

Interfacial Synthesis of Coordination Nanosheets and Their Functions

Hiroshi Nishihara

Department of Chemistry, School of Science, The University of Tokyo,

7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan

nishihara@chem.s.u-tokyo.ac.jp

Single-layer 2D materials have attracted much attention because of their unique physical and chemical properties. We have synthesized coordination nanosheets (CONASHs) comprising metal ions and organic π -ligands by the interfacial coordination reactions.^{1,2} For example, a liquid–liquid interfacial reaction of nickel(II) acetate in an aqueous phase with benzenehexathiol in an organic phase produced semiconducting sheets containing bis(dithiolato)nickel moieties with one micrometer thickness. A single-layer nanosheet with 0.6 nm thickness was successfully synthesized using a gas–liquid interfacial reaction. Modulation of the oxidation state and the electronic conductivity of the coordination nanosheet was achieved using redox reactions. Bis(dithiolato)palladium nanosheet was prepared by a modified interfacial method inhibiting the formation of Pd nanoparticles.

A series of multilayered coordination nanosheets comprising 1,3,5-tris(4-(2,2':6',2''-terpyridyl)phenyl)benzene and iron(II) or cobalt(II) ions was synthesized by liquid/liquid interfacial coordination reactions. The resultant nanosheet had a flat, smooth morphology and was several hundreds of nanometers thick. Upon its deposition on an indium tin oxide (ITO) electrode, the nanosheets underwent a reversible and robust redox reaction ($\text{Fe}^{3+}/\text{Fe}^{2+}$ or $\text{Co}^{2+}/\text{Co}^{+}$) accompanied by a distinctive color change. Electrochromism was achieved in a solidified device composed of the nanosheet, a pair of ITO electrodes, and a polymer-supported electrolyte. The combination of Fe^{2+} and Co^{2+} nanosheets in one device deposited on each ITO electrode demonstrated dual-electrochromic behavior.

We also synthesized coordination nanosheets featuring a photoactive bis(dipyrrinato)zinc(II) complex motif by an interfacial reaction between a three-way dipyrin ligand and zinc(II) ions.⁷ The bis(dipyrrinato)zinc(II) nanosheet deposited on a SnO_2 electrode functions as a photoanode in a photoelectric conversion system.

References

- [1] R. Sakamoto, K. Takada, X. Sun, T. Pal, T. Tsukamoto, E. J. H. Phua, A. Rapakousiou, K. Hoshiko, H. Nishihara, *Coord. Chem. Rev.* **2016**, 320-321, 118-128, and the references therein.
- [2] H. Maeda, R. Sakamoto, H. Nishihara, *Langmuir* **2016**, 32, 2527-2840 (Feature Article), and the references therein.

Multi-stability based on intramolecular electron transfers

Masayuki Nihei, Yoshihiro Sekine, Hiroki Okamoto, Karin Shiroyanagi, Hiroki Oshio

Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba

Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

nihei@chem.tsukuba.ac.jp

Multi-stable system, exhibiting switchable electronic states by external stimuli, is a promising candidate for switching devices and memories in the molecular electronics. Although there are numerous examples of multi-stable molecules, the controlled multi-stability still remains challenging. The multi-stability is originating from a close proximity of the energy levels of each electronic states; therefore, the rational control of the Gibbs free energy for the states is required. We report here a series of cyanide-bridged multi-nuclear metal complexes, exhibiting controlled multi-stabilities (Fig. 1).^{[1]-[4]} They exhibit external stimuli-induced electron transfers between the metal centers accompanied with spin transitions of the cobalt ions; here we call this phenomenon as electron-transfer-coupled spin transition (ETCST). We systematically investigated the thermal ETCST behavior of a series of cyanide-bridged multi-nuclear complexes, and the transition temperatures can be rationally controlled by chemical modifications. In addition, we have found a light-induced single molecule magnetism in solid state and a protonation-induced ETCST in solution, which are based on the precise control of intramolecular electron transfers. Dimensionally controlled assembly of the ETCST-active molecules will be also presented.

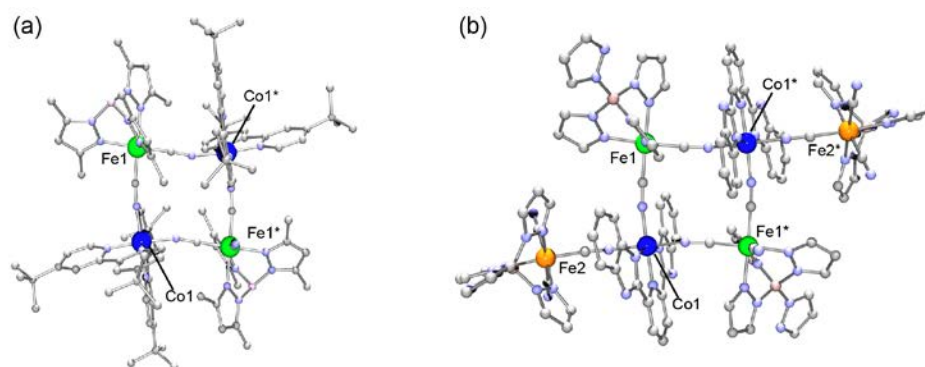


Fig. 1. Structures of cyanide-bridged $[\text{Co}_2\text{Fe}_2]$ (a) and $[\text{Co}_2\text{Fe}_4]$ (b) complexes.

Reference:

- [1] M. Nihei, Y. Sekine, N. Suganami, H. Oshio, *Chem. Lett.* **2010**, 39, 978.
- [2] M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami, H. Oshio, *J. Am. Chem. Soc.* **2011**, 133, 3592.
- [3] M. Nihei, Y. Okamoto, Y. Sekine, N. Hoshino, T. Shiga, I. P.-C. Liu, H. Oshio, *Angew. Chem. Int. Ed.*, **2012**, 51, 6361.
- [4] Y. Sekine, M. Nihei, R. Kumai, H. Nakao, Y. Murakami, H. Oshio, *Chem. Commun.*, **2014**, 50, 4050.

Talk Title: Where the Rubber Meets the Road - polyMOFs

Presenter: Seth M. Cohen, University of California, San Diego

Abstract

As porous, crystalline solids, metal-organic frameworks (MOFs) have limited options for materials processing and fabrication. To alleviate this limitation, different strategies to integrate MOFs with processible polymer materials have been explored, such as the use of mixed matrix membranes (MMMs). The direct preparation of porous materials from polymers is challenging because the packing of polymer chains results in a dense, non-porous arrangement. However, we demonstrate the transformation of an amorphous, linear, non-porous, flexible organic polymer into a 3-dimensional, highly porous, crystalline solid, as the organic component of a MOF. A polymer with aromatic dicarboxylic acids in the backbone functioned as a polymer-ligand upon annealing with metal ions to generate a polymer-metal-organic-framework (polyMOF). These materials uproot the dogma that MOFs must be prepared from small, rigid ligands. Similarly, polyMOFs contradict conventional polymer chemistry by demonstrating that linear and amorphous polymers can be readily coaxed into a highly crystalline, porous, 3-dimensional structure via coordination chemistry. polyMOFs are compatible with a variety of MOF architectures including IRMOF-1 type, Cu-paddlewheel type, and UiO-66 type structures. polyMOFs demonstrate interesting gas sorption behavior and demonstrate exceptional water stability attributed to the hydrophobicity of polymer ligands, as well as the cross-linking of the polymer chains within the MOF. Overall, the polyMOF strategy shows promise as a new class of materials that bridge the gap between polymers and porous solids. We are also examining the use of block copolymers to form polyMOFs in order to achieve polyMOF materials with truly polymer-like processing properties, but with high surface areas reminiscent of MOFs.

References

Corinne A. Allen and Seth M. Cohen, "Exploration of Chemically Crosslinked Metal-organic Frameworks" *Inorg. Chem.* **2014**, *53*, 7014-7019. DOI: 10.1021/IC500951B

Zhenjie Zhang, Ha Thi Hoang Nguyen, Stephen A. Miller, and Seth M. Cohen, "polyMOFs: A New Class of Interconvertible Polymer-MOF Hybrid Materials" *Angew. Chem. Int. Ed.* **2015**, *54*, 6152-6157. DOI: 10.1002/ANIE.201504077.

Zhenjie Zhang, Ha Thi Hoang Nguyen, Stephen A. Miller, Ann Ploskonka, Jared DeCoste, and Seth M. Cohen*, "polyMOFs as Water Tolerant Materials for Selective Carbon Dioxide Separations" *J. Am. Chem. Soc.* **2016**, *138*, 920-925. DOI: 10.1021/JACS.5B11034.

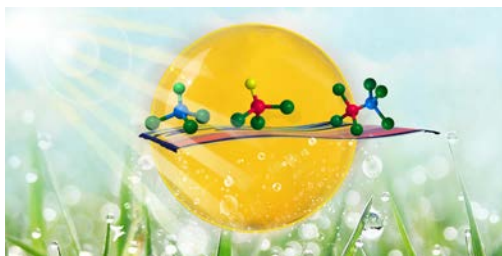
Artificial Photosynthetic Systems for Chemical Transformation

Li-Zhu Wu

*Technical Institute of Physics and Chemistry, the Chinese Academy of Sciences,
Beijing 100190, P.R. China*

lzwu@mail.ipc.ac.cn

With the increasing concern over the global energy crisis and the greenhouse effect caused by carbon dioxide emission, the development of carbon-neutral and renewable-energy solutions has attracted considerable interest in both the scientific and industrial communities. Solar energy conversion via natural or artificial photosynthesis requires three main components (Scheme 1). First, antenna/reaction center complexes absorb sunlight and convert the excitation energy to electrochemical energy (redox equivalents). Then, a water oxidation complex uses this redox potential to catalyze conversion of water to protons, electrons stored as reducing equivalents, and oxygen. A second catalytic system uses the reducing equivalents to make fuels such as carbohydrates, lipids, or hydrogen. In this presentation, we will compile the following four stories to illustrate a few approaches that may be useful in the design of artificial photosynthetic systems for chemical transformation. (1) Artificial photosynthetic systems for hydrogen evolution by [FeFe]-hydrogenases mimics; (2) Artificial photocatalysts made by earth-abundant metal salts and quantum dots *in situ* under visible light irradiation; (3) Artificial quantum dots photocathodes for hydrogen evolution by water-splitting under visible light irradiation; (4) Artificial photosynthetic systems for chemical transformation under visible light.



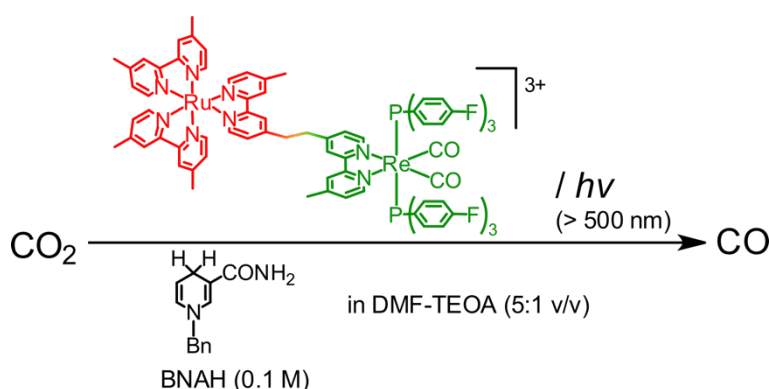
Scheme 1. Artificial photosynthetic system for solar energy conversion

Photocatalytic CO₂ reduction using multinuclear metal complexes

(Tokyo Institute of Technology) TAMAKI, Yusuke

Reductive conversion of CO₂ into energy-rich compounds using solar light as an energy source has been intensively investigated in recent years as one of promising solutions to global warming and shortage of fossil resources. We have already reported that the multinuclear complexes consisting of [Ru(N[^]N)₃]²⁺ (N[^]N = diimine ligand) photosensitizer unit and Re(I) carbonyl complex as a catalyst unit photocatalyzed the reduction of CO₂ to CO under visible-light irradiation using 1-benzyl-1,4-dihydronicotinamide (BNAH) as a sacrificial electron donor.^[1] Although these systems exhibited relatively high efficiency, durability, and selectivity, large part of the reaction mechanisms was unclear.

In this presentation, therefore, significant improvement of photocatalytic abilities^[2] and development of the photocatalytic system with the novel function, i.e., the reduction of low concentration of CO₂,^[3] based on the clarification of parts of the reaction mechanisms will be shown. For example, the oxidized products of BNAH were clarified and the electron balance of the photocatalysis was revealed. Since the accumulation of oxidized products of BNAH was found to inhibit the photocatalysis, using a new sacrificial electron donor intensively increased photocatalytic activities.



[1] (a) Gholamkhash, B.; Ishitani, O. et al. *Inorg. Chem.* **2005**, *44*, 2326. (b) Tamaki, Y.; Ishitani, O. et al. *Faraday Discuss.* **2012**, *155*, 115.

[2] Tamaki, Y.; Ishitani, O. et al. *J. Catal.* **2013**, *304*, 22.

[3] Tamaki, Y.; Morimoto, T.; Ishitani, O. et al. *submitted*.

Inorganic materials for photocatalytic water splitting and CO₂ reduction

A. Kudo^{a,b}

^a Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Japan

^b Photocatalysis international Research Center, Research Institute for Science and Technology, Tokyo University of Science, Japan

E-mail: a-kudo@rs.kagu.tus.ac.jp

Water splitting and CO₂ fixation of uphill reactions can be regarded as artificial photosynthesis, because light energy is converted to chemical energy. In the present paper, we introduce various metal oxide and sulfide photocatalysts and photoelectrochemical cells aiming at artificial photosynthesis.¹⁾

Rh and Sb-codoped SrTiO₃ photocatalyst loaded with IrO₂ is active for water splitting into H₂ and O₂ under visible light and simulated sunlight irradiations as a single particle type photocatalyst. This photocatalyst responds to 500 nm.²⁾ SrTiO₃:Rh of a H₂-evolving photocatalyst and BiVO₄ of an O₂-evolving photocatalyst construct various type of Z-schematic photocatalyst systems with Fe³⁺/Fe²⁺, [Co(bpy)₃]^{3+/2+}, [Co(phen)₃]^{3+/2+}, and a conductive reduced graphene oxide (RGO) as an electron mediator and even without an electron mediator. It is noteworthy that a sheet photocatalyst consisting of SrTiO₃:Rh,La and BiVO₄ powders with a Au contacting layer shows a quite high activity.³⁾

Metal sulfide photocatalysts that are normally unstable for water splitting into H₂ and O₂ in the absence of an electron donor can be employed for Z-schematic photocatalyst systems for water splitting. Z-schematic photocatalyst systems combining metal sulfide photocatalysts as a H₂-evolving photocatalyst with TiO₂ (RGO/TiO₂)⁴⁾ and BiVO₄+Co complex (an electron mediator) as an O₂-evolving photocatalyst show activity for water splitting into H₂ and O₂.⁵⁾ These photocatalyst materials can also be employed for photoelectrochemical system for solar water splitting.^{5,6)}

Ag/BaLa₄Ti₄O₁₅ and Ag/KCaSrTa₅O₁₅ photocatalysts with wide bandgaps show activities for CO₂ reduction to form CO and HCOOH in an aqueous medium without any sacrificial reagents.⁷⁾ O₂ evolved with a stoichiometric amount indicating that water reacts as an electron donor indicating that an uphill reaction of CO₂ reduction accompanied with water oxidation was achieved. CuGaS₂-RGO/BiVO₄ of a Z-scheme photocatalyst system is active for water splitting and CO₂ reduction to CO under visible light irradiation without any sacrificial reagents. This is the first time to demonstrate CO₂ reduction using water as an electron donor in a powdered photocatalyst system with visible light response.⁸⁾

References

- 1) A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, **2009**, 38, 253.
- 2) R. Asai, H. Nemoto, Q. Jia, K. Saito, A. Iwase, A. Kudo, *Chem. Commun.* **2014**, 50, 2543.
- 3) Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. Sharp, A. Kudo, T. Yamada, and K. Domen, *Nature Mater.*, **2016**, 15, 611.
- 4) K. Iwashina, A. Iwase, Y. Hau Ng, R. Amal, A. Kudo, *J. Am. Chem. Soc.*, **2015**, 137, 604.
- 5) T. Kato, Y. Hakari, S. Ikeda, Q. Jia, A. Iwase, A. Kudo, *J. Phys. Chem. Lett.*, **2015**, 6, 1042.
- 6) Q. Jia, K. Iwashina, A. Kudo, *Proc. Natl. Acad. Sci. USA*, **2012**, 109, 11564.
- 7) K. Iizuka, T. Wato, Y. Miseki, K. Saito, and A. Kudo, *J. Am. Chem. Soc.*, **2011**, 133, 20863.
- 8) A. Iwase, S. Yoshino, T. Takayama, Y. H. Ng, R. Amal, A. Kudo, *J. Am. Chem. Soc.*, **2016**, 138, 10260.

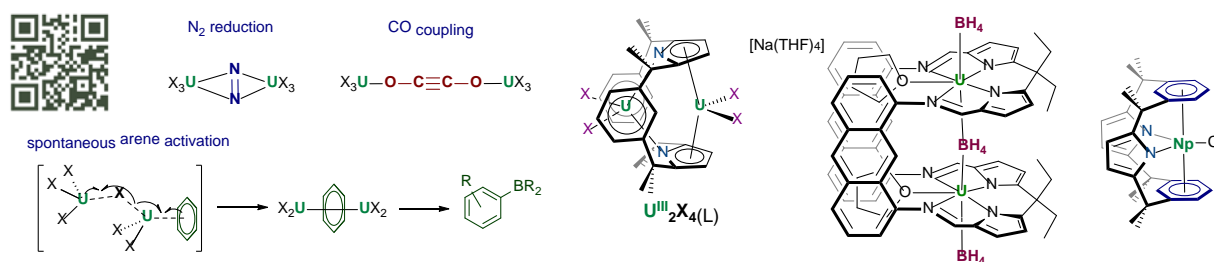
Architectural control of f-block organometallics for small molecule activation

Marketa Suvova,^a Nicola L. Bell^a Charlotte J. Stevens,^a Michal Dutkiewicz,^a Joy H. Farnaby,^a Jason B. Love,^a Roberto Caciuffo,^b Christos Apostolidis,^b Olaf Walter,^b Nikolas Kaltsoyannis,^c Michael G. Gardiner,^d Simon Parsons,^a & Polly L Arnold^{*a}

EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, The King's Buildings, Edinburgh, EH9 3JJ, UK. Polly.Arnold@ed.ac.uk. b. European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany. c. Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. d. School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Australia.

The activation of small, traditionally inert molecules by metal complexes contributes to our fundamental understanding of metal-ligand bonding and can open up new areas of catalysis. We will present new uranium complexes with simple, bulky ligands that enable the binding and reductive activation of small molecules such as N₂, and can promote C-O cleavage and C-C and C-B bond formation in carbon oxides and aromatic hydrocarbons. We will discuss new results arising from using larger, constraining ligands to preorganise and control these multi-electron reactions.

Arguably more importantly, the study of interactions of f-block cations with softer ligands provides important contributions to the understanding of covalency in f-element ligand bonding that is needed for nuclear waste handling. Time allowing, the electronic structure and magnetic behaviours of sets of new electron-rich, organometallic samarium, uranium and neptunium complexes will be compared.



Selected references

1. M. S. Dutkiewicz, J. H. Farnaby, C. Apostolidis, E. Colineau, O. Walter, N. Magnani, M. G. Gardiner, J. B. Love, N. Kaltsoyannis, R. Caciuffo, P. L. Arnold *Nature Chem.* **2016**, *8*, 797.
2. P. L. Arnold, A. Prescimone, J. H. Farnaby, S. M. Mansell, S. Parsons, N. Kaltsoyannis, *Angew. Chem. Int. Ed.* **2015**, *54*, 6735
3. P. L. Arnold, C. J. Stevens, J. H. Farnaby, M. G. Gardiner, G. S. Nichol, J. B. Love, *J. Am. Chem. Soc.* **2014**, *136*, 10218.
4. P. L. Arnold, J. H. Farnaby, R. C. White, N. Kaltsoyannis, M. G. Gardiner, J. B. Love, *Chem. Sci.* **2014**, *5*, 756;
5. P. L. Arnold, S. M. Mansell, D. McKay, and L. Maron, *Nature Chem.*, **2012**, *4*, 668.
6. S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* **2011**, *133*, 9036.

Polyaromatic Micelles as New Supramolecular Capsules

Michito Yoshizawa

Laboratory for Chemistry and Life Science

Chemistry and Life Science Laboratory

Tokyo Institute of Technology

E-mail: yoshizawa.m.ac@m.titech.ac.jp

Micelles are spherical assemblies of linear amphiphilic molecules and one of the oldest classes of supramolecules bearing wide-ranging applications. We have recently developed new amphiphilic molecules with a bent polyaromatic framework and two hydrophilic pendants.^[1] In water, the bent amphiphiles spontaneously and quantitatively assemble into spherical micelles providing polyaromatic shells through effective aromatic-aromatic interactions and hydrophobic effects. Here we report the utility of the polyaromatic micelles as new supramolecular capsules for encapsulating nanocarbons (e.g., fullerene C₆₀ and carbon nanotube) and metal-complexes (e.g., metallo-phthalocyanines and porphyrins) in water.^[2,3]

References

- [1] a) K. Kondo, A. Suzuki, M. Akita, M. Yoshizawa, *Angew. Chem. Int. Ed.*, **2013**, 52, 2308–2312; b) Y. Okazawa, K. Kondo, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.*, **2015**, 137, 98–101; c) Y. Okazawa, K. Kondo, M. Akita, M. Yoshizawa, *Chem. Sci.*, **2015**, 6, 5059–5062.
- [2] K. Kondo, M. Akita, T. Nakagawa, Y. Matsuo, M. Yoshizawa, *Chem. Eur. J.*, **2015**, 21, 12741–12746.
- [3] a) K. Kondo, M. Akita, M. Yoshizawa, *Chem. Eur. J.*, **2016**, 21, 1937–1940; b) T. Omagari, A. Suzuki, M. Akita, M. Yoshizawa, *J. Am. Chem. Soc.*, **2016**, 138, 499–502.

Chemistry of Sandwich Clusters

Tetsuro MURAHASHI

*Department of Chemical Science and Engineering, School of Materials and Chemical Technology,
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, JAPAN*

The sandwich structure is one of the fundamental structural motifs for transition metal complexes. Most of sandwich complexes contain a mononuclear metal moiety between parallel cyclic unsaturated hydrocarbon ligands. On the other hand, it had been difficult to synthesize stable sandwich complexes in which a metal assembly is sandwiched between two parallel unsaturated hydrocarbons. Our group discovered that multinuclear sandwich complexes exist as isolable molecules (Figure 1).^{1,2} It has been shown that a wide range of $p\pi$ -conjugated unsaturated hydrocarbons, such as linear π -conjugated polyenes, monocyclic aromatic hydrocarbons, and polycyclic arenes form multinuclear sandwich complexes. Several unique chemical properties of multinuclear sandwich complexes stemming from the (π -conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures have been elucidated.

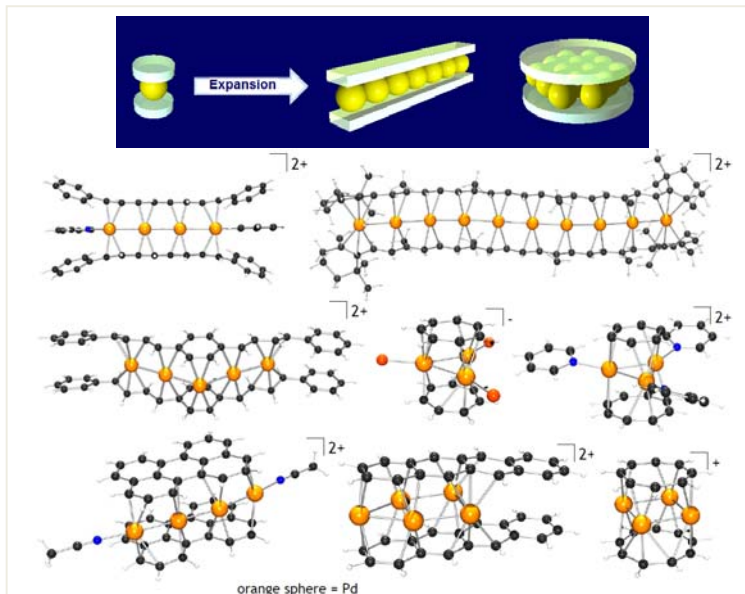


Figure 1. The concept and some examples of dimensionally extended sandwich complexes.

In this presentation, recent development

in the chemistry of multinuclear sandwich complexes will be overviewed; e.g., tailor-made construction of metal assembly in organometallic sandwich framework,^{3,5,6} and elucidation of unique dynamic structural changes induced by redox reactions.⁴

1. T. Murahashi, E. Mochizuki, Y. Kai, H. Kurosawa, *J. Am. Chem. Soc.* **1999**, 121, 10660.
2. T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki, H. Kurosawa, *Science*, **2006**, 313, 1104.
3. T. Murahashi, R. Inoue, K. Usui, S. Ogoshi, *J. Am. Chem. Soc.* **2009**, 131, 9888.
4. T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi, H. Kurosawa, *Nature Chem.* **2012**, 4, 52.
5. S. Horiuchi, Y. Tachibana, M. Yamashita, K. Yamamoto, K. Masai, K. Takase, T. Matsutani, S. Kawamata, Y. Kurashige, T. Yanai, T. Murahashi, *Nature Commun.* **2015**, 6, 6742.
6. Y. Ishikawa, S. Kimura, K. Takase, K. Yamamoto, Y. Kurashige, T. Yanai, T. Murahashi, *Angew. Chem. Int. Ed.* **2015**, 54, 2482.