

# Development of Functional Metal Complexes for Artificial Photosynthesis

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Artificial photosynthesis is a solar energy conversion technology that mimics natural photosynthesis, and poised to be one of the next big breakthroughs in energy. Our group studies chemistry of transition metal complexes for the realization of artificial photosynthesis. Efforts have focused on development of new catalysts for multi-electron transfer reactions and understanding the reaction mechanism. During the last year, we reported (i) a mononuclear ruthenium complex showing multiple proton-coupled electron transfer toward multi-electron transfer reactions,<sup>1)</sup> (ii) kinetics and DFT studies on water oxidation catalyzed by a mononuclear ruthenium complex,<sup>2)</sup> and (iii) two-step photoexcitation of a platinum complex to produce hydrogen from water.<sup>3)</sup> We also demonstrated (iv) the self-assembly of microstructures from dinuclear ruthenium complexes and their structural transformation.<sup>4)</sup> The research projects (i), (ii) and (iv) are introduced in this report.

## 1. A Mononuclear Ruthenium Complex Showing Multiple Proton-Coupled Electron Transfer toward Multi-Electron Transfer Reactions<sup>1)</sup>

Proton-coupled electron transfer (PCET) is an important chemical process that involves the concerted transfer of a proton ( $H^+$ ) and an electron ( $e^-$ ). It is widely employed to achieve multi-electron transfer reactions such as water oxidation by photosystem II and nitrogen fixation by nitrogenase as well as solar energy conversion in artificial photosynthesis, since high-energy intermediates and/or electrostatic charge buildup during the reactions are generally avoided by going through PCET processes.

In this context, we synthesized and characterized a new ruthenium(II) complex,  $[Ru(trpy)(H_2bim)(OH_2)](PF_6)_2$  (**1**)

( $H_2bim = 2,2'$ -biimidazole and  $trpy = 2,2':6',2''$ -terpyridine), where the  $H_2bim$  and  $M-OH_2$  moieties in the molecule are expected to serve as proton-dissociation sites. Electrochemical studies in aqueous solutions under various pH conditions afforded the Pourbaix diagram (potential versus pH diagram) of **1**, where the  $pK_a$  values found from the diagram agree well with those determined spectrophotometrically. It was also found that **1** demonstrates four-step PCET reactions to give the four-electron oxidized species,  $[Ru^{IV}(trpy)(bim)(O)]^{2+}$ , without electrostatic charge buildup during the reactions (Figure 1). The multiple PCET ability of **1** would be applicable to various multi-electron oxidation reactions. Catalysis of electrochemical water oxidation was indeed evaluated in the initial attempt to demonstrate multi-electron oxidation reactions, revealing that the water oxidation potential for **1** is lower than that for 2,2'-bipyridine analogue,  $[Ru(trpy)(bpy)(OH_2)]^{2+}$  (**2**) ( $bpy = 2,2'$ -bipyridine), which is known as an active catalyst for water oxidation.



**Figure 1.** A schematic view of the four-step PCET reaction of **1** to give the four-electron oxidized species,  $[Ru^{IV}(trpy)(bim)(O)]^{2+}$ .

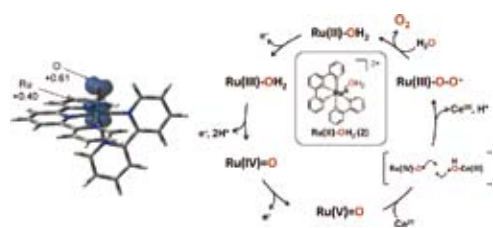
## 2. Kinetics and DFT Studies on the Mechanism of Water Oxidation Catalyzed by Mononuclear Ruthenium Complexes<sup>2)</sup>

Visible light-induced water splitting is one promising

approach for artificial photosynthesis. This solar-to-fuels conversion consists of the two half-cell reactions; reduction of water to  $\text{H}_2$  ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) and oxidation of water to  $\text{O}_2$  ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ). Particularly, development of molecular catalysts for  $\text{O}_2$  evolution has been considered more difficult than the hydrogen side, since the  $\text{O}_2$  evolution requires removal of four protons and four electrons.

We previously provided two important aspects with regard to this issue as follows. (i) Mononuclear ruthenium catalysts can be classified into two groups based on the rate law observed. One obeys  $d[\text{O}_2]/dt = k[\text{catalyst}][\text{Ce}^{4+}]$  and the other obeys  $d[\text{O}_2]/dt = k[\text{catalyst}]^2$ , where the rate is first- and second-order to the catalyst concentration, respectively. (ii) A radical coupling of the oxo atom from Ru catalyst and the radical-like O(hydroxo) atom from hydroxocerium(IV) species plays an important role in the O–O bond formation in the former monoruthenium-catalyzed  $\text{O}_2$  evolution reactions. However, our previous studies has not provided the spectroscopic evidence of the highest-valence intermediate for the Ru species prior to the O–O bond formation.

In this work, the reaction mechanism of the  $\text{Ce}^{4+}$ -driven water oxidation catalyzed by  $[\text{Ru}(\text{trpy})(\text{bpy})(\text{OH}_2)]^{2+}$  (**2**,  $\text{Ru}^{\text{II}}\text{-OH}_2$ ). As a result, the  $\text{Ru}^{\text{V}}=\text{O}$  species, together with other intermediates in the multi-step electron transfer processes, were spectrophotometrically followed by use of the global kinetic analysis using the singular value decomposition (SVD) method. We also demonstrate that each spectral component can be rationally reproduced by TD-DFT (time-dependent density functional theory) calculation. Moreover, it is also found that the  $\text{Ru}^{\text{V}}=\text{O}$  species can be written as the resonance structure of the  $\text{Ru}^{\text{IV}}\text{-O}^\bullet$  species ( $\text{Ru}^{\text{V}}=\text{O} \leftrightarrow \text{Ru}^{\text{IV}}\text{-O}^\bullet$ ), indicating that the  $\text{Ru}^{\text{V}}=\text{O}$  species bears a substantial radical character at the O(oxo) atom. This study suggests that a radical-radical coupling of  $\text{Ru}^{\text{V}}=\text{O}$  and hydroxocerium(IV) species predominates the major path leading to the dioxygen formation.



**Figure 2.** (Left) The optimized structure of the  $\text{Ru}^{\text{V}}=\text{O}$  species in the doublet state. The distribution of the Mulliken atomic spin density is also overlaid. The spin density is located on the 3d orbital of the ruthenium ion (+0.40) and the 2p orbital of the O(oxo) atom (+0.61). (Right) A proposed catalytic cycle of the  $\text{Ce}^{4+}$ -driven water oxidation catalyzed by **2**.

#### Award

KONDO, Mio; The 5<sup>th</sup> Shiseido Female Researcher Science Grant (2012).

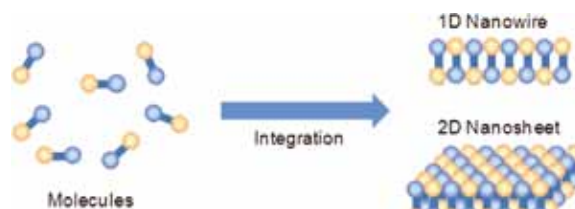
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### 3. Self-Assembly of Tubular Structures from Dinuclear Ruthenium Complexes and Their Structural Transformation<sup>4)</sup>

Controlled self-assembly of metal complexes is of high scientific and technological importance for the development of multi-functional materials and devices. Among various types of metal complexes, mixed-valence complexes have attracted much attention because of their wide range of interesting physical and chemical properties from charge-transfer interactions between metal ions linked via bridging ligands. In particular, low-dimensional assembly of such mixed-valence complexes gives rise to specific electronic, magnetic, and optical properties. Ideally, the characteristics of such systems would be tunable by controlling the spatial arrangement of the mixed-valence complexes, resulting in electric interaction among metal complexes without linkage of covalent or coordination.

In this work, we have demonstrated that the lipid-packaged mixed-valence complex displays morphological changes with aging of the solution in dichloromethane. Formation of a bilayer structure causes morphological evolution from microtapes to microtubes, giving rise to changes in absorption spectral intensities. Moreover, these morphological and spectral changes can be reversed by standing or shaking. The technique of combination of lipid molecules and *discrete* coordination compounds makes it possible to design flexible, reversible and signal responsive supramolecular coordination systems. The concept of lipid packaging could also be expanded of other useful coordination compounds, and should allow us to further develop the nanochemistry of coordination materials.



**Figure 3.** Schematic illustration of the assembly of discrete metal complexes for constructing nanostructures.

#### References

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