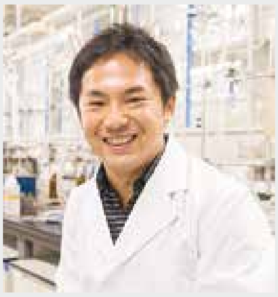
Development of Functional Metal Complexes for Artificial Photosynthesis

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
2019	Professor, Osaka University

Award

2017	The 13th (FY 2016) JSPS Prize
2019	The 25th Gold Medal Prize

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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 the research field. Our group studies the development of functional metal complexes toward the realization of artificial photosynthesis. Specific areas of research include (i) creation of cluster catalysts for multi-electron transfer reactions, (ii) frontier-orbital engineering of metal complexes for multi-electron transfer reactions, (iii) application of proton-coupled electron transfer toward multi-electron transfer reactions, (iv) electrochemical analysis of catalytic reactions, (v) development of novel photo-induced electron transfer systems, (vi) establishment of electrochemical method for the photoreactions of metal complexes in homogeneous solutions, and (vii) development of framework catalysts for small molecule conversion via the self-assembly of catalyst modules.

Figure 1. An overview of our work.

Selected Publications

- V. K. K. Praneeth, M. Kondo, M. Okamura, T. Akai, H. Izu and S. Masaoka, "Pentanuclear Iron Catalysts for Water Oxidation: Substituents Provide Two Routes to Control Onset Potentials," *Chem. Sci.* **10**, 4628–4639 (2019).
- S. K. Lee, M. Kondo, M. Okamura, T. Enomoto, G. Nakamura and S. Masaoka, "Function-Integrated Ru Catalyst for Photochemical CO_2 Reduction," *J. Am. Chem. Soc.* **140**, 16899–16903 (2018).
- P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, "Development of a Framework Catalyst for Photocatalytic Hydrogen Evolution," *Chem. Commun.* **54**, 1174–1177 (2018).
- 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).
- 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. Development of Function-Integrated Ru Catalyst for Photochemical CO_2 Reduction[1)]

The efficient conversion of solar energy into storable chemical fuels or useful chemicals is one of the major challenges in the 21st century. Particularly, visible-light driven photocatalytic reduction of CO_2 has attracted considerable attention because this technology can produce fuels and chemicals and counteract CO_2 emissions. The reaction is typically achieved by a system using a combination of two distinct functional units: A visible-light absorbing chromophore (photosensitizer, PS) and a catalyst (Cat). These systems require photoinduced electron transfer (ET) from the PS to the Cat to drive the reaction, and catalysis is largely affected by the efficiency of the ET process. Accordingly, optimization of the ET process with convergent modification of PS and Cat units is indispensable for efficient catalytic reactions.

A function-integrated catalyst, which can act as both PS and Cat, is a valuable alternative for photocatalytic CO_2 reduction. In this type of system, light absorption and subsequent CO_2 reduction proceed within one molecular unit. Thus, a reaction without an ET event between PS and Cat units can be achieved. However, the development of function-integrated catalysts that have (i) strong absorption in the visible-light region, (ii) high reaction rate, and (iii) high stability is still challenging.

In this study, we report efficient, visible-light-driven CO_2 reduction catalyzed by a function-integrated photocatalyst. The key to our success is the use of a phosphine-substituted Ru(II) polypyridyl complex, *trans(P,MeCN)*-[Ru^{II}(tpy) (pqn) (MeCN)]$^{2+}$ (**RuP**, tpy = 2,2′:6′,2″-terpyridine; pqn = 8-(diphenylphosphanyl)quinoline, Figure 2). **RuP** exhibits an intense band at 475 nm due to MLCT transitions. Additionally, **RuP** catalyzes electrochemical CO_2 reduction at one of the lowest overpotentials among homogeneous catalysts. These two characteristics of **RuP** enabled the development of a function-integrated system with a catalytic performance superior to that of best-in-class counterparts.

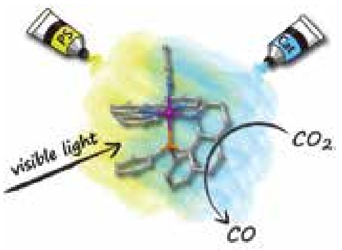

Figure 2. Function-integrated catalyst for visible-light driven CO_2 reduction.

2. Water Oxidation Reaction Catalyzed by Pentanuclear Iron Complexes[2)]

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. Recently, we demonstrated that a pentanuclear iron complex [$Fe^{II}_4Fe^{III}(\mu_3\text{-}O)(bpp)_6$]$^{3+}$, [**$Fe_5$-H**]$^{3+}$ (Hbpp = bis(pyridyl)pyrazole), can serve as a highly active catalyst for electrocatalytic water oxidation. The reaction rate and durability of [**Fe_5-H**]$^{3+}$ are the highest among iron-based water oxidation catalysts reported thus far. However, a relatively large onset potential is required for the catalysis. Therefore, the development of a novel strategy for designing catalysts that can drive the reaction at low onset potentials is essential.

Here, we report two approaches for decreasing the onset potential of pentairon water oxidation systems. Two approaches involving the installation of substituents onto the Hbpp ligand have been demonstrated. Two kinds of ligands, one with electron-donating and the other with electron-withdrawing groups at the 4-position of the Hbpp have been employed, and the new pentairon complexes were constructed utilizing these ligands. The newly synthesized complexes catalysed the oxidation of water with high Faradaic efficiencies, and the onset potentials of these complexes were lower than that of the parent complex. Mechanistic insights revealed that there are two methods for decreasing onset potentials: Control of the redox potentials of the pentairon complex and control of the reaction mechanism (Figure 3).

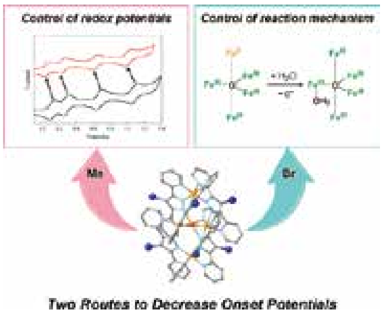

Figure 3. Two routes to control onset potentials of water oxidation in pentanuclear iron complexes.

References

1) S. K. Lee, M. Kondo, M. Okamura, T. Enomoto, G. Nakamura and S. Masaoka, *J. Am. Chem. Soc.* **140**, 16899–16903 (2018).
2) V. K. K. Praneeth, M. Kondo, M. Okamura, T. Akai, H. Izu and S. Masaoka, *Chem. Sci.* **10**, 4628–4639 (2019).

Awards

MASAOKA, Shigeyuki; The 25th Gold Medal Prize (2019).
IZU, Hitoshi; Elsevier Best Poster Prize, 15th International Symposium on Applied Bioinorganic Chemistry (2019).
ENOMOTO, Takafumi; The School of Physical Sciences Dean’s Award, SOKENDAI (2018).
LEE, Sze Koon; SOKENDAI Award (2018).
CHINAPONG, Pondchanok; The School of Physical Sciences Dean’s Award, SOKENDAI (2018)