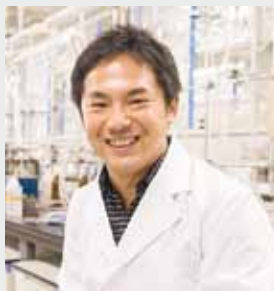


# Development of Functional Metal Complexes for Artificial Photosynthesis

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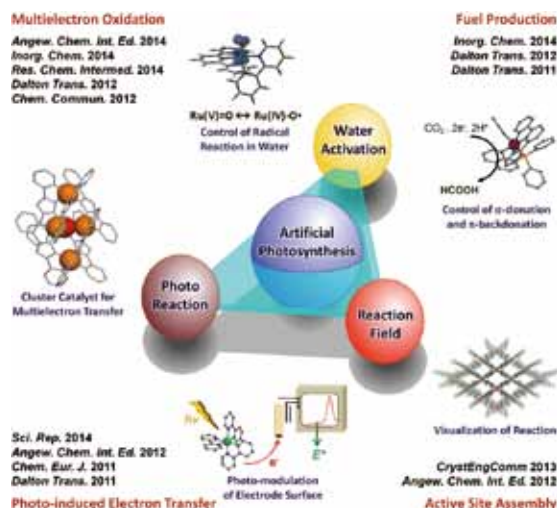
2002 JSPS Research Fellow (DC2)  
2004 Research Assistant (Postdoc), University of Liverpool  
2005 Research Associate, Kyushu University  
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2011 Associate Professor, Institute for Molecular Science  
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Artificial 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.

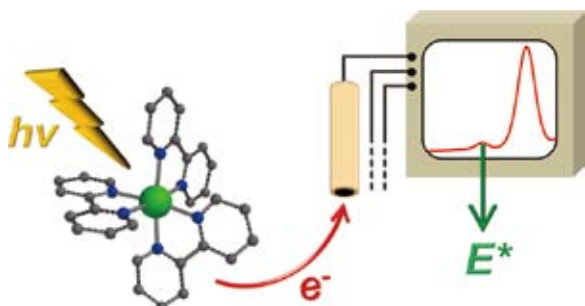
#### Selected Publications

- M. Yoshida, M. Kondo, 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. Kanaïke and S. Masaoka, "Arene-Perfluoro-arene Interactions for Crystal Engineering of Metal Complexes: Controlled Self-Assembly of Paddle-Wheel Dimers," *CrystEngComm* **15**, 6122–6126 (2013).
- M. Okamura, M. Yoshida, R. Kuga, K. Sakai, M. Kondo and S. Masaoka, "A Mononuclear Ruthenium Complex Showing Multiple Proton-Coupled Electron Transfer toward Multi-Electron Transfer Reactions," *Dalton Trans.* **41**, 13081–13089 (2012).
- A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka and K. Sakai, "Kinetics and DFT Studies on Water Oxidation by  $Ce^{4+}$  Catalyzed by  $[Ru(terpy)(bpy)(OH_2)_2]^{2+}$ ," *Chem. Commun.* **48**, 239–241 (2012).

## 1. Electrochemical Response of Metal Complexes in Homogeneous Solution under Photoirradiation<sup>1)</sup>

Photoinduced electron transfer (PET) is a key process in reactions that convert light energy to electrical or chemical energy, both in natural and artificial systems. The efficiency of PET, which largely affects the performance of these systems, is correlated with the redox properties of the photoexcited molecule, which transfers electrons or holes during the PET reaction. Hence, determining the redox potentials of photoexcited molecules is of great significance not only for understanding the mechanisms of PET reactions but also for achieving highly efficient light-energy conversion systems. Electrochemical analysis under photoirradiation should enable the measurement of the redox potentials of excited species. However, reports of the direct electrochemical detection of photoexcited molecules have been limited to only a few examples in which specialized photoelectrochemical instrumentation was required. This limitation may be due to the difficulty to avoid the complication of voltammogram profiles that arises from the unintended side effects of photoirradiation, such as temperature increases and enhanced mass transfer. Thus, the redox potentials of excited states have more commonly been indirectly estimated using the 0-0 transition energy ( $E_{00}$ ) or the quenching rate constant ( $k_q$ ). Therefore, the establishment of a versatile methodology for electrochemical measurements under photoirradiation will provide new insights into PET phenomena.

To establish a simple method for directly determining the redox potentials of the photoexcited states of metal complexes, electrochemical measurements under several conditions were performed. The electrochemical response was largely influenced not only by the generation of photoexcited molecules but also by the convection induced by photoirradiation, even when the global temperature of the sample solution was unchanged. The suppression of these unfavourable electrochemical responses was successfully achieved by adopting well-established electrochemical techniques. Furthermore, as an initial demonstration, the photoexcited state of a Ru-based metal complex was directly detected, and its redox potential was determined using a thin layer electrochemical method.

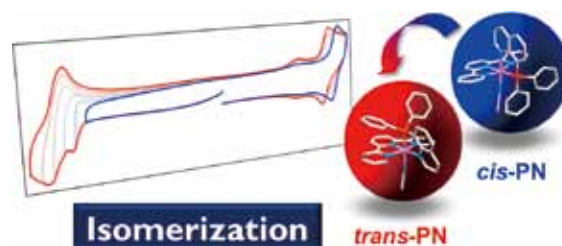


**Figure 2.** Schematic illustration of electrochemical measurement of a metal complex under photoirradiation.

## 2. Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand<sup>2)</sup>

Ruthenium(II) polypyridine complexes with a single labile ligand have been widely studied as catalysts for many chemical reactions including water oxidation, CO<sub>2</sub> reduction, and photoinduced chemical conversions. One of the key strategies in developing ruthenium polypyridine catalysts with novel properties and reactivities is the introduction of phosphine ligands because their  $\sigma$ -donating and  $\pi$ -accepting abilities can influence electronic structures of the ruthenium center. However, few studies examining substitution of phosphine for pyridine moiety have been reported; there have been only a few works of diphosphine-coordinated ruthenium(II) polypyridine complexes, and no crystal structures have been reported. Thus, the investigation of phosphine-substituted ruthenium(II) polypyridine complexes with a single labile is important not only for the design and development of new catalysts but also for an understanding of their basic properties.

We report the synthesis, structural characterization, and electrochemical and spectroscopic properties of a series of ruthenium(II) polypyridine complexes containing 8-(diphenylphosphanyl)quinoline (Pqn), *trans*-(P,MeCN)-[Ru(trpy)(Pqn)(MeCN)](PF<sub>6</sub>)<sub>2</sub> (*trans*-PN) and *cis*-(P,MeCN)-[Ru(trpy)(Pqn)(MeCN)](PF<sub>6</sub>)<sub>2</sub> (*cis*-PN), or 1,2-bis(diphenylphosphanyl)benzene (dppbz), [Ru(trpy)(dppbz)(MeCN)](PF<sub>6</sub>)<sub>2</sub> (PP). Effects of the number and position of phosphine donors on the structures and electronic properties were investigated on the basis of comparisons with [Ru(trpy)(bpy)(MeCN)](PF<sub>6</sub>)<sub>2</sub> (NN). The electrochemical measurements of these complexes showed distinct behavior in their reduction reactions; reduction of *cis*-PN resulted in *cis*-*trans* isomerization to *trans*-PN, and that of PP proceeded via a two electron-transfer reaction. The mechanism of these electrochemical behaviors was explained in conjunction with the liberation of a monodentate labile ligand.



**Figure 3.** Cyclic voltammograms showing redox-induced *cis*-*trans* isomerization from *cis*-PN to *trans*-PN.

### References

- 1) A. Fukatsu, M. Kondo, M. Okamura, M. Yoshida and S. Masaoka, *Sci. Rep.* **4**, 5327 (2014).
- 2) G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi, M. Kondo and S. Masaoka, *Inorg. Chem.* **53**, 7214–7226 (2014).

### Award

OKAMURA, Masaya; Student Lecture Award, The 63<sup>rd</sup> Conference of Japan Society of Coordination Chemistry (2013).