2nd OUS Frontier Symposium

Functional Complexes and Their New Applications
March 3, 2023

KAKE Educational Institution ● 50th Anniversary Hall
Okayama University of Science,
Okayama, Japan

Organized by Institute of Frontier Science and Technology, Okayama University of Science

---

Scientific Program

13:00
Opening Ceremony Haruo Akashi (Director, Institute of Frontier Science and Technology)

13:05 – 13:55
Guest Lecturer 1 Chairperson: Haruo Akashi
Shie-Ming Peng (National Taiwan University)
From Metal-Metal Multiple Bonds to Helical Metal Strings

13:55 – 14:45
Guest Lecturer 2 Chairperson: Minoru Mitsumi
Hitoshi Ishida (Kansai University)
Photocatalytic CO_2 Reduction by Ruthenium Complexes towards Artificial Photosynthesis

14:45 – 15:15 Coffee Break

15:15 – 16:05
Guest Lecturer 3 Chairperson: Haruo Akashi
Akitaka Ito (Kochi University of Technology)
Controlling Photofunctionalities of Metal Complexes by Electrostatic Interactions

16:05
Closing Ceremony Yoshiko Minami (Vice President, Okayama University of Science)

To join, register here → https://zoom.us/meeting/register/tJIqfuuuqjwsHtSwT7f3MspcToh0SyAnlz96

You will be taken to a Zoom website where you will fill in your first and last names and an email address. Clicking "Register" takes you to another Zoom page containing the Date & Time, Meeting ID, Passcode, and a Zoom link. You will also receive a confirmation email with the same information.

The information you submit will be used solely for participating in the 2nd OUS Frontier Symposium.

From Metal-Metal Multiple Bonds to Helical Metal Strings

Shie-Ming Peng*

Department of Chemistry, National Taiwan University, Taipei Taiwan
Institute of Chemistry, Academia Sinica, Taipei Taiwan
*E-mail: smpeng@ntu.edu.tw

The study of metal string complexes with 1-D transition metal frameworks (Fig.1) began in the early 1990s. Since these complexes provide great insight into multiple metal-metal bonds, and may have potential applications as molecular wires (Fig.2), this field of research has grown in the past 20 years. As such, the electronic structure of the simplest trinuclear complexes, the supporting ligand systems, and single molecular conductance of metal string complexes are discussed. This review will introduce the development of this field and summarize some important results in the newly designed heteronuclear metal string complexes (HMSCs). These molecules may be of great interest in studying the nature of heterometallic electronic effects and molecular electronic applications.

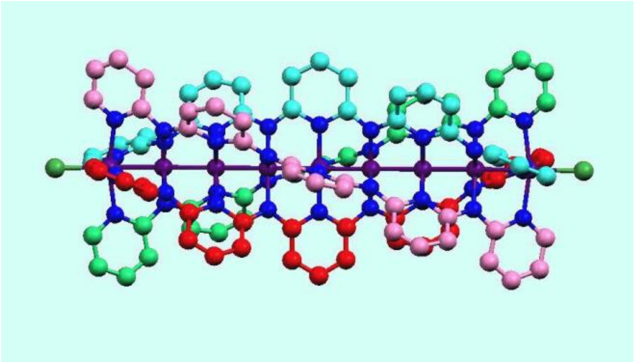

Figure 1: Molecular Model of Metal String Complex with Quadruple Ligands

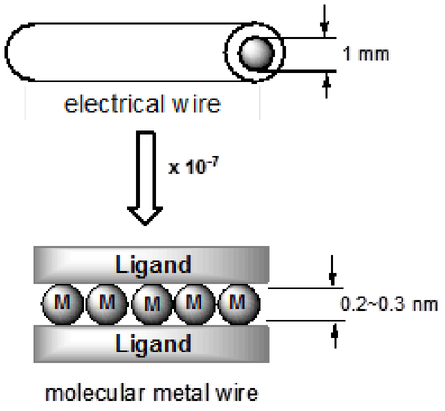

Figure 2: An Electric Wire and a Miniature Molecular Metal Wire

[1] Ismayilov RH, Wang WZ, Lee GH, Yeh CY, Hua SA, Song Y, Rohmer MM, Bénard M, **Peng SM,** *Angew. Chem. Int. Ed.*, **2011**, *50*, 2045-2048.

[2] Hua SA, Cheng MC, Chen C-h, and **Peng SM,** *Eur. J. Inorg.* **2015**, *Micro Review*, *15*, 2498.

[3] Ting TC, Hsu LY, Huang MJ, Horng EC, Lu HC, Hsu CH, Jiang CH, Jin BY, **Peng SM** and Chen Ch, *Angew. Chem. Int. Ed.*, **2015**, *54*, 15734-15738.

[4] Liu YC, Hua SA, Cheng MC, Yu LC, Demeshko S, Dechert S, Meyer F, Lee GH, Chiang MH, **Peng SM,** *Chem-Eur J*, **2018**, *24(45)*, 11649-11666.

[5] Cheng MC, Huang RX, Liu YC, Chiang MH, Lee GH, Song Y, Lin TS, **Peng SM**, *Dalton Trans.*, **2020**, *49(22)*, 7299-7303.

Photocatalytic CO_2 Reduction by Ruthenium Complexes towards Artificial Photosynthesis

Hitoshi Ishida*

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka, Japan

*E-mail: ishida.h@kansai-u.ac.jp

Photocatalytic CO_2 reduction is attracting much attention from the viewpoints of the utilization of solar energy and recycling of CO_2 and is expected as a central technology in artificial photosynthesis.[1] In this lecture, the catalytic abilities of *trans*(Cl)-Ru(bpy)$(CO)_2Cl_2$ (bpy: 2,2'-bipyridine) and the derivatives for CO_2 reduction will be described (Figure 1).[2] The reaction mechanism is elucidated in many parts but remains unknown in some features.[3]

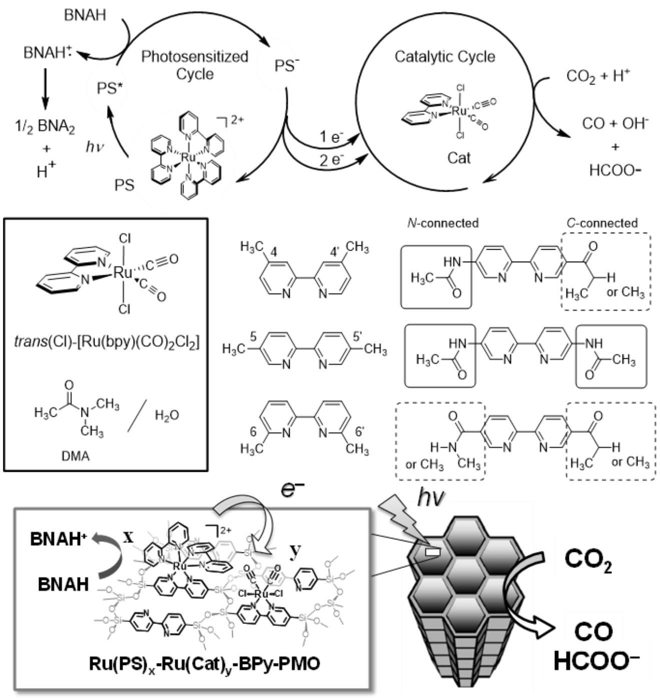

Figure 1. Photocatalytic CO_2 Reduction by *trans*(Cl)-[Ru(bpy)$(CO)_2Cl_2$] and the derivatives.

The photocatalytic CO_2 reduction proceeds by irradiating visible light (> 400 nm) in the *N*-dimethylacetamide (DMA)/water (9:1 v/v) solution containing $[Ru(bpy)_3]^{2+}$ as the photo-sensitizer, 1-benzyl-1,4-dihydronicotinamide (BNAH) as the electron donor and the catalyst. The reaction mechanism does not only depend on the electronic structures of the catalysts but also the reaction conditions such as the catalyst concentrations. It also depends on the electron-injection speeds from the one-electron reduced species of photo-sensitizer to the catalyst.

The application of the photocatalytic CO_2 reduction towards artificial photosynthesis will be discussed.

[1] Ishida, H. (**2018**), Electrochemical / Photochemical CO_2 Reduction Catalyzed by Transition Metal Complexes, in "*Carbon Dioxide Chemistry, Capture and Oil Recovery*", Iyad Karamé, Janah Shaya, Hassan Srour (Eds), InTech, pp. 17-40, DOI: 10.5772/intechopen. 75199.

[2] Ishida, H., et al., *ChemPhotoChem*, **2018**, *2*, 314-322; *Chem. Eur. J.*, **2017**, *23*, 10301-10309; *Faraday Discussions*, **2017**, *198*, 263-277; *Chem. Eur. J.*, **2015**, *21*, 10049-10060; *Chem. Sci.*, **2015**, *6*, 3063-3074; *Inorg. Chem.*, **2014**, *53*, 3326-3332.

[3] Kuramochi, Y.; Osamu Ishitani, O.; Ishida, H., *Coord. Chem. Rev.* **2018**, *373*, 333-356.

Controlling Photofunctionalities of Metal Complexes by Electrostatic Interactions

Akitaka Ito[1,2,*]

[1] *Graduate School of Engineering, Kochi University of Technology, Kami, Kochi, Japan*
[2] *Research Center for Molecular Design, Kochi University of Technology, Kami, Kochi, Japan*
*E-mail: ito.akitaka@kochi-tech.ac.jp

Metal-to-ligand charge transfer (MLCT) excited states of $d\pi^6$-type transition metal complexes represented by $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) have been utilized in various photochemical applications such as solar–energy conversion systems, light-emitting devices and sensing owing to their intense visible-light absorption and phosphorescence from the long-lived triplet excited state [1]. Therefore, controlling their photofunctionalities (e.g., light absorption, emission and photoinduced reaction behaviors) is of primary importance. There are numerous reports on synthetic tuning of the electronic structures of a complex by varying a combination of metal center and ligands and/or by introducing a functional group(s) in a ligand(s) [2]. In addition to such synthetic strategy, surrounding environment is another important factor to characterize the photofunctionalities of a metal complex [3]. Here, we focused on electric charges of metal complexes and succeeded in tuning photophysical/photochemical properties of ionic metal complexes by hybridizing with ionic nanospheres, a class of ion-exchange resins with a diameter of <300 nm.

Polypyridyl ruthenium(II)/osmium(II) and cyclometalated iridium(III) complexes doped in the ionic nanospheres exhibited intense and long-lived emission arising from decreased nonradiative decay rate constants. Such long-lived excited states of the metal complexes in the nanospheres are advantageous for photosensitized reactions, and multiple ionic species can be doped in a nanosphere. In practice, emission from $[Ru(bpy)_3]^{2+}$ in the nanosphere was reduced in the presence of codoped methyl viologen dication (MV^{2+}), and >60% quenching was obtained even by 100 nmol/mg MV^{2+} (almost equivalent to $[Ru(bpy)_3]^{2+}$ content) [4]. Similar efficient photoinduced reaction was also observed in the energy-transfer systems.

[1] Thompson, D. W.; Ito, A.; Meyer, T. J. *Pure Appl. Chem.* **2013**, *85*, 1257.: Ito, A.; Iwamura, M.; Sakuda, E. *Coord. Chem. Rev.* **2022**, *467*, 214610.

[2] Ito, A.; Kang, Y.; Saito, S.; Sakuda, E.; Kitamura, N. *Inorg. Chem.* **2012**, *51*, 7722.: Ito, A.; Kobayashi, N.; Teki, Y. *Inorg. Chem.* **2017**, *56*, 3794.: Ito, A.; Matsui, Y. *Inorg. Chem.* **2019**, *58*, 10436 [Supplementary Cover].

[3] Ito, A.; Stewart, D. J.; Fang, Z.; Brennaman, M. K.; Meyer, T. J. *Proc. Natl. Acad. Sci.* **2012**, *109*, 15132.: Ito, A.; Meyer, T. J. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13731.: Ito, A.; Fang, Z.; Brennaman, M. K.; Meyer, T. J. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4880.

[4] Yamamoto, H.; Taomoto, M.; Ito, A.; Kosumi, D. *J. Photochem. Photobiol. A: Chem.* **2020**, *401*, 112771.