

INORGANIC CHEMISTRY

Annual Research Highlights

(1) "Electronic properties of surface-attached molecular wires"

Surface junction effects on the electron conduction of *p*-phenylene-bridged bis(terpyridine)iron oligomers terminated with a ferrocene moiety were quantitatively analyzed by employing three different surface-anchoring terpyridine ligands. The dependence of the electron-transfer rate constant for oxidation of the terminal ferrocene moiety, k_{et} , on the distance between the electrode surface and the ferrocene moiety, x , showed that the attenuation factor, β_d , which indicates the degree of reduction of k_{ct} with x , was 0.018 in all cases. However, the absolute k_{et} value depended strongly on both electronic and steric factors of the surface-anchoring ligand.

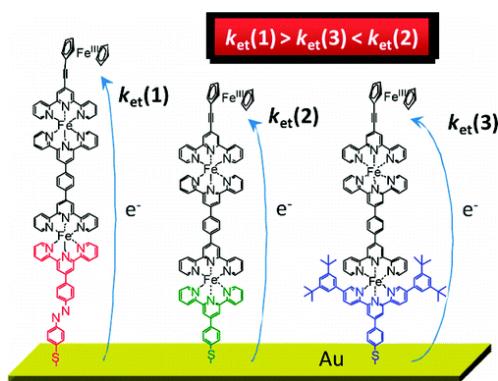


Fig. 1. Molecular wire prepared by stepwise complexation between iron ion and terpyridine moiety.

1.(1)-8) *J. Am. Chem. Soc.*, **132**, 4524-4525 (2010).

(2) "Photosensing system composed of photosystem I, molecular wire, gold nanoparticle and electrode"

We have developed a system that mimics photosynthesis and harnesses the flow of electrons to produce a voltage change on gold electrode. The device is potentially sensitive enough to detect even a single photon, making it useful as a light sensor.

Photosystem I is a complex assembly of molecules having pockets in which molecules of vitamin K₁ can sit. We prepared 2 nm sized gold nanoparticles and attached molecules similar to vitamin K₁ to their surface. They then anchored the gold particles to a gold wafer measuring about 17 μm on each side, and finally added photosystem I without vitamin K₁. The gold nanoparticles bearing the vitamin K₁ mimic reconstituted into the vacant pockets in the photosystem I, forming an electrical connection between the complex and the gold wafer. When the system was immersed in a solution of sodium ascorbate as a source of electrons, the voltage at the wafer

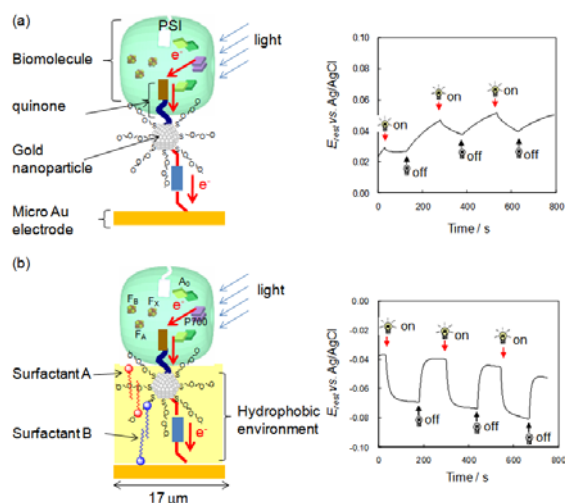


Fig. 2. Structure of biophotosensor and its photocurrent changes. (a) In the absence of surfactant. (b) In the presence of surfactant.

jumped by ca. 200 mV under the irradiation of red light.

The addition of two surfactants to the system significantly improved the response, causing a faster and larger change in voltage. We concluded that the hydrophobic moiety of the surfactants around the gold nanoparticles helps to repel water molecules that interfere with the charge storage into nanoparticles.

1.(1)-9) *Chem. Commun.*, **46**, 2557-2559 (2010).

(3) "New metal complexes responding to external stimuli"

We developed a new copper(I) complex using 4-methyl-2-pyridyl-pyrimidine and diphosphine as ligands. This complex exhibited geometric bistability based on inversion of the pyrimidine, which led to dual luminescence behavior. The dynamics of inversion were sensitive to temperature and solvent, suggesting that the excitation process could be tuned using the inversion process.

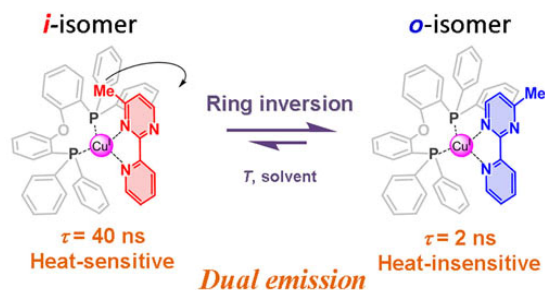


Fig. 3 Conceptual diagram showing the dual luminescence behaviors based on pyrimidine ring inversion

1.(1)-5) *J. Am. Chem. Soc.*, **132**, 9579-9581 (2010).

1.(1)-11) *Chem. Lett.*, **39**, 204-205 (2010).

研究ハイライト

(1) 電極表面に固定した分子ワイヤの電子機能

分子回路設計を目指すには、分子構造体内の電子移動特性と同時に、その信号を取り出すインターフェースとしての接合部位の電子移動効率が重要なファクターとなる。我々は種々の電極接合部位を用いて逐次ボトムアップ法による錯体ワイヤを形成し、それらの電子移動特性の世代依存性から接合部位と分子内の電子の通過過程それぞれの定量評価に成功した (図1)。

図1に示す3種の錯体ワイヤは、電極接合部分に異なる分子を用いているが、それから1世代ずつ伸張させたワイヤ部分の構造は同一である。接合部位にアゾベンゼンを介する場合 (図1左)、強い界面ワイヤの電子カップリングにより長い分子長にもかかわらず最も高い電子注入効率を示す。また、同等の共役系でも立体障害基を導入しワイヤを孤立化させると (図1右)、電子注入効率は増大し、基板固定部への電解質のアプローチが電荷注入効率に大きく影響することがわかった。

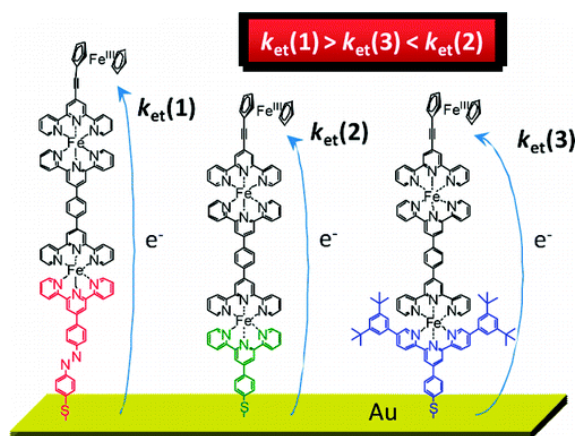


図1 テルピリジン基を逐次積層させた分子ワイヤ

1.(1)-8) *J. Am. Chem. Soc.* **2010**, *132*, 4524-4525.

(2) 生体分子とナノ粒子を接続した高感度光センサー

100%の光電変換効率を持つ光合成ユニットを利用して、人工材料と組み合わせた新たな光電変換システムの構築を行った。具体的には好熱性藍色細菌から光化学系I (PSI) を抽出し、電子伝達部位として機能しているビタミン K₁を人工キノン型分子ワイヤで置換し、そのワイヤを電極基板に接合した系であり、光照射によりPSI内で発生した電子を分子ワイヤを通して電極基板へと導き、外部信号として取り出した。本研究では、2種類の界面活性剤により金

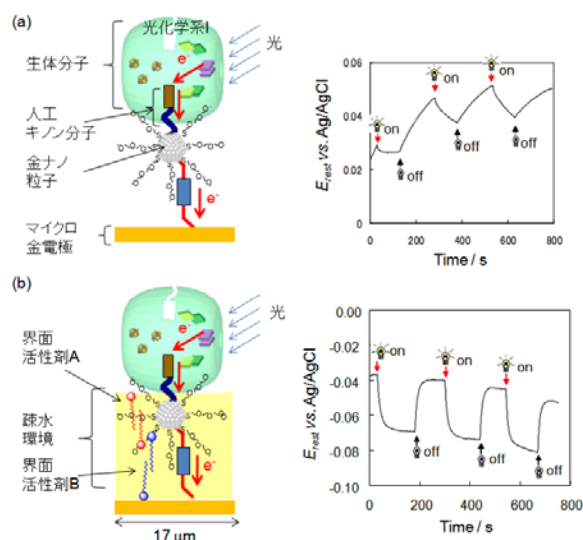


図2. (a) バイオ光センサーの構造と光電流の変化。(b) 界面活性剤添加時の光電流変化

ナノ粒子周囲の疎水性を制御し、生体-人工分子-金ナノ粒子 (直径 1.7 ± 0.1 nm) 連結体に適用することによって、界面活性剤が存在しない場合と比較して (図2(a))、光電変換応答の高速化および高感度化 (SN比の増大) に成功した (図2(b))。本研究で用いた電極は $17 \mu\text{m}$ 平方のマイクロサイズであるが、電極をさらにナノサイズまで小型化することにより、室温で少数フォトンを検出できる系が達成できると期待される。

1.(1)-9) *Chem. Commun.* **2010**, *46*, 2557-2559.

(3) 外場応答性錯体の創製

4-メチル-2-ピリジルピリミジンとジホスフィンを配位子とする新規銅一価錯体を開発した (図3)。この錯体はピリミジンの反転による相安定性に基づく二重発光を示した。反転の動的挙動は温度と溶媒に依存しており、その光励起過程を反転により制御し得ることを明らかとした。



図3. ピリミジン環反転に基づく二重発光

1.(1)-5) *J. Am. Chem. Soc.* **2010**, *132*, 9579-9581.

1.(1)-11) *Chem. Lett.* **2010**, *39*, 204-205.

1. 原著論文

(1) Refereed Journals

- 1) A. Lesbani, H. Kondo, Y. Yabusaki, M. Nakai, Y. Yamanoi, H. Nishihara, "Integrated Palladium-Catalyzed Arylation of Heavier Group 14 Hydrides", *Chem. Eur. J.*, **16**, 13519-13527 (2010).
- 2) A. Lesbani, H. Kondo, J.-i. Sato, Y. Yamanoi, H. Nishihara, "Facile synthesis of hypersilylated aromatic compounds by palladium-mediated arylation reaction", *Chem. Commun.*, **46**, 7784-7786 (2010).
- 3) Y. Shishino, T. Yonezawa, K. Kawai, H. Nishihara, "Molten matrix sputtering synthesis of water-soluble luminescent Au nanoparticles with a large Stokes shift", *Chem. Commun.*, **46**, 7211-7213 (2010).
- 4) K. P. Rao, T. Kusamoto, F. Toshimitsu, K. Inayoshi, S. Kume, R. Sakamoto, H. Nishihara, "Double Protonation of 1,5-Bis(triarylaminoethynyl)anthraquinone To Form a Paramagnetic Pentacyclic Dipyrylium Salt", *J. Am. Chem. Soc.*, **16**, 12472-12479 (2010).
- 5) M. Nishikawa, K. Nomoto, S. Kume, K. Inoue, M. Sakai, M. Fujii, H. Nishihara, "Dual Emission Caused by Ring Inversion Isomerization of a 4-Methyl-2-pyridyl-pyrimidine Copper(I) Complex", *J. Am. Chem. Soc.*, **132**, 9579-9581 (2010).
- 6) Y. Yabusaki, N. Ohshima, T. Kusamoto, H. Kondo, Y. Yamanoi, H. Nishihara, "Versatile Synthesis of Blue Luminescent Siloles and Germales and Hydrogen Bond-Assisted Color Alteration", *Chem. Eur. J.*, **16**, 5581-5585 (2010).
- 7) Y. Ochi, M. Suzuki, T. Imaoka, M. Murata, H. Nishihara, Y. Einaga, K. Yamamoto, "Controlled Storage of Ferrocene Derivatives as Redox-Active Molecules in Dendrimers", *J. Am. Chem. Soc.*, **132**, 5061-5069 (2010).
- 8) T. Kurita, Y. Nishimori, F. Toshimitsu, S. Muratsugu, S. Kume, H. Nishihara, "Surface Junction Effects on the Electron Conduction of Molecular Wires", *J. Am. Chem. Soc.*, **132**, 4524-4525 (2010).
- 9) M. Miyachi, Y. Yamanoi, Y. Shibata, H. Matsumoto, A. Nakazato, M. Konno, K. Ito, Y. Inoue, H. Nishihara, "A Photosensing System Composed of Photosystem I, Molecular Wire, Gold Nanoparticle, and Double Surfactants in Water", *Chem. Commun.*, **46**, 2557-2559 (2010).
- 10) R. Sakamoto, M. Nishikawa, T. Yamamura, S. Kume, H. Nishihara, "A new special pair model comprising meso-di-*p*-anisylaminoporphyrin: enhancement of visible-light absorptivities and quantification of electronic communication in mixed-valent cation radical", *Chem. Commun.*, **46**, 2028-2030 (2010).
- 11) S. Umeki, S. Kume, H. Nishihara, "Acid-Base Responsive Photoelectric Conversion of a Hydroxyazobenzene-appended Bipyridine-Copper Complex System", *Chem. Lett.*, **39**, 204-205 (2010).
- 12) W.-W. Zhang, M. Kondo, T. Fujita, K. Namiki, M. Murata, H. Nishihara, "Thioacetyl-Terminated Ferrocene-Anthraquinone Conjugates: Synthesis, Photo- and Electrochemical Properties Triggered by Protonation-Induced Intramolecular Electron Transfer", *Molecules*, **15**, 150-163 (2010).
- 13) T. Kusamoto, S. Kume, H. Nishihara, "Cyclization of TEMPO Radicals Bound to Metalladithiolene Induced by SOMO-HOMO Energy-Level Conversion", *Angew. Chem. Int. Ed.*, **49**, 529-531 (2010).

2. 総説・解説

- 1) M. Miyachi, H. Nishihara, "Redox and Photo Functions of Metal Complex Oligomer and Polymer Wires on the Electrode Macromolecules Containing metal and Metal-Like Elements", Vol. 10, Wiley, 387-412 (2010).
- 2) R. Sakamoto, H. Nishihara "π-Conjugated photochromic molecular systems exhibiting multiple functionalities" in *Molecular Electronic and Related Materials- Control and Probe with Light*, Trans-World Research Network, India, Chapter 11, 223-242 (2010).

3. 著書

- 1) 坂本良太、西原 寛, "電気化学"、第4章, 金属錯体の機器分析、三共出版、2010.

4. その他

- 1) 西原 寛, いよいよ国際化学オリンピック (ICHO) 日本大会, 化学と教育, **58**, 103 (2010).