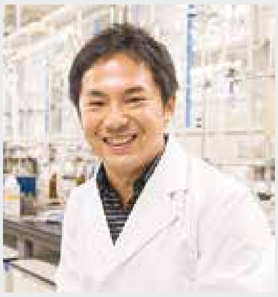
Development of Functional Metal Complexes for Artificial Photosynthesis

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
  OKAMURA, Masaya
  VIJAYENDRAN, Praneeth
Graduate Student
  ITOH, Takahiro
  OKABE, Yuki
  CHINAPANG, Pondchanok
  FUKATSU, Arisa
  LEE, Sze Koon
  IZU, Hitoshi
  ENOMOTO, Takafumi
  USHIJIMA, Riku
  MATSUI, Chihiro
Technical Fellow
  KUGA, Reiko
  KANAIKE, Mari
  SHIBATA, Akane
Secretary
  TANIWAKE, Mayuko
  NOGAWA, Kyoko

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.

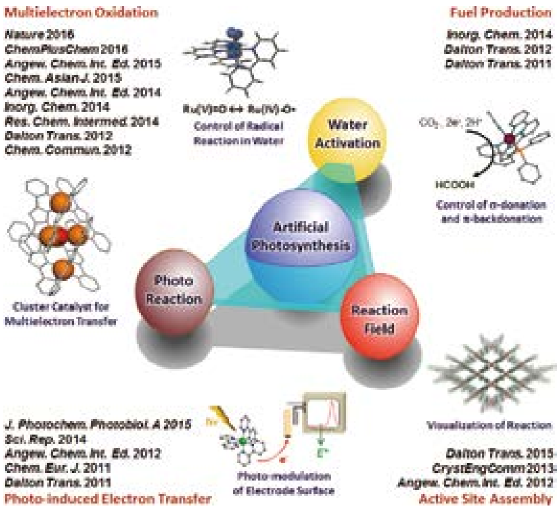


Figure 1. An overview of our work.

Selected Publications

- M. 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 -SO_3^- Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- T. Itoh, M. Kondo, H. Sakamoto, K. Wakabayashi, M. Kanaike, K. Itami and S. Masaoka, "Porous Frameworks Constructed by Non-Covalent Linking of Substitution-Inert Metal Complexes," *Dalton Trans.* **44**, 15334–15342 (2015).
- A. Fukatsu, M. Kondo, Y. Okabe and S. Masaoka, "Electrochemical Analysis of Iron-Porphyrin-Catalyzed CO_2 Reduction under Photoirradiation," *J. Photochem. Photobiol. A* **313**, 143–148 (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. A Pentanuclear Iron Catalyst Designed for Water Oxidation[1)]

Water oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is considered the main bottleneck in the production of chemical fuels from sunlight and/or electricity. In nature, the oxidation of water is efficiently catalysed by the oxygen-evolving complex (OEC) in photosystem II (PSII). Because extraction of the OEC is extremely difficult, various synthetic molecular catalysts have been investigated over the last decades. However, the development of efficient, robust and abundant metal-based molecular catalysts remains a challenge. In this work, we show a water oxidation reaction catalysed by a pentanuclear iron complex. Electrochemical analysis revealed that the pentairon complex exhibits rich redox flexibility with six different oxidation states between Fe^{II}_5 and Fe^{III}_5, in which the Fe^{III}_5 state is the active species for oxidising water. A computational investigation indicated that the O–O bond formation proceeds from the mixed-valence $Fe^{II}_2Fe^{III}(Fe^{IV}{=}O)_2$ intermediate with a reaction barrier of less than 10 kcal mol^{-1}. The turnover frequency of the water oxidation catalyst was determined to be 1,900 s^{-1}, which is considerably greater than that of the OEC (100–400 s^{-1}). Our findings indicate that efficient water oxidation catalysts can be created based on multinuclear iron complexes with redox flexibility and adjacent water-activation sites.

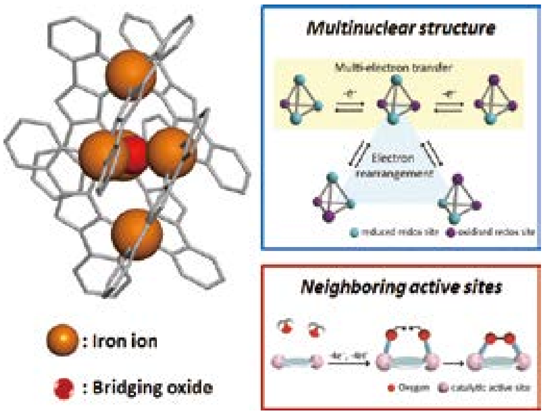


Figure 2. Structure (a) and characteristics (b) of the Fe_5 catalyst.

2. Electrochemical Analysis of Iron-Porphyrin-Catalyzed CO_2 Reduction under Photoirradiation[2)]

To understand the mechanisms of solar-to-fuel conversion reactions, electrochemical responses of catalysts should be investigated under photoirradiation because the electrochemical process proceeds subsequent to the photochemical process. However, in general, the electrochemical and photochemical properties of molecular catalysts are separately evaluated using different experimental setups. In this study, the photochemical reaction of a metal-complex-based catalyst was analyzed by electrochemical measurements. A well-known catalyst for the CO_2 reduction reaction, *meso*-tetraphenylporphyrin iron(III) chloride (**Fe(tpp)Cl**), was selected as the target analyte. Although the analysis of the electrochemical response of **Fe(tpp)Cl** under photoirradiation with conventional cyclic voltammetry (CV) was not allowed, the adaptation of thin layer cyclic voltammetry (TLCV) enabled us to detect the photochemical reaction of **Fe(tpp)Cl**. The influence of photoirradiation on the electrochemical property of **Fe(tpp)Cl** was investigated both under Ar and CO_2 atmospheres. Although the thin layer cyclic voltammograms of **Fe(tpp)Cl** upon photoirradiation under an Ar atmosphere were almost the same as those measured in the dark, the measurements under a CO_2 atmosphere clearly indicated the change of the electrochemical response upon photoirradiation. The detailed analysis of this phenomenon revealed that the photoinduced decarbonylation reaction regenerates the original [Fe^{II}(tpp)] complex under photoirradiation.

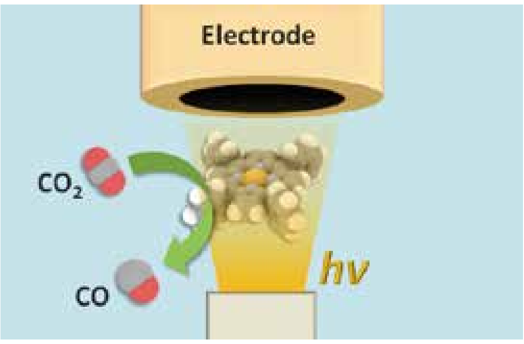


Figure 3. Electrochemical CO_2 reduction under photoirradiation.

References

1) 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, *Nature* **530**, 465–468 (2016).

2) A. Fukatsu, M. Kondo, Y. Okabe and S. Masaoka, *J. Photochem. Photobiol. A* **313**, 143–148 (2015).

Awards

ENOMOTO, Takafumi; Outstanding Student Prize, Tokai Branch of the Chemical Society of Japan (2016).

LEE, Sze Koon; Poster Award, The Winter School of Asian-Core Program (2016).

ENOMOTO, Takafumi; Poster Award, The 27th Symposium on Photochemistry and Photophysics of Coordination Compounds (2016).

FUKATSU, Arisa; IZU, Hitoshi; ENOMOTO, Takafumi; Presentation Award, SOKENDAI Physical Science Student Seminar (2016).

ENOMOTO, Takafumi; Adobe Award (the excellence award), SOKENDAI Physical Science Student Seminar (2016).