

INORGANIC CHEMISTRY

Annual Research Review

(1) “Synthesis and multi-dimensional physical properties of photochromic metal complexes”

New photochromic complexes comprising transition metal complex moieties with unique electronic and optic properties and azobenzene moieties with photoisomerization properties were synthesized and their physical properties and functions were investigated. We have found several new phenomena that had not been observed for regular organic azobenzenes. For example, 3-ferrocenylazobenzene undergoes reversible trans-cis photoisomerization with a single green light source and redox change between Fe^{II} and Fe^{III} (Fig. 1). This new phenomenon is realized by the trans-to-cis isomerization caused by MLCT (from Fe d to azobenzene π^* orbital) band irradiation with green light when the ferrocene moiety is in the reduced form (Fe^{II}) and by the cis-to-trans isomerization caused by azobenzene $n-\pi^*$ band irradiation with green light when the ferrocene moiety is oxidized (Fe^{III}) and the MLCT band diminishes.

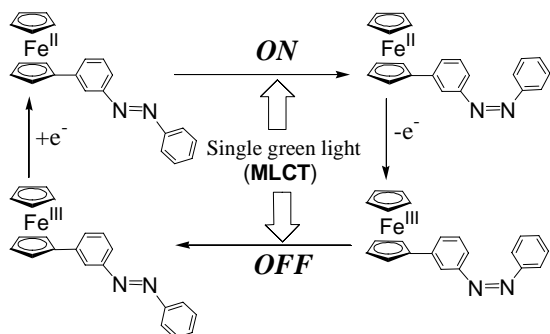


Fig. 1. Reversible trans-cis isomerization of 3-ferrocenylazobenzene with a single green light source and the redox change.

$\text{Pt}(\text{II})$ complexes with a terpyridylazobenzene ligand (tpyAB), $\text{PtL}(\text{tpyAB})\cdot n\text{A}^-$ ($\text{L} = \text{Cl}$, pyridine) undergo reversible trans-cis photoisomerization and their luminescence properties are changed markedly by the isomerization; no emission is observed in the trans form, but significant emission occurs in the cis form. Accordingly, they promise to be doubly photo-functional materials, showing complete off-on switching of emission linked to trans-cis conformation change.

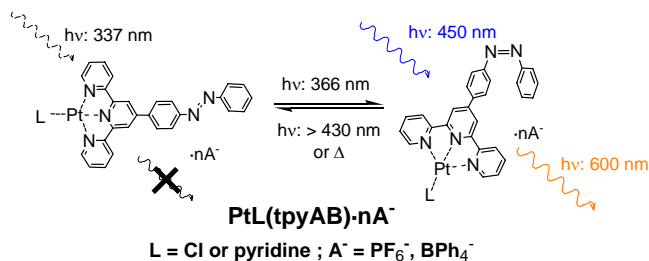


Fig. 2. Photochemical control of photoluminescence properties of azobenzene-bound Pt terpyridine complexes.

- A-2) *Coord. Chem. Rev.*, **226**, 125-135 (2002)
- A-7) *Macromol. Symp*, **186**, 93-98 (2002)
- A-9) *J. Kor. Electrochem. Soc.*, **5**, 189-191 (2002)
- A-10) *Inorg. Chem.*, **41**, 7143-7150 (2002)
- B-1) Shokubai, **44**, 328-333 (2002)

(2) “Synthesis and electrochemical deposition of metal nanoparticles”

Synthesis of new metal nanoparticles and their assembly on the solid surface were investigated. Palladium nanoparticles protected by alkyl thiolates with a core diameter 1.3-3.9 nm were synthesized by the treatment of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with tetraalkylammonium bromide and LiBET_3H in THF, followed by the addition of alkanethiols. The factors to control the mean size and its deviation were clarified. We have also demonstrated that a combination of electro-oxidative deposition of palladium nanoparticles attached with bifero-cene-terminated thiolates and that of gold nanoparticles with same thiolates forms a thin redox-active composite film with a layered hybrid structure.

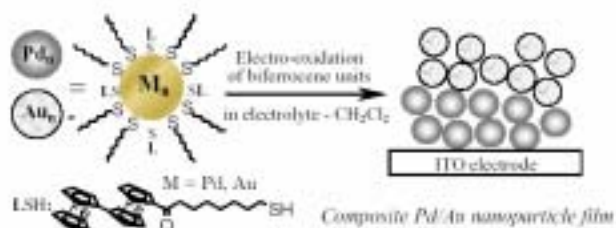


Fig. 3. Electrochemical construction of an alternating multi-layered structure of palladium and gold nanoparticles attached with bifero-cene moieties

- A-1) *Langmuir*, **18**, 1413-1418 (2002)
- A-8) *Chem. Commun.*, **2002**, 2578-2579
- B-3) *Adv. Inorg. Chem.*, **53**, 41-86 (2002)

研究レビュー

(1) フォトクロミック金属錯体の合成と多元物性

電子、光物性に特徴をもつ金属錯体と光異性化による大きな構造変化を示すアゾベンゼンを連結した種々のフォトクロミック金属錯体を合成し、両者の物性、機能の複合化について検討した。その結果、有機アゾベンゼン類では見出されていなかった新しい現象を見出した。例えば、3-フェロセニルアゾベンゼンでは、フェロセンの酸化還元特性および鉄 d 軌道からアゾベンゼンπ*軌道への可視光吸収をアゾベンゼンの異性化と組み合わせることによって、単一緑色光での可逆な *tans*-*cis* 異性化を実現した(図1)。すなわち、フェロセン部位が Fe^{II} の還元状態では、緑色光による MLCT 励起によって *tans*-to-*cis* の異性化が起こり、その後フェロセンを酸化してフェロセニウム(Fe^{III})にすると、MLCT 吸収が消滅し、緑色光ではアゾベンゼン部位の n-π* バンドを励起することから *cis*-to-*tans* の異性化が進行する。

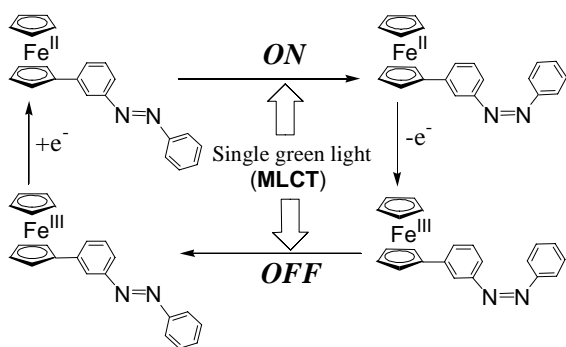


図1 3-フェロセニルアゾベンゼンにおける、単一緑色光とレドックスの組合せによる可逆異性化

また、発光特性をしめす白金テルピリジン錯体とアゾベンゼンを結合した錯体に、PtL(tpyAB)•nA (L = Cl, pyridine)においては、アゾ基が *trans* 体時には発光がクエンチされるが、*cis* 体ときには600nmの発光を示すことを見出し、光入力(アゾ基の光異性化)によって、光出力を制御できる新しい分子系であることを示した(図2)。

その他の研究結果も合わせて、フォトクロミック錯体の多重物性・機能分子としての有用性を示した。

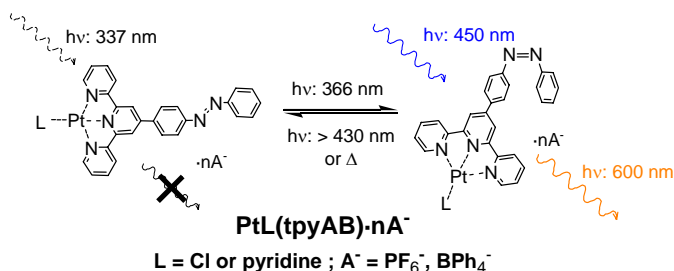


図2 アゾベンゼン共役白金テルピリジン錯体における発光特性の光制御

- A-2) *Coord. Chem. Rev.*, **226**, 125-135 (2002)
- A-7) *Macromol. Symp.*, **186**, 93-98 (2002)
- A-9) *J. Kor. Electrochem. Soc.*, **5**, 189-191 (2002)
- A-10) *Inorg. Chem.*, **41**, 7143-7150 (2002)
- B-1) *触媒*, **44**, 328-333 (2002)

(2) 金属ナノ粒子の合成と電析配列

様々な特異な物理的、化学的性質を示し、次世代のナノ素材として期待されている金属ナノ粒子についてその合成と界面配列について検討した。パラジウムナノ粒子については有機溶媒単一相 super hydride を用いる還元による、単分散粒径のアルカンオール修飾 Pd ナノ粒子の合成法を開発した。また、ピフェロセンのチオール誘導体を修飾した金およびパラジウムのナノ粒子の電気化学的界面凝集を組み合わせた交互積層法により、ヘテロ金属ナノ粒子多重積層膜の作製に成功した(図3)。このヘテロ積層膜では、電子移動の方向制御が行えることを示した。

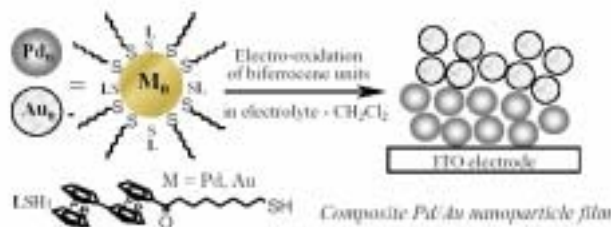


図3 金ナノ粒子とパラジウムナノ粒子の電気化学的界面凝集を利用した交互積層膜の作製

- A-1) *Langmuir*, **18**, 1413-1418 (2002)
- A-8) *Chem. Commun.*, **2002**, 2578-2579
- B-3) *Adv. Inorg. Chem.*, **53**, 41-86 (2002)

A. Original Papers

- 1) I. Quiros, M. Yamada, K. Kubo, J. Mizutani, M. Kurihara, and H. Nishihara: "Preparation of Alkyl Thiolate-Protected Palladium Nanoparticles and Their Size Dependence on Synthetic Conditions", *Langmuir*, **18**, 1413-1418 (2002).
- 2) M. Kurihara and H. Nishihara, "Azo- and quinone-conjugated redox complexes — photo- and proton-coupled intramolecular reactions based on d- π interaction", *Coord. Chem. Rev.*, **226**, 125-135 (2002).
- 3) H. Nishihara, M. Murata, K. Kojima, T. Fijita, K. Kubo, and M. Kurihara: "Synthesis of Ferrocene-Quinone Conjugated Oligomers and Polymers and Their Protonation-Induced Intramolecular Electron- Transfer Reaction", *Polym. Mater. Sci. Eng.*, **2002**, 86 -87.
- 4) (S. Takagi), (T. Sahashi), (K. Sako), K. Mizuno, M. Kurihara, and H. Nishihara: "Synthesis of New Primidine Based Compounds and Their Peculiar Emission Behaviors", *Chem. Lett.*, **2002**, 628-629.
- 5) M. Kurihara, A. Hirooka, S. Kume, (M. Sugimoto), and H. Nishihara: "Redox-conjugated Reversible Isomerization of Ferrocenylazobenzene with a Single Green Light", *J. Am. Chem. Soc.*, **124**, 8800-8801 (2002).
- 6) S. R. Korupolu, (N. Mangayarkarasi), (P. S. Zacharias), J. Mizutani, and H. Nishihara: "Synthesis, Structure and DNA Cleavage Activity of New Trinuclear Zn₃ and Zn₂Cu Complexes of a Chiral Macrocyclic Structural Correlation with the Active Center of P1 nuclease", *Inorg. Chem.*, **41**, 4099-4101 (2002).
- 7) H. Nishihara, M. Nihei, A. Hirooka, and M. Kurihara: "Photo- and Protonation-Induced Changes in Structures and Physical Properties of Azo-Conjugated Metal Complex Systems", *Macromol. Symp*, **186**, 93-98 (2002).
- 8) M. Yamada and H. Nishihara: "Electrochemical construction of an alternating multi-layered structure of palladium and gold nanoparticles attached with biferrocene moieties", *Chem. Commun.*, **2002**, 2578-2579.
- 9) S. Kume, M. Kurihara, and H. Nishihara, "A Large Trans/cis Conversion Ratio in Redox-conjugated Single-light Reversible Isomerization of a Cobalt Complex with meta-Bipyridylazobenzene Ligands", *J. Kor. Electrochem. Soc.*, **5**, 189-191 (2002).
- 10) T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, (N. Tamai), (T. Kawai), (M. Irie), and H. Nishihara, "Photoluminescence Switching of Azobenzene-Conjugated Pt(II) Terpyridine Complexes by Trans-Cis Photoisomerization", *Inorg. Chem.*, **41**, 7143-7150 (2002).
- 11) (Y. Kobayashi), (Y. Yoshida), M. K. Kubo, (Y. Yamada), (A. Yoshida), (H. Ogawa), (H. Ueno), and (K. H. Asahi): "In-beam Mossbauer study of Fe-57 using a secondary Mn-57 beam and ion implantation", *Eur. Phys. J. A*, **13**, 243-246 (2002).
- 12) T. Yonezawa, (S. Onoue), (N. Kimizuka): "Metal Coating of DNA Molecules by Cationic, Metastable Gold Nanoparticles", *Chem. Lett.*, **2002**, 1172-1173.

B. Reviews

- 1) 西原 寛, 村田昌樹: 「フォトクロミック金属錯体」, 触媒, **44**, 328-333 (2002).
H. Nishihara and M. Murata: "Photochromic Metal Complexes", *Shokubai*, **44**, 328-333 (2002).
- 2) 西原 寛: 「五十路を超えたフェロセン化学の新展開」, 化学, **57**, 24-25 (2002).
H. Nishihara: "New development of ferrocene chemistry over 50 years", *Kagaku*, **57**, 24-25 (2002).
- 3) H. Nishihara: "Redox Chemistry and Functionalities of Conjugated Ferrocene Systems", *Adv. Inorg. Chem.*, **53**, 41-86 (2002).

- 4) 米澤 徹：「湿式法による制御された金属ナノ粒子の調製と応用 - 規則配列への展開 - 」，日本化学会，コロイドおよび界面化学部会 ニュースレター，**27**(4), 2-4 (2002).
T. Yonezawa: “Preparation of Metal Nanoparticles with a controlled structure by wet methods and their applications – Development of Ordered Arrangement”, Newsletter; Colloid and Interface Science Division, Chemical Society of Japan, **27**(4), 2-4 (2002).

D. Books

- 1) 米澤 徹：「「自己組織化」で実現する化学分野のナノテクノロジー」，「図解 ナノテク活用技術のすべて」，川合知二監修，工業調査会，東京，pp.211-214，2002年11月
T. Yonezawa: “Nanotechnology in Chemistry – Realized by “Self-Assembly””, “All about Application Engineering of Nanotechnology”, T. Kawai Ed., Kogyochosakai, Tokyo, pp. 211-214 (2002.11).