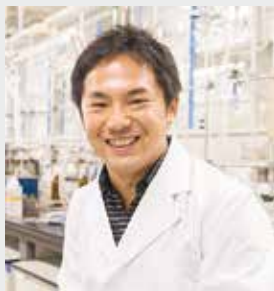


Development of Functional Metal Complexes for Artificial Photosynthesis

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry



MASAOKA, Shigeyuki
Associate Professor
[masaoka@ims.ac.jp]

Education

1999 B.S. Doshisha University
2004 Ph.D. Kyoto University

Professional Employment

2002 JSPS Research Fellow (DC2)
2004 Research Assistant (Postdoc), University of Liverpool
2005 Research Associate, Kyushu University
2007 Assistant Professor, Kyushu University
2009 JST PRESTO Researcher
2011 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Member

Assistant Professor
KONDO, Mio
Post-Doctoral Fellow
VIJAYENDRAN, Praneeth
Graduate Student
OKAMURA, Masaya
ITOH, Takahiro
OKABE, Yuki
CHINAPANG, Pondchanok
FUKATSU, Arisa
FUKAHORI, Yukino
IZU, Hitoshi
ENOMOTO, Takafumi
USHIJIMA, Riku
Technical Fellow
KUGA, Reiko
KANAIKE, Mari
SHIBATA, Akane
Secretary
TANIWAKE, Mayuko
NOGAWA, Kyoko

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Artificial photosynthesis is a solar energy conversion technology that mimics natural photosynthesis, and considered to be one of the next big breakthroughs in energy. Our group studies the development of functional metal complexes toward the realization of artificial photosynthesis. Specific areas of research include (i) synthesis of ruthenium-based molecular catalysts for water oxidation and carbon dioxide reduction, (ii) creation of cluster catalysts for multi-electron transfer reactions, (iii) mechanistic investigation into water oxidation catalyzed by metal complexes, (iv) application of proton-coupled electron transfer toward multi-electron transfer reactions, (v) electrochemical evaluation of the activity of molecular catalysts for water oxidation and carbon dioxide reduction, (vi) electrochemical measurement of metal complexes in homogeneous solutions under photoirradiation, and (vii) development of reaction fields via self-assembly of molecular catalysts.

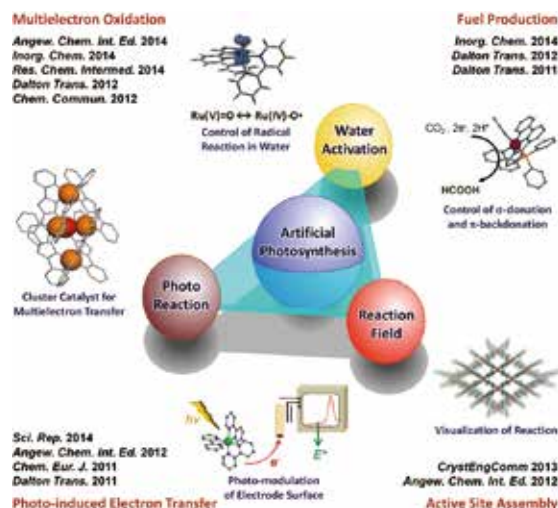


Figure 1. An overview of our work.

Selected Publications

- M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant $-SO_3^-$ Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- M. Okamura and S. Masaoka, "Design of Mononuclear Ruthenium Catalysts for Low-Overpotential Water Oxidation," *Chem. –Asian J. [Focus Review]* **10**, 306–315 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).
- G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi,

- M. Kondo and S. Masaoka, "Electrochemical Behavior of Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand," *Inorg. Chem.* **53**, 7214–7226 (2014).
- A. Fukatsu, M. Kondo, M. Okamura, M. Yoshida and S. Masaoka, "Electrochemical Response of Metal Complexes in Homogeneous Solution under Photoirradiation," *Sci. Rep.* **4**, 5327 (2014).
- T. Itoh, M. Kondo, M. Kanaike and S. Masaoka, "Arene-Perfluoroarene Interactions for Crystal Engineering of Metal Complexes: Controlled Self-Assembly of Paddle-Wheel Dimers," *CrystEngComm* **15**, 6122–6126 (2013).

1. Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant SO_3^- Groups¹

Rational molecular design of catalytic systems capable of smooth O–O bond formation is critical to the development of efficient catalysts for water oxidation. In this work, we developed a new ruthenium complex which bears pendant SO_3^- groups in the secondary coordination sphere: $[\text{Ru}(\text{terpy})(\text{bpys})(\text{OH}_2)]$ ($\text{terpy} = 2,2':6',2''$ -terpyridine, $\text{bpys} = 2,2'$ -bipyridine-5,5'-bis(methanesulfonate)). Water oxidation driven by a Ce^{4+} oxidant is distinctly accelerated upon introduction of the pendant SO_3^- groups in comparisons to the parent catalyst, $[\text{Ru}(\text{terpy})(\text{bpy})(\text{OH}_2)]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine). Spectroscopic, electrochemical, and crystallographic investigations concluded that the pendant SO_3^- groups promote the formation of an O–O bond via the secondary coordination sphere on the catalyst, whereas the influence of the pendant SO_3^- groups on the electronic structure of the $[\text{Ru}(\text{terpy})(\text{bpy})(\text{OH}_2)]^{2+}$ core is negligible. The results of this work indicate that modification of the secondary coordination sphere is a valuable strategy for the design of water oxidation catalysts.

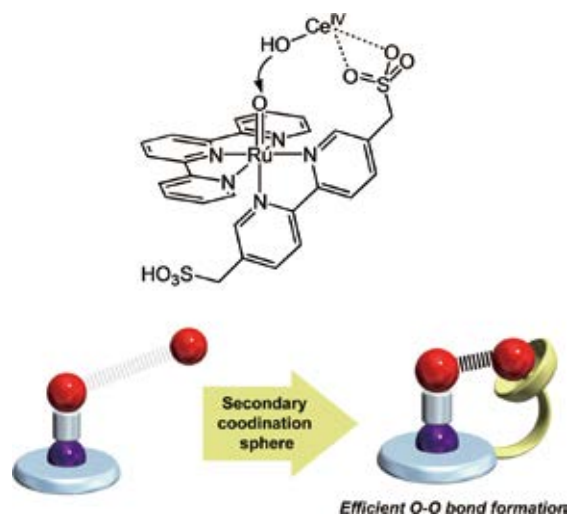


Figure 2. Schematic illustration of efficient O–O bond formation through modification of the secondary coordination sphere.

2. Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex²

Mixed-valence (MV) complexes are excellent model systems for the investigation of electron-transfer phenomena in biophysical processes such as photosynthesis and in artificial electronic devices based on conjugated materials. Given that

the electronic properties of MV states could be strictly controlled by the oxidation state of the dinuclear core, systematic investigations on the several oxidation states of dinuclear metal complexes are an interesting and important research topic. In this work, a series of $[\{(\text{terpy})(\text{bpy})\text{Ru}\}(\mu\text{-O})\{\text{Ru}(\text{bpy})(\text{terpy})\}]^{n+}$ ($[\text{RuORu}]^{n+}$, $\text{terpy} = 2,2':6',2''$ -terpyridine, $\text{bpy} = 2,2'$ -bipyridine) was systematically synthesized and characterized in three distinct redox states ($n = 3, 4,$ and 5 for $\text{Ru}^{\text{II,III}}_2$, $\text{Ru}^{\text{III,III}}_2$, and $\text{Ru}^{\text{III,IV}}_2$, respectively). The crystal structures of $[\text{RuORu}]^{n+}$ ($n = 3, 4, 5$) in all three redox states were successfully determined. X-ray crystallography showed that the Ru–O distances and the Ru–O–Ru angles are mainly regulated by the oxidation states of the ruthenium centers. X-ray crystallography and ESR spectra clearly revealed the detailed electronic structures of two mixed-valence complexes, $[\text{Ru}^{\text{III}}\text{ORu}^{\text{IV}}]^{5+}$ and $[\text{Ru}^{\text{II}}\text{ORu}^{\text{III}}]^{3+}$, in which each unpaired electron is completely delocalized across the oxo-bridged dinuclear core. These findings allow us to understand the systematic changes in structure and electronic state that accompany the changes in the redox state.

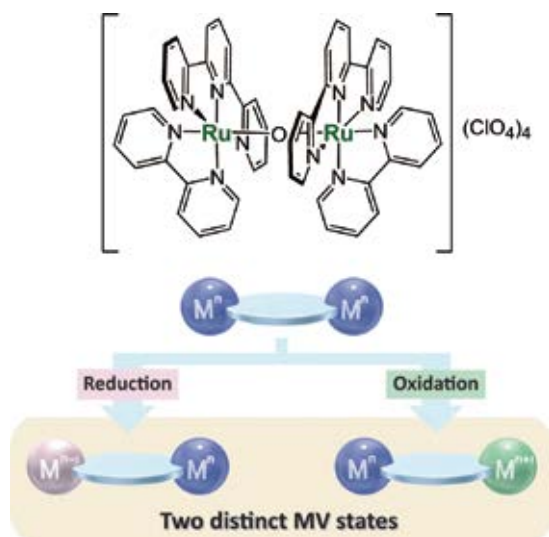


Figure 3. Two distinct MV states derived from a homovalent dimer.

References

- 1) M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant SO_3^- Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- 2) M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

Awards

FUKATSU, Arisa; Excellent Poster Award, International Conference on Artificial Photosynthesis (2014).
 IZU, Hitoshi; Excellent Poster Award, The 4th CSJ Chemistry Festa (2014).
 ITOH, Takahiro; CrystEngComm Poster Prize (2014).
 ITOH, Takahiro; Poster Award, The 64th Conference of Japan Society of Coordination Chemistry (2014).