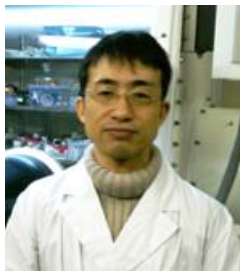


Molecular Design Laboratory



Masakazu Hirotsu (Associate Professor)

- [Current Research Interests](#)
- [Selected Publications](#)

1. Current Research Interests

- (i) Activation of Chemical Bonds by Transition-Metal Complexes ([1](#), [3](#))
- (ii) Metal Complexes Involved in Multi-Step Electron Transfer Reactions in Biological Systems ([2](#), [3](#))
- (iii) Thiophene-Based Functional Materials ([1](#), [2](#))
- (iv) Molecular Switching Materials: Structural, Magnetic, and Catalytic Properties ([5](#))

(1) Reactions of Thiophene-Based Materials. Metal-mediated activation of strong bonds, such as C–C, C–H, C–O, and C–X (X = halogen), is a vital research area related to the catalytic transformation of organic molecules. Carbon-sulfur bonds are also activated on metal centers to provide useful reaction pathways for novel sulfur-containing compounds. The C–S bond cleavage of thiophenes is an industrially important process in catalytic hydrodesulfurization (HDS) that removes sulfur from organosulfur compounds in petroleum feedstocks. The reactions of dibenzothiophenes (DBT) with organometallic compounds are of particular interest because dibenzothiophenes are especially resistant to desulfurization, which causes serious problems for further HDS. However, the rich sulfur-metal chemistry originating from HDS would provide new ways to produce S-containing functional materials.

We have used pyridyl-substituted dibenzothiophenes, 4-(2'-pyridyl)dibenzothiophene (PyDBT) and its derivatives, as ligand precursors in order to facilitate the metalation reaction. For example, the reaction of PyDBT with $[\text{Ru}_3(\text{CO})_{12}]$ gave the diruthenium(II) complex $[\text{Ru}(\mu\text{-PyBPT-}\kappa^3\text{N,C,S})(\text{CO})_2]_2$, where PyBPT denotes a dianion of 3'-(2''-pyridyl)-1,1'-biphenyl-2-thiol (Figure 1). The N,C,S-tridentate ligand PyBPT provides a pincer structure consisting of two metallacycles. The precoordination of the pyridyl group, including the N,S-chelating mode, accelerates the oxidative addition of the C–S bond by increasing the accessibility of the C–S bond to the vacant site on the metal center.



Figure 1. Formation of thiolate-containing pincer structures by C–S bond cleavage.

Another way to utilize C–S cleavage reactions is modification of C–S cleaved ligands in

transition-metal complexes. A thiolate-bridged diiron carbonyl complex derived from benzothiophene, $[\text{Fe}_2(\mu\text{-SC}_6\text{H}_4\text{CHCH})(\text{CO})_6]$, which was reported by Rauchfuss et al. (*Organometallics*, 1988, 7, 1171), reacted with terminal alkynes under photoirradiation conditions to afford diiron carbonyl complexes of π -conjugated thiolate ligands as alkyne insertion products (Figure 2). Various functional groups were introduced on the extended carbon chain. This reaction process involves insertion of CO and/or migration of coordinating functional groups via C–N or C–O bond cleavage.

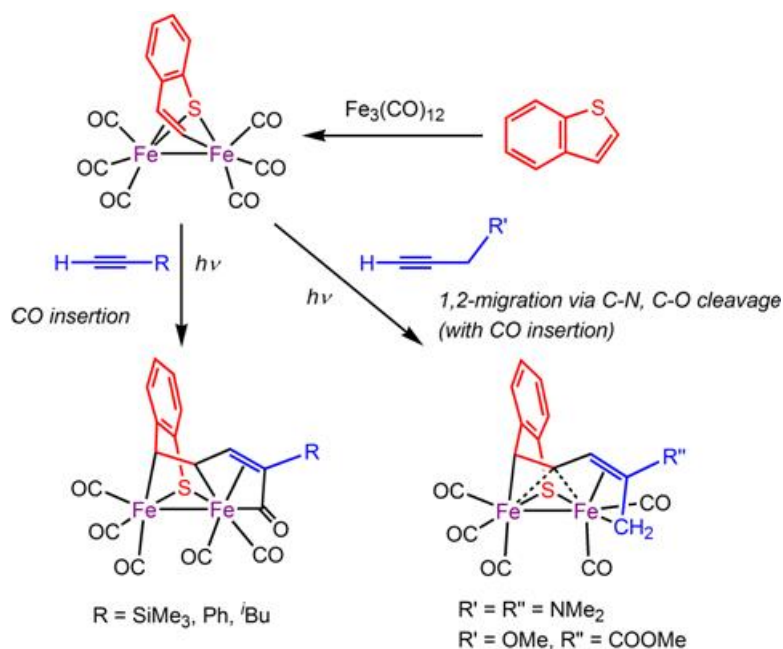


Figure 2. Reactions of a diiron complex containing C–S cleaved benzothiophene with alkynes.

(2) Mimics of [FeFe]-Hydrogenase Active Sites. Thiolate iron complexes are found in the active site of hydrogenases, which catalyze the formation and consumption of dihydrogen in biological systems. The active site of [FeFe]-hydrogenases consists of a diiron center bridged by a dithiolate ligand and a $\{4\text{Fe}_4\text{S}\}$ cubane cluster. The diiron center has carbonyl and cyanide ligands, and one of the two Fe ions is connected to the $\{4\text{Fe}_4\text{S}\}$ cluster via a cysteinyl residue (Figure 1a). A binding site for substrates is in the diiron unit, and the $\{4\text{Fe}_4\text{S}\}$ cluster is involved in electron transfer in the catalytic cycle of [FeFe]-hydrogenases.

We synthesized a thiolate-bridged diiron carbonyl complex $[\{\text{Fe}(\mu\text{-PyBPT-}\kappa^3\text{N,C,S})(\text{CO})_2\}\text{Fe}(\text{CO})_3]$ by the photochemical reaction of PyDBT with $[\text{Fe}(\text{CO})_5]$ (Figure 1b). An $\text{Fe}(\text{CO})_3$ unit in the PyBPT complex is bound to the thiolate-containing metallacycle to form a carbon- and sulfur-bridged dinuclear structure with an Fe–Fe bond, which is similar to the diiron unit of the [FeFe]-hydrogenase active site. The C,S-bridged diiron complex and its Schiff base and oxazoline derivatives showed electrocatalytic ability for proton reduction.

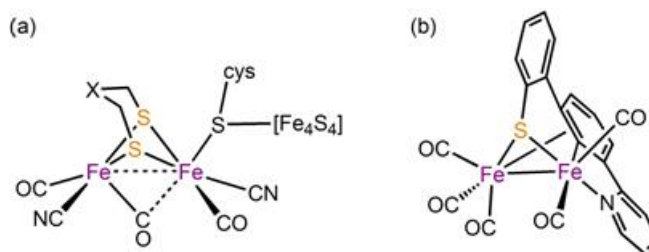


Figure 3. Structures of (a) the active site of [FeFe]-hydrogenases in the oxidized state and (b) a diiron complex with an S,C,N-tridentate ligand.

(3) N_2 Activation. Biological reduction of dinitrogen to ammonia is catalyzed by nitrogenase enzymes under ambient conditions, which is an essential process in the biochemical nitrogen

cycle. The N₂ binding and reduction proceed at the FeMo-cofactor in nitrogenase, in which the iron centers are surrounded by the sulfur donor atoms. The structure of the FeMo-cofactor has been revealed by crystallographic studies, and synthetic approaches are currently underway to obtain the structural model. In addition, the reduction and functionalization of the coordinated N₂ using early- to middle-transition-metal complexes have become an active research area. However, the mechanistic details of the N₂ reduction on the FeMo-cofactor are still unclear.

We recently reported that sulfur-bridged Ta₂M₂ complexes (M = Mo, Cr) containing a four-electron-reduced dinitrogen ligand, [Cp*Ta(μ-SC₆H₄Me)₂M(CO)₄]₂(μ-η¹:η¹-N₂) (Cp* = η⁵-C₅Me₅), were synthesized from the ditantalum complex [Cp*Ta(SC₆H₄Me)₂]₂(μ-η¹:η¹-N₂), which was obtained by a one-pot reaction using [Cp*TaCl₄], di-*p*-tolyl disulfide, and KC₈ under dinitrogen (Figure 4). Crystal structures of the Ta₂ and Ta₂M₂ complexes revealed the analogy of the Ta–N–N–Ta moieties. This new synthetic procedure provides various types of S-bridged multinuclear N₂ complexes, which should be useful for investigating the reactivity of N₂ incorporated in sulfur rich metal clusters.

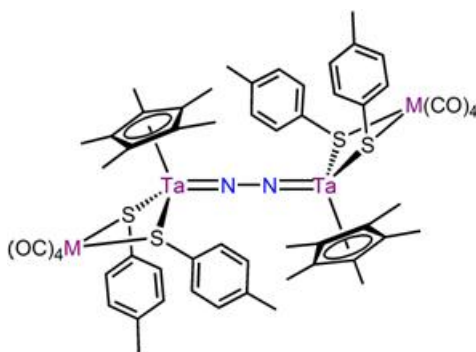


Figure 4. Structure of S-bridged Ta₂M₂ complexes with N₂⁴⁻ (M = Mo, Cr).

(4) Mimics of Oxygen Evolving Center in Photosystem II. Photosynthetic water oxidation is catalyzed by the oxygen evolving complex (OEC) in photosystem II (PSII). X-ray diffraction studies of PSII revealed that the active site of the OEC has a Mn₄CaO₅ cluster. A variety of tetranuclear manganese clusters were synthesized to model the OEC active site, and their structural, spectroscopic, and magnetic properties were investigated. We recently designed 5,5'-(9,9-dimethylxanthene-4,5-diyl)bis(salicylaldehyde) (H₂xansal). The xansal-based Schiff base ligands secure two Mn ions in close proximity. This bimetallic platform is applicable to the tetrametallic one by dimerization. We synthesized Mn₄ complexes by using a xansal-based ligand derived from H₂xansal and 3-amino-1-propanol. Figure 5 shows an acetate-bridged Mn₄ complex, which has an incomplete double-cubane structure of Mn₄O₆. This complex is a potential starting material for the model of the OEC active site, because the defective site could be occupied by a Ca²⁺ ion to form a Mn₃CaO₄ cubane structure binding a fourth Mn ion.

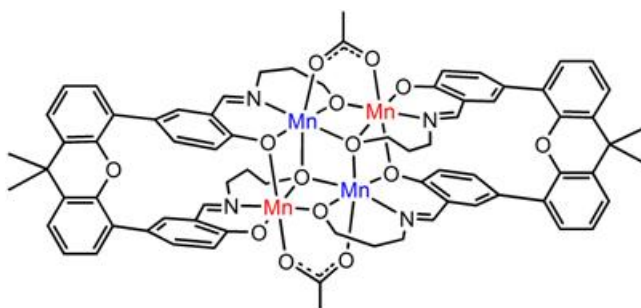


Figure 5. Structure of a tetramanganese(II,II,III,III) complex supported by xanthene-bridged Schiff base ligands.

(5) Multimetallic Catalysts. Chiral sulfoxides are useful building blocks in asymmetric synthesis of organic compounds. Enantioselective oxidation of sulfides catalyzed by transition metal complexes is an efficient method to prepare chiral sulfoxides. In the last two decades, metal complex catalysts containing chiral salen-type Schiff base ligands have been developed for the asymmetric sulfoxidation reactions, showing moderate to high enantioselectivity. On the other hand, chiral multimetallic complexes have recently been designed as efficient asymmetric catalysts which cause proximity effect. If two metal centers in a catalyst act as an enantioselective Lewis-acid center to catch a sulfide and as an enantioselective oxidation site, respectively, the sulfide is expected to be oxidized to the corresponding chiral sulfoxide in high enantioselectivity by the cooperative effect.

Several dimeric salen-type complexes, in which the monomeric units are connected by organic linkages, have been synthesized, and their catalytic properties have been investigated. However, structurally characterized salen-type complex dimers with a face-to-face arrangement are very rare. We have synthesized an optically active dinuclear manganese(III) complex with a cyclic ligand, in which two salen-type units are anchored by two 9,9-dimethylxanthene-4,5-diyl spacers (Figure 6). The chiral dimanganese complex was found to have a face-to-face structure in close proximity and showed catalytic activity for the asymmetric oxidation of sulfides by iodobenzene. The enantioselectivity was improved by the addition of 4-(dimethylamino)pyridine (DMAP) to the reaction system, which was not effective for the corresponding mononuclear catalyst.

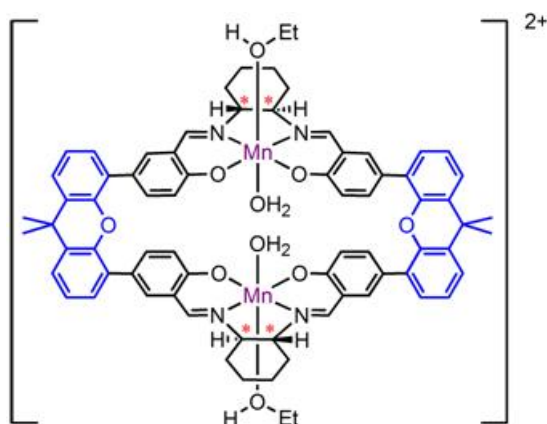


Figure 6. Structure of a chiral dimanganese(III,III) complex.

2. Selected Publications

1. "Skeletal Modification of Benzothiophene Mediated by Iron Carbonyls: Insertion of Terminal Alkynes with Migration of Amino and Alkoxy Groups" Kyohei Kobayashi, Masakazu Hirotsu, Isamu Kinoshita, *Organometallics*, **2013**, 32 (18), 5030-5033.
2. "Titanium and manganese complexes supported by a xanthene-bridged bis(tripodal N₂O₂) ligand: isomerization, intramolecular hydrogen bonding and metal-binding ability" Masakazu Hirotsu, Keisuke Kawamoto, Rika Tanaka, Yuji Nagai, Keiji Ueno, Yoshio Teki, Isamu Kinoshita, *Dalton Trans.*, **2013**, 42 (34), 12220-12227.
3. "Carbon- and Sulfur-Bridged Diiron Carbonyl Complexes Containing N,C,S-Tridentate Ligands Derived from Functionalized Dibenzothiophenes: Mimics of the [FeFe]-Hydrogenase Active Site" Masakazu Hirotsu, Kiyokazu Santo, Hideki Hashimoto, Isamu Kinoshita, *Organometallics*, **2012**, 31 (21), 7548-7557.
4. "Design, synthesis, magnetic properties of a π -radical ligand with photo-excited high-spin state and its Fe(II) complex. The first stage of a new strategy for LIESST materials." Koichi Katayama, Masakazu Hirotsu, Isamu Kinoshita, Yoshio Teki, *Dalton Trans.*, **2012**, 41 (43), 13465-13473.
5. "Anion-Controlled Assembly of Four Manganese Ions: Structural, Magnetic, and Electrochemical Properties of Tetramanganese Complexes Stabilized by Xanthene-Bridged Schiff Base Ligands" Masakazu Hirotsu, Yuu Shimizu, Naoto Kuwamura, Rika Tanaka, Isamu Kinoshita, Ryoichi Takada, Yoshio Teki, Hideki Hashimoto, *Inorg. Chem.*, **2012**, 51 (2), 766-768.

6. "Sulfur-Bridged Ta-M (M = Mo, Cr) Multinuclear Complexes Bearing a Four-Electron-Reduced Dinitrogen Ligand" R. Takada, M. Hirotsu, T. Nishioka, H. Hashimoto, I. Kinoshita, *Organometallics*, **2011**, 30 (16), 4232-4235.
7. "Carbon-sulfur bond cleavage reactions of dibenzothiophene derivatives mediated by iron and ruthenium carbonyls" M. Hirotsu, C. Tsuboi, T. Nishioka, I. Kinoshita, *Dalton Trans.*, **2011**, 40 (4), 785-787.
8. "Manganese(II), Nickel(II), and Palladium(II) Complexes of a Terpyridine-Like Ligand Containing a Sulfur Linkage, and an Analogous NCN Pincer Palladium(II) Complex: Synthesis, Characterization, and Pd-Catalyzed Reactions" M. Hirotsu, Y. Tsukahara, I. Kinoshita, *Bull. Chem. Soc. Jpn.*, **2010**, 83 (9), 1058-1066.
9. "Synthesis and characterization of xanthene-bridged Schiff base dimanganese(III) complexes: bimetallic catalysts for asymmetric oxidation of sulfides" M. Hirotsu, N. Ohno, T. Nakajima, C. Kushibe, K. Ueno, I. Kinoshita, *Dalton Trans.*, **2010**, 39 (1), 139-148.
10. "Steric, geometrical and solvent effects on redox potentials in salen-type copper(II) complexes" M. Hirotsu, N. Kuwamura, I. Kinoshita, M. Kojima, Y. Yoshikawa, K. Ueno, *Dalton Trans.*, **2009**, (37), 7678-7683.
11. "Ruthenium and Rhodium Complexes with Thiolate-Containing Pincer Ligands Produced by C-S Bond Cleavage of Pyridyl-Substituted Dibenzothiophenes" M. Shibue, M. Hirotsu, T. Nishioka, I. Kinoshita, *Organometallics*, **2008**, 27 (17), 4475-4483.
12. "A Thiocalix[3]pyridine Copper(I) Complex as a Highly Active Catalyst for the Olefin Aziridination Reaction" Y. Tsukahara, M. Hirotsu, S. Hattori, Y. Usuki, I. Kinoshita, *Chem. Lett.*, **2008**, 37 (4), 452-453.
13. "Extreme N-N Bond Elongation and Facile N-Atom Functionalization Reactions within Two Structurally Versatile New Families of Group 4 Bimetallic "Side-on-Bridged" Dinitrogen Complexes for Zirconium and Hafnium" M. Hirotsu, P. P. Fontaine, P. Y. Zavalij, L. R. Sita,* *J. Am. Chem. Soc.*, **2007**, 129 (42), 12690-12692.
14. "Dinitrogen Activation at Ambient Temperatures: New Modes of H₂ and PhSiH₃ Additions for an "End-On-Bridged" [Ta(IV)]₂(μ-η¹:η¹-N₂) Complex and for the Bis(μ-nitrido) [Ta(V) (μ-N)]₂ Product Derived from Facile N-N Bond Cleavage" M. Hirotsu, P. P. Fontaine, A. Epshteyn, P. Y. Zavalij, L. R. Sita,* *J. Am. Chem. Soc.*, **2007**, 129 (30), 9284-9285.
15. "Synthesis of a Cofacial Schiff-Base Dimanganese(III) Complex for Asymmetric Catalytic Oxidation of Sulfides" M. Hirotsu, N. Ohno, T. Nakajima, K. Ueno, *Chem. Lett.*, **2005**, 34 (6), 848-849.