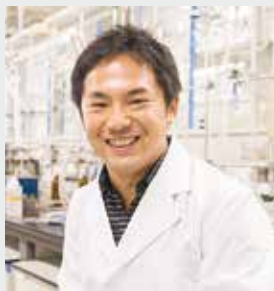


# Development of Functional Metal Complexes for Artificial Photosynthesis

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



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### 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

### Award

2017 The 13<sup>th</sup> (FY 2016) JSPS Prize

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TASAKI, Masahiro

### Technical Fellow

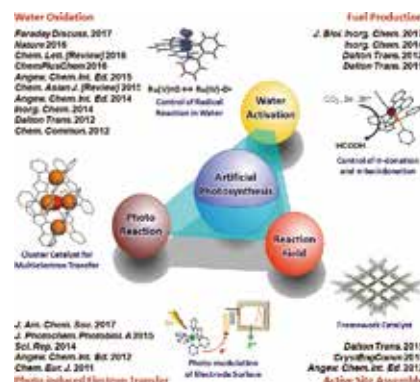
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SHIBATA, Akane  
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**Keywords** Metal Complex, Water Oxidation, Artificial Photosynthesis

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, M. Okamura, M. Kanaike, S. Haesuwannakij, H. Sakurai and S. Masaoka, "Fe, Ru, and Os Complexes with the Same Molecular Framework: Comparison of Structures, Properties and Catalytic Activities," *Faraday Discuss.* **198**, 181–196 (2017).
- V. K. K. Praneeth, M. Kondo, P.-M. Woi, M. Okamura and S. Masaoka, "Electrocatalytic Water Oxidation by a Tetranuclear Copper Complex," *ChemPlusChem* **81**, 1123–1128 (2016).
- M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, "A Pentanuclear Iron Catalyst Designed for Water Oxidation," *Nature* **530**, 465–468 (2016).
- M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant  $-\text{SO}_3^-$  Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (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).

## 1. Fe, Ru, and Os Complexes with the Same Molecular Framework: Comparison of Structures, Properties and Catalytic Activities<sup>1)</sup>

Water oxidation ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) is a key reaction in energy conversion in natural and artificial photosynthesis. The development of artificial water oxidation catalysts (WOCs) has attracted growing interest in recent years due to the urgent need to solve the world's energy problems. Metal complexes containing group 8 metal centres (Fe, Ru, or Os) and water coordination sites can be regarded as the most attractive candidates for molecular WOCs, because such metal-aqua species can generate high-valent metal-oxo species, which are the key intermediates triggering the formation of the O–O bond, via stepwise electron removal involving concomitant proton loss.

In this study, we present the syntheses, crystal structures, spectroscopic and electrochemical properties, and water oxidation activities of a series of Fe(II), Ru(II), and Os(II) complexes bearing a pentadentate ligand and a monodentate ligand. The nature of the metal ions are extracted and discussed by comparing the difference of the structure, properties and reactivities among a series of group 8 metal complexes with the same molecular framework. The results will provide new insight into the design and development of group 8 metal-based molecular catalysts for water oxidation.



Figure 2. Crystal structures of the Fe, Ru, and Os Complexes.

## 2. Electrocatalytic Water Oxidation by a Tetranuclear Copper Complex<sup>2)</sup>

Cu-based WOCs have attracted much interest among researchers due to the low cost and biological relevance of Cu.<sup>3)</sup> One of the most attractive targets in this field of research can be considered to be discrete multinuclear Cu complexes

due to their homogeneity and multinuclearity. However, there are only a few reports on water oxidation catalysis by discrete multinuclear Cu complexes.

In this study, a novel tetranuclear copper-based water oxidation catalyst was designed and synthesized by using a new multinucleating ligand containing two proton dissociation sites, 1,3-bis(6-hydroxy-2-pyridyl)-1H-pyrazole. The copper complex showed electrocatalytic activity for water oxidation reactions under aqueous basic conditions (pH 12.5) with an overpotential of approximately 500 mV. UV/Vis absorption and energy-dispersive X-ray (EDX) spectroscopic techniques coupled with electrochemical analyses of the catalyst system strongly suggest that the tetranuclear copper complex works as a homogeneous system under the conditions used. The results demonstrate the utility of a discrete tetranuclear copper complex in water oxidation reactions.

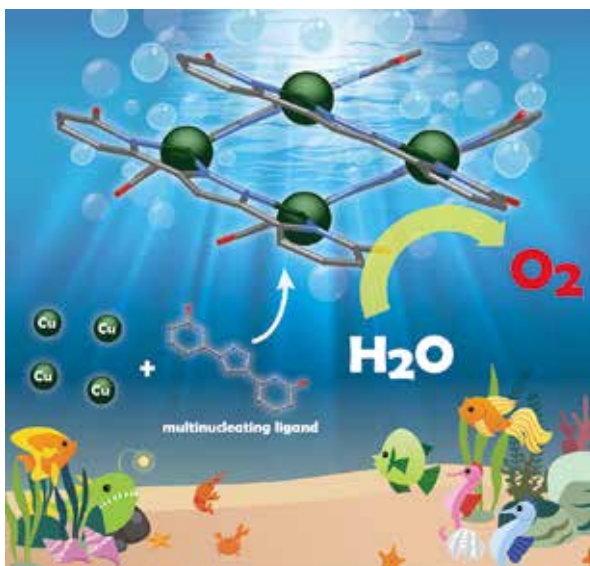


Figure 3. Water oxidation by the tetranuclear copper complex.

### References

- 1) M. Yoshida, M. Kondo, M. Okamura, M. Kanaike, S. Haesuwannakij, H. Sakurai and S. Masaoka, *Faraday Discuss.* **198**, 181–196 (2017).
- 2) V. K. K. Praneeth, M. Kondo, P.-M. Woi, M. Okamura and S. Masaoka, *ChemPlusChem* **81**, 1123–1128 (2016).
- 3) M. Kondo and S. Masaoka, *Chem. Lett. [Highlight Review]* **45**, 1220–1231 (2016).

### Awards

MASAOKA, Shigeyuki; The 13<sup>th</sup> (FY 2016) JSPS Prize (2017).

KONDO, Mio; Morita Science Research Award (2017).

CHINAPANG, Pondchanok; Excellent Poster Award, International Conference on Artificial Photosynthesis (2017).

IZU, Hitoshi; Excellent Poster Award, International Conference on Artificial Photosynthesis (2017).

ENOMOTO, Takafumi; Poster Award, 6<sup>th</sup> CSJ Chemistry Festa (2016).

OKAMURA, Masaya; KONDO, Mio; MASAOKA, Shigeyuki; Special Prize of the Nature Industry Award (2016).

ENOMOTO, Takafumi; Poster Prize, the 66<sup>th</sup> JSCC Symposium (2016).

ENOMOTO, Takafumi; Dalton Transactions Award (2016).