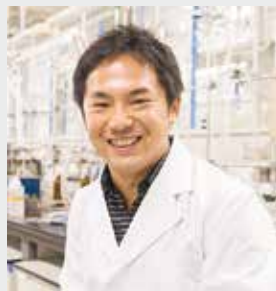


Development of Functional Metal Complexes for Artificial Photosynthesis

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Education

1999 B.S. Doshisha University
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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
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Keywords

Metal Complex, Multi-Electron Transfer Reactions, 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 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.

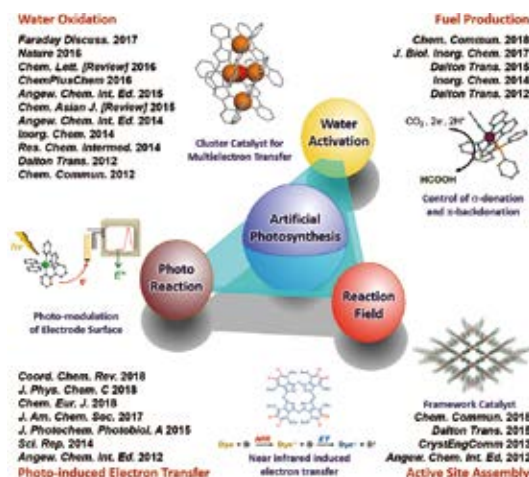


Figure 1. An overview of our work.

Selected Publications

- S. K. Lee, M. Kondo, G. Nakamura, M. Okamura and S. Masaoka, "Low-Overpotential CO₂ Reduction by Phosphine-Substituted Ru(II) Polypyridyl Complex," *Chem. Commun.* **54**, 6915–6918 (2018).
- T. Enomoto, M. Kondo, M. Asada, T. Nakamura and S. Masaoka, "Near-IR Light-Induced Electron Transfer via Dynamic Quenching," *J. Phys. Chem. C* **122**, 11282–11287 (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 -SO₃⁻ 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. Low-Overpotential CO₂ Reduction by Phosphine-Substituted Ru(II) Polypyridyl Complex¹⁾

Catalytic CO₂ reduction into liquid fuels and commodity chemicals under benign condition has drawn tremendous attention, not only as a means to decrease the competition for limited fossil fuel reserves but also help to reduce the concentration of atmospheric CO₂. There are a continuously increasing number of molecular catalysts to convert CO₂ into fuels, such as HCOOH and deeply reduced products. In addition, the reduction of CO₂ to carbon monoxide (CO) is also favourable because a wide variety of fuels and commodity chemicals can be produced from CO via Fischer–Tropsch synthesis. Therefore, the development of a catalyst that can convert CO₂ to CO is an attractive research target.

In this study, we investigated electrochemical CO₂ reduction by a polypyridyl Ru complex with a mixed phosphine-pyridine and a labile ligands. Electrochemical measurements and controlled potential electrolysis revealed that the complex can promote electrocatalytic CO₂ reduction to produce CO at a lower overpotential than those of the relevant metal-complex-based catalysts. Mechanistic investigations using spectroscopic measurements clarified that the introduction of a phosphine donor at the *trans* position to the labile ligand is the key to reduce the overpotential for CO₂ reduction. In other words, a simple introduction of a phosphine moiety to the ligand largely affect the reactivity of the Ru centre, which collectively allow the complex to reduce CO₂ at a low overpotential. The results presented in this work provides a novel versatile strategy to reduce the overpotential of molecular catalysts for CO₂ reduction, which is possibly applicable to a wide variety of catalytic systems.

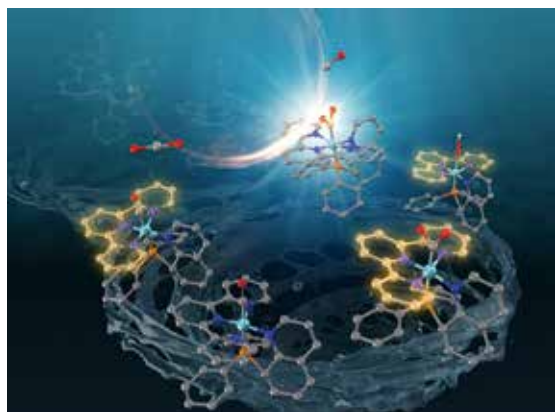


Figure 2. CO₂ reduction catalyzed by the ruthenium complex.

2. Development of a Framework Catalyst for Photocatalytic Hydrogen Evolution²⁾

The photocatalytic production of H₂ from water is a promising way to provide a sustainable and environmentally friendly chemical fuels. Thus far, considerable efforts have been devoted to the development of molecular-based homogeneous photocatalytic systems. However, homogeneous systems are considered unsuitable for future practical applications because of their moderate reusability and stability, for which heterogeneous photocatalytic systems are rather advantageous.

In this study, we propose an effective approach to construct a heterogeneous photocatalytic system based on the supramolecular assembly of molecular catalyst modules. In this system, a discrete catalyst module, which has a metal-complex-based catalytic centre (catalytic node) and intermolecular interaction sites (molecular connector), can be assembled into an ordered structure via non-covalent interactions to afford a heterogeneous framework catalyst. Therefore, our system provides two prominent features: (1) well-defined catalytic sites attributed to the molecular-based modules and (2) reusability and high durability based on the heterogeneous nature. The controlled self-assembly of a catalyst module composed of a Rh(II) paddle-wheel dimer bearing 1,8-naphthalimide-based moieties afforded a novel heterogeneous framework catalyst. The framework catalyst exhibited long-lived activity for photocatalytic hydrogen production from water and was easily reused without considerable loss of catalytic activity. The present work offer novel strategy constructing molecular-based heterogeneous catalytic systems for small molecular conversions.

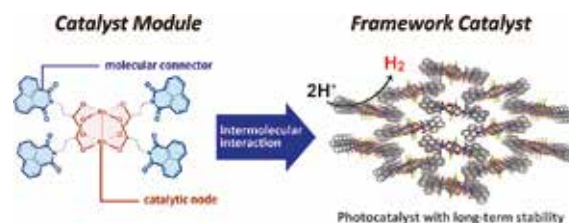


Figure 3. Construction of a framework catalyst via the self-assembly of catalyst modules.

References

- 1) S. K. Lee, M. Kondo, G. Nakamura, M. Okamura and S. Masaoka, *Chem. Commun.* **54**, 6915–6918 (2018).
- 2) P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, *Chem. Commun.* **54**, 1174–1177 (2018).

Awards

KONDO, Mio; Chemical Society of Japan Award for Young Women Chemists (2018).
 KONDO, Mio; The 7th Young Scientists Award of National Institutes for Natural Sciences (2018).
 CHINAPANG, Pondchanok; CSJ Student Presentation Award 2017, The 98th CSJ Annual Meeting (2018).
 CHINAPANG, Pondchanok; Poster Prize, the 67th JSCC Symposium (2017).
 LEE, Sze Koon; Chemistry Letters Young Award, The 4th Japan-Taiwan-Singapore-Hong Kong Quadrilateral Symposium on Coordination Chemistry (2017).
 IZU, Hitoshi; Oral Award, Interdisciplinary Symposium for Up-and-Coming Material Scientists 2017 (ISUMS2017) (2017).
 IZU, Hitoshi; Poster Award, The 50th symposium on Chemical and Biochemical Oxidation (2017).