

INORGANIC CHEMISTRY

Annual Research Highlights

(1) “Photo- and electro-functions of surface-attached molecular wires”

We have developed a new bottom-up method to prepare metal complex oligomer wires utilizing stepwise coordination reactions of metal ions and bridging ligands on the ligand-attached electrode surface. This method has an advantage to prepare a given number of different kinds of metal complex units on the surface. Using this method, we have fabricated redox molecule-terminated molecular wires with different lengths and analyzed their long-range electron transport abilities. We found that π -conjugated redox metal complex oligomer wires exhibit superior electron transport abilities (Fig. 1).

By connecting photosystem I (PSI) of cyanobacteria, with molecular wires by the reconstruction method followed by attaching to the electrode, we fabricated bio-conjugated photon sensor.

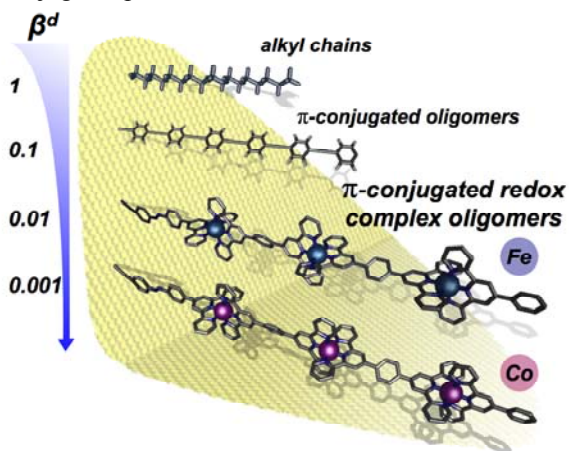


Fig. 1. Long-range electron transport abilities of π -conjugated redox metal complex molecular wires in comparison with other wires.

- 1.(1)-11) *Chem. Asian J.*, **4**, 1361-1367 (2009).
 1.(1)-2) *J. Naosci. Nanotech.*, **9**, 1722-1726 (2009)
 1.(1)-6) *Angew. Chem. Int. Ed.*, **48**, 1585-1587 (2009).

(2) “New structures and unique properties of metalladithiolenes”

A new and convenient method to synthesize group 9 metalladithiolene triangular trinuclear complexes using benzenehexathiol was developed. By comparing the molecular structures and physical properties of Co, Rh and Ir complexes, the degree of conjugation among the three metal centers was clarified. Reaction of rhodadithiolene dinuclear complex with molybdenum carbonyl afforded a new cage-type Rh_4Mo_2 complex (Fig. 2). A Rh_2Mo complex underwent one-step $2e^-$ reduction in contrast to the analogous Co_2Mo complex causing two-step $1e^-$ reduction. This unique reaction was interpreted as intramolecular ECE reaction (Fig. 3).

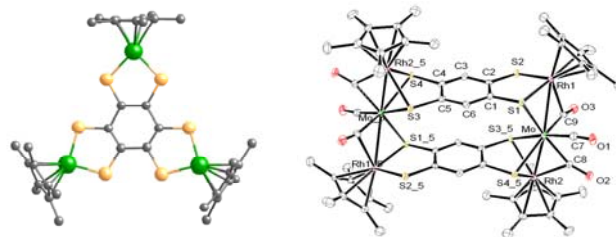


Fig. 2. Molecular structures of triangular Ir_3 and cage-type Rh_4Mo_2 metalladithiolene clusters determined by single-crystal X-ray diffraction analysis.

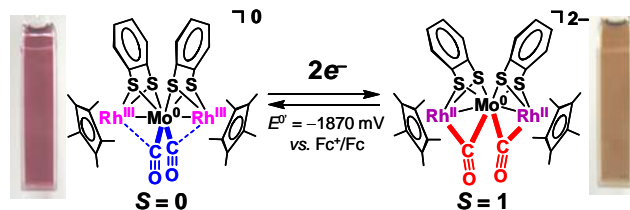


Fig. 3. One-step two-electron redox reaction of a Rh_2Mo metalladithiolene cluster.

- 1.(1)-4) *J. Am. Chem. Soc.*, **131**, 1388-1389 (2009).
 1.(1)-7) *Dalton Trans.*, 1939-1943 (2009).
 1.(1)-10) *Angew. Chem. Int. Ed.*, **48**, 3858-3861 (2009).

(3) “New metal complexes responding to external stimuli”

A new Fe(II) complex showing photo-magnetic effect, a Pt(II) complex with tristability controlled by three different wavelength lights, a pyrylium complex with strong intramolecular donor-acceptor interaction which can be switched with alcohol and acid, and copper complexes containing 4-methyl-2-pyridylpyrimidine ligand of which ring inversion changes the Cu(II)/Cu(I) redox potential were developed.

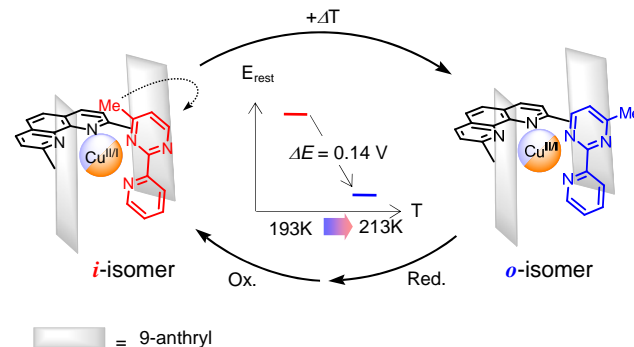


Fig. 4. A Cu(I) complex exhibiting the correlation of redox potentials with coordinating pyrimidine ring inversion.

- 1.(1)-1) *Dalton Trans.* 280-284 (2009).
 1.(1)-3) *Chem. Eur. J.* **15**, 1429-1439 (2009).
 1.(1)-8) *Chem. Commun.*, 1993-1995 (2009).
 1.(1)-9) *J. Am. Chem. Soc.*, **131**, 3830-3831 (2009).
 1.(1)-12) *J. Am. Chem. Soc.*, **131**, 12112-12124 (2009).
 1.(1)-13) *J. Am. Chem. Soc.*, **131**, 14198-14199 (2009).

研究ハイライト

(1) 電極表面に固定した分子ワイヤの光・電子機能

電極表面に配位子を有する自己集合単分子膜を形成し、その上に金属イオン、架橋配位子を交互に結合させることにより、任意の金属イオンと配位子の並び方と数と物理構造を制御した分子ワイヤが構築できる。今回、この方法で作製した π 共役レドックス錯体分子ワイヤが極めて高い長距離電子輸送能を持つことを明らかにした (図1)。

生体コンポーネントである藍色細菌のフォトシステム I (PSI) を再構成法により分子ワイヤと連結し、電極に固定する方法を用いて、フォトセンサーの作製に成功した。

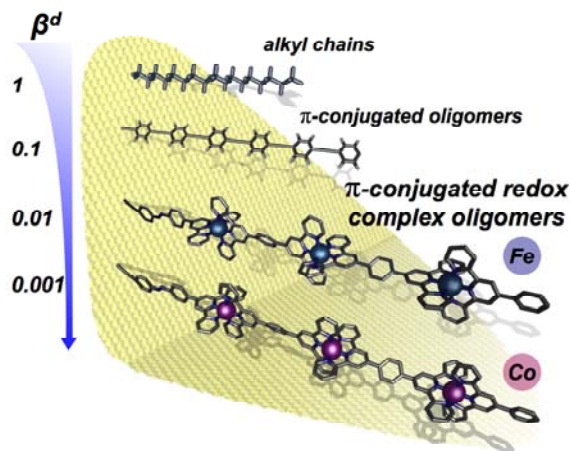


図1. π 共役レドックス錯体分子ワイヤの長距離電子輸送能の他の分子ワイヤとの比較。

- 1.(1)-11) *Chem. Asian J.*, **4**, 1361-1367 (2009).
- 1.(1)-2) *J. Naosci. Nanotech.*, **9**, 1722-1726 (2009)
- 1.(1)-6) *Angew. Chem. Int. Ed.*, **48**, 1585-1587 (2009).

(2) メタラジチオレンの新構造創製と新物性発現

9族元素のメタラジチオレンの環状三核錯体のベンゼンヘキサチオールを用いる汎用合成法を確立し、合成した新規錯体の結晶構造と電子・光・レドックス特性の金属元素依存性を明らかにした。またロダジチオレン複核錯体とモリブデンカルボニル錯体の反応により Rh_4Mo_2 の6核かご型錯体を新規合成した (図2)。また Rh_2Mo 3核錯体がすでに報告した同形の Co_2Mo 錯体と異なり、1段階2電子移動を起こすことを見出し、その反応機構の解明を行い、分子内ECE機構であることを明らかにした (図3)。またTEMPOラジカルを結合したジチオラト配位子の白金への配位による SOMO-HOMO 逆転現象を見出した。

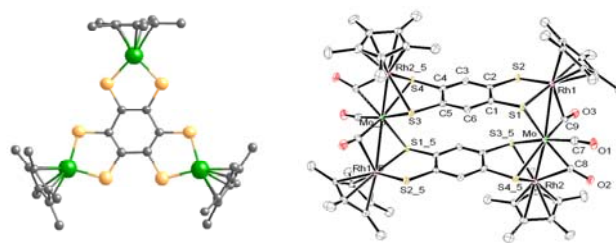


図2. X線構造解析による Ir_3 三角形および Rh_4Mo_2 かご型メタラジチオレン錯体の分子構造。

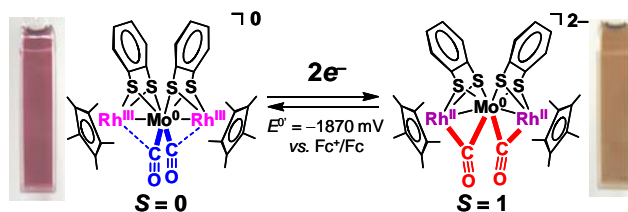


図3. Rh_2Mo クラスタ錯体の1段階2電子移動。

- 1.(1)-4) *J. Am. Chem. Soc.*, **131**, 1388-1389 (2009).
- 1.(1)-7) *Dalton Trans.*, 1939-1943 (2009).
- 1.(1)-10) *Angew. Chem. Int. Ed.*, **48**, 3858-3861 (2009).

(3) 外場応答性錯体の創製

光で磁性が変化する鉄(II)錯体、異なる3波長の光で3状態間を可逆的に変換するアズベンゼン共役白金錯体、アルコールと酸で可逆的に構造変換するドナーアクセプター(ピリリウム)共役錯体、ならびに熱によるピリミジン環反転に伴いレドックス電位が可逆に変化する4-メチル-2-ピリジルピリミジン銅(I)錯体を創製した。

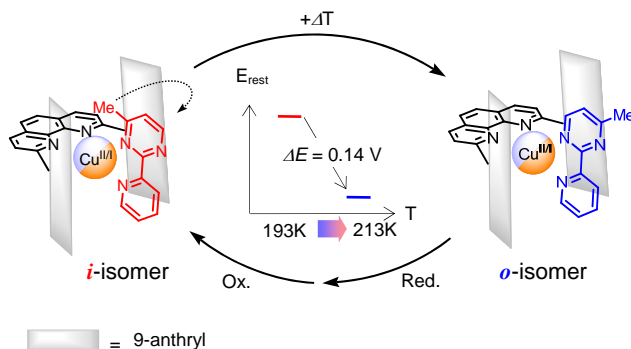


図4. ピリミジン環反転とレドックス電位が連動する銅(I)錯体

- 1.(1)-1) *Dalton Trans.* 280-284 (2009).
- 1.(1)-3) *Chem. Eur. J.* **15**, 1429-1439 (2009).
- 1.(1)-8) *Chem. Commun.*, 1993-1995 (2009).
- 1.(1)-9) *J. Am. Chem. Soc.*, **131**, 3830-3831 (2009).
- 1.(1)-12) *J. Am. Chem. Soc.*, **131**, 12112-12124 (2009).
- 1.(1)-13) *J. Am. Chem. Soc.*, **131**, 14198-14199 (2009).

1. 原著論文

(1) Refereed Journals

- 1) Y. Hasegawa, S. Kume, and H. Nishihara, "Reversible Light-induced Magnetization Change in an Azobenzene-attached Pyridylbenzimidazole Complex of Iron(II) at Room Temperature", *Dalton Trans.* 280-284 (2009).
- 2) M. Miyachi, Y. Yamanoi, T. Yonezawa, H. Nishihara, M. Iwai, M. Konno, M. Iwai, and Y. Inoue, "Surface immobilization of PSI using vitamin K₁-like molecular wires for fabrication of a bio-photoelectrode", *J. Naosci. Nanotech.*, **9**, 1722-1726 (2009).
- 3) R. Sakamoto, S. Kume, M. Sugimoto, and H. Nishihara, "Trans-Cis Photoisomerization of Azobenzene-Conjugated Dithiolato-Bipyridine-Pt(II) Complexes: Extension of Photoresponse to Longer Wavelengths and Photo-Controllable Tristability", *Chem. Eur. J.*, **15**, 1429-1439 (2009).
- 4) S. Muratsugu, K. Sodeyama, F. Kitamura, M. Sugimoto, S. Tsuneyuki, S. Miyashita, T. Kato, and H. Nishihara, "Two-electron Reduction of a Rh-Mo-Rh Dithiolato Complex to Form a Triplet Ground State Associated with a Change in CO Coordination Mode", *J. Am. Chem. Soc.*, **131**, 1388-1389 (2009).
- 5) S. I. Allakhverdiev, V. D. Kreslavski, V. Thavasi, S. K. Zharmukhamedov, V. V. Klimov, T. Nagata, H. Nishihara, and S. Ramakrishna, "Hydrogen photoproduction by use of photosynthetic organisms and biomimetic systems", *Photochem. Photobiol. Sci.*, **8**, 148-156 (2009).
- 6) N. Terasaki, N. Yamamoto, T. Hiraga, Y. Yamanoi, T. Yonezawa, H. Nishihara, T. Ohmori, M. Sakai, M. Fujii, A. Tohri, M. Iwai, Y. Inoue, S. Yoneyama, M. Minakata, I. Enami, "Plugging a Molecular Wire into Photosystem I: Reconstitution of the Photoelectric Conversion System on a Gold Electrode", *Angew. Chem. Int. Ed.*, **48**, 1585-1587 (2009).
- 7) Y. Shibata, B.H. Zhu, S. Kume, and H. Nishihara, "Development of a versatile synthesis method for trinuclear Co(III), Rh(III), and Ir(III) dithiolene complexes, and their crystal structures and multi-step redox properties", *Dalton Trans.*, 1939-1943 (2009).
- 8) M. Kondo, M. Uchikawa, S. Kume, and H. Nishihara, "Alcohol- and acid-causing reversible switching of near-infrared absorption and luminescence in a donor-acceptor conjugated system", *Chem. Commun.*, 1993-1995 (2009).
- 9) K. Nomoto, S. Kume, and H. Nishihara, "A Single Molecular System Gating Electron Transfer by Ring Inversion of a Methylpyridylpyrimidine Ligand on Copper", *J. Am. Chem. Soc.*, **131**, 3830-3831 (2009).
- 10) B.-H. Zhu, Y. Shibata, S. Muratsugu, Y. Yamanoi, and H. Nishihara, "A Cyclic Hexanuclear Heterometalladithiolene Cluster [$\{(\text{Cp}^*\text{Rh})_2\text{Mo}(\mu\text{-CO})_2(\text{CO})\}_2(\text{S}_2\text{C}_6\text{H}_2\text{S}_2)_2$] with Two π -Conjugated $\text{S}_2\text{C}_6\text{S}_2$ Bridges: Synthesis, Crystal Structure, and Properties", *Angew. Chem. Int. Ed.*, **48**, 3858-3861 (2009).
- 11) Y. Nishimori, K. Kanaizuka, T. Kurita, T. Nagatsu, Y. Segawa, F. Toshimitsu, S. Muratsugu, M. Utsuno, S. Kume, M. Murata, and H. Nishihara, "Superior Electron-Transport Ability of π -Conjugated Redox Molecular Wires Prepared by the Stepwise Coordination Method on a Surface", *Chem. Asian J.*, **4**, 1361-1367 (2009).
- 12) M. Kondo, M. Uchikawa, K. Namiki, W.-W. Zhang, S. Kume, E. Nishibori, H. Suwa, S. Aoyagi, M. Sakata, M. Murata, Y. Kobayashi, and H. Nishihara, "Counterion-Dependent Valence Tautomerization of Ferrocenyl-Conjugated Pyrylium Salts", *J. Am. Chem. Soc.*, **131**, 12112-12124 (2009).
- 13) S. Kume, K. Nomoto, T. Kusamoto, and H. Nishihara, "Intramolecular Electron Arrangement with a Rotative Trigger", *J. Am. Chem. Soc.*, **131**, 14198-14199 (2009).

2. 総説・解説

- 1) 山野井慶徳、西原 寛：「ヒドロシラン類をケイ素導入源とした芳香族ケイ素化合物の新規合成法」, 有機合成化学協会誌, **67**, 778-786 (2009).

- 2) 西原 寛：「メタラジチオレン錯体の多核化と多重機能化」, *Organometallic News* 146-151 (2009).
- 3) 雨宮健太, 近藤寛, 太田俊明：「軟 X 線エネルギー分散型表面 XAFS 法による表面化学反応の時分割追跡」, *表面科学*, **25**, 345-350 (2005).

K. Amemiya, H. Kondoh, T. Ohta, "Time resolved trace of surface reaction by soft x-ray energy dispersive surface XAFS method", *Surface Science*, **25**, 345-350 (2005).

3. 著書

- 1) K. Kanaizuka and H. Nishihara: "Bottom-Up Fabrication of Redox-Containing Metal Complex Polymers on an Electrode Surface" in "Bottom-Up Nanofabrication", edited by H. S. Nalwa and K. Ariga, (Amer. Sci. Pub., 2009), pp. 429-445.
- 2) 西原 寛, 高木 繁, 森山広思：「レイナーキャナム無機化学」(東京化学同人, 2009).
- 3) 西原 寛, 荒牧国次：「腐食と防食」 in 「第3版 現代界面コロイド化学の基礎 原理・応用・測定ソリューション」(丸善, 2009), pp. 207-210.
- 4) 西原 寛,：「化学のいま」 in 「東大式現代科学用語ナビ キーワードでわかるサイエンスの「いま」」(化学同人, 2009), pp. 46-49.
- 5) 西森慶彦, 西原 寛：「錯体多次元集合界面」 in 「配位空間の化学 - 最新技術と応用 - 」(シーエムシー出版, 2009), pp. 223-231.

4. その他

- 1) H. Nishihara, "Report on the 5th Japan-US conference, PRiME2008", *Electrochemistry*, **77**, 85-86 (2009).
- 2) H. Nishihara, "Female researchers relay essay. Male teachers and "Men and Women cooperative participation". *Electrochemistry*, **77**, 1053-1054 (2009).
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- 5) H. Nishihara, T. Yonezawa, Y. Shishino, S. Suzuki, K. Hase, "Method for manufacture of plastic optical products containing uniformly dispersed metal compound refractive index controllers independently of monomer types", Jpn. Kokai Tokkyo Koho (2009), 11pp., JP2009221255.
- 6) H. Nishihara, T. Yonezawa, Y. Yamanoi, Y. Yamamoto, Y. Kobori, S. Oshima, Y. Kobayashi, S. Maekawa, "Hydrogen storage material containing palladium and organic compounds", PCT Int. Appl. (2009), 32pp., WO2009154200.