during the photolysis, revealing that one of the axial sites of the $Rh_2$ core is responsible for the hydrogenic activation. The quenching of $Ru^*(bpy)_3^{2+}$ by **9** was also investigated by luminescence spectroscopy. The rate of $H_2$ evolution was found to decrease upon increasing the concentration of **9**, indicating that the quenching of $Ru^*(bpy)_3^{2+}$ by the $Rh(II)_2$ species rather than by $MV^{2+}$ becomes predominant at the higher concentrations of **9**. The DFT calculations were carried out for several possible reaction paths proposed (*e.g.*, $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+$ and $[Rh^{II}_2(\mu\text{-}OAc)_4(H_2O)] + H^+ + e^-$). It is suggested that the initial step is a proton-coupled electron transfer (PCET) to the $Rh(II)_2$ dimer leading to the formation of a Rh(II)Rh(III)–H intermediate. The $H_2$ evolution step is suggested to proceed either *via* the transfer of another set of $H^+$ and $e^-$ to the Rh(II)Rh(III)–H intermediate or *via* the homolytic radical coupling through the interaction of two Rh(II)Rh(III)–H intermediates.



R = $CH_3$, L = $H_2O$ (**9**)
R = $CH_2OH$, L = $H_2O$ (**10**)
R = $CF_3$, L = acetone (**11**)

$[Rh^{II,II}_2(bpy)_2(OAc)_4]$ (**12**)

**Figure 3.** Structures of carboxylate-bridged dirhodium(II) catalysts for photochemical water reduction.

### References

1) M. Yoshida, S. Masaoka, J. Abe and K. Sakai, *Chem. –Asian J.* **5**, 2369–2378 (2010).
2) J. Kiyota, J. Yokoyama, M. Yoshida, S. Masaoka and K. Sakai, *Chem. Lett.* **39**, 1146–1148 (2010).
3) S. Tanaka, S. Masaoka, K. Yamauchi, M. Annaka and K. Sakai, *Dalton Trans.* **39**, 11218–11226 (2010).

### Awards

MASAOKA, Shigeyuki; The 25th Young Scholar Lectures in the 91th Annual Meeting of CSJ (2011).
KONDO, Mio; Poster Award at 60th Anniversary Conference on Coordination Chemistry in OSAKA (2010).
KONDO, Mio; The 27th Inoue Research Award for Young Scientists (2010).

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