

Annual Research Highlights

(1) Construction of π -Conjugated Nickel Bis(dithiolene) Complex Nanosheet

A π -conjugated nanosheet comprising planar nickel bis(dithiolene) complexes was synthesized by a bottom-up method. A liquid–liquid interfacial reaction using benzenehexathiol in the organic phase and nickel(II) acetate in the aqueous phase produced a semiconducting bulk material with a thickness of several micrometers. Powder X-ray diffraction analysis revealed that the crystalline portion of the bulk material comprised a staggered stack of nanosheets. A single-layer nanosheet was successfully realized using a gas–liquid interfacial reaction. Atomic force microscopy and scanning tunneling microscopy confirmed that the π -conjugated nanosheet was single-layered. Modulation of the oxidation state of the nanosheet was possible using chemical redox reactions.

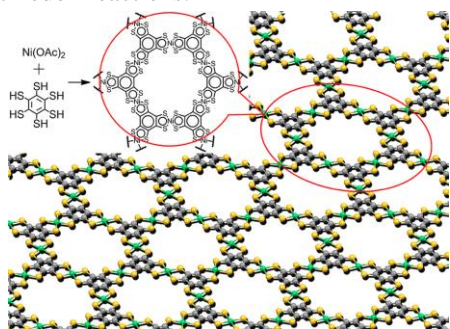


Fig. 1 Structure of π -Conjugated Bis(dithiolene) Complex Nanosheet

1.(1)-16) *J. Am. Chem. Soc.*, **135**, 2462-2465 (2013)

2.-1) *日本結晶学会誌*, **55**, 323-330 (2013)

2.-3) *Dalton Trans.*, **42**, 15825 (2013)

(2) π -Conjugated Trinuclear Metalladithiolenes with a Triphenylene Backbone

Previously, we synthesized π -conjugated trinuclear metalladithiolene complexes based on benzenehexathiol. We report trinuclear complexes with a triphenylene backbone. A reaction with triphenylenehexathiol and group 9 metal precursors in the presence of triethylamine gives rise to trinuclear complexes. The planar structure of Ir complex is determined using single crystal X-ray diffraction analysis. The ligand-to-metal charge transfer bands of trinuclear complexes move to longer wavelengths compared with those of mononuclear ones. Electrochemical measurements disclose that the one-electron and two-electron reduced mixed-valent states are stabilized thermodynamically. UV–vis–NIR spectroscopy for the reduced species of Co complex identifies intervalence charge transfer bands for mono anion and dianion, substantiating the existence of electronic communication among the three metal nuclei. These observations prove that the triphenylene backbone transmits π -conjugation among the three

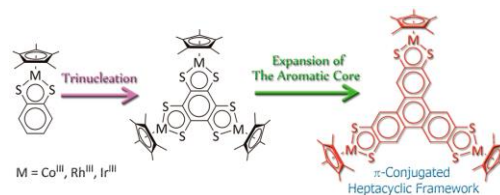


Fig. 2 Structure of π -Conjugated Trinuclear Metalladithiolenes with a Triphenylene Backbone metalladithiolene units.

1.(1)-7) *Inorg. Chem.*, **52**, 7411-7416 (2013)

(2) Photo- and electrochemical properties of triarylamine-conjugated bis(dipyrinato)zinc(II) complexes

Dipyrins and their complexes are known for their excellent photochemical properties, serving as chromophores. Molecules appended with triarylamine moieties often exhibit enhanced absorptivities and intramolecular charge transfer transitions. In this context, we synthesized hybrids of triarylamine and bis(dipyrinato)zinc(II) complexes to investigate their photo- and electrochemical properties.

Bis(dipyrinato)zinc(II) complexes with triarylamine at the meso position of dipyrin **1** and **2** were synthesized (Fig. 3 (a)). X-ray crystallographic analysis revealed that their zinc centers adopt tetrahedral coordination spheres; their adjacent triarylamine and dipyrin subunits are orthogonal to each other. Their UV-vis absorption spectra were simple overlays of the absorption bands of the triarylamine and dipyrin moieties of the complexes. On the other hand, cyclic voltammograms of triarylamine-conjugated complexes showed complicated redox waves. The results show the presence of electronic interactions between the triarylamine and dipyrin units (Fig. 3 (b)).

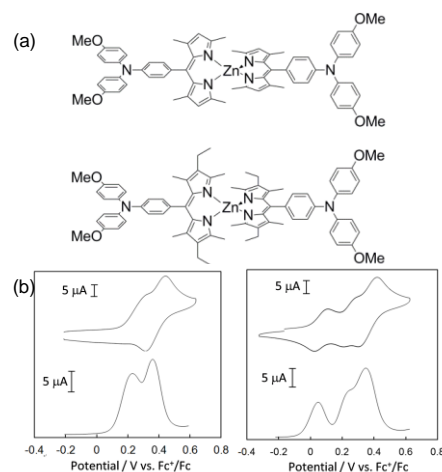


Fig. 3 (a) Chemical structures and (b) cyclic voltammograms (scan rate: 0.1 Vs^{-1} , electrolyte/solvent: 0.1 M $n\text{-Bu}_4\text{ClO}_4/\text{dichloromethane}$, concentration: ca. 0.5 mM) of triarylamine-conjugated complexes **1** and **2**.

1.(1)-19) *Chem. Asian J.*, **8**, 723-727 (2013)

1.(1)-20) *Electrochemistry*, **81**, 337-339 (2013)

研究ハイライト

(1) π 共役ニッケルビスジチオレン錯体ナノシートの構築

原子一つ分の厚さを有する二次元的に広がった構造を有する物質はナノシートと呼ばれ、3次元的なバルク物質とは異なる物理的、化学的な性質を有し種々の分野で盛んに研究が進められている。我々はこれまでのトップダウン的な合成とは異なり、 π 共役系ジチオレン多核錯体の知見を用いて二次元的に π 共役系を拡張したボトムアップ型 π 共役系ニッケルビスジチオレン金属錯体ナノシートの作製を行った。合成に際し金属イオンと有機配位子とを界面上で二次元的に反応させる二層界面合成法を開発し、多層および単層の金属錯体ナノシートをボトムアップ的に合成することに成功した。さらに得られたナノシートが化学的に還元できることならびにその電気伝導度の変化を明らかにし、トップダウン型ナノシートでは困難であったナノシートの物性制御を達成した。

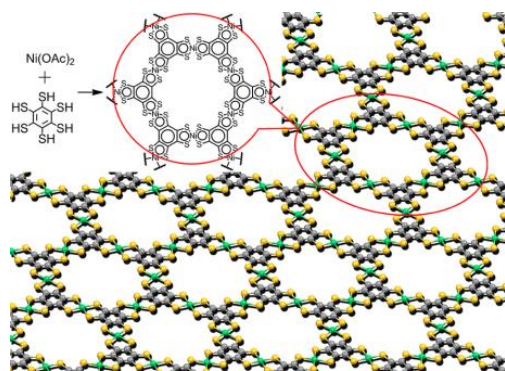


図1 π 共役ジチオレン錯体ナノシートの構造

- 1.(1)-16) *J. Am. Chem. Soc.*, **135**, 2462-2465 (2013)
- 2.-1) *日本結晶学会誌*, **55**, 323-330 (2013)
- 2.-3) *Dalton Trans.*, **42**, 15825 (2013)

(2) トリフェニレン骨格を有する π 共役系第九族メタラジチオレン三核錯体の構築

多核の金属錯体は混合原子価やスピンフラストレーションの発現等、特徴的な物性を示すことから注目を集めている。当研究室ではメタラジチオレン錯体の持つ平面的に広がった π 共役構造に着目し、トリフェニレン骨格を有するメタラジチオレン三角形三核錯体を用いて、より金属間距離が広がった錯体上における金属-金属間相互作用の発現に成功した。サイクリックボルタメトリーにおいて三核錯体の安定な一価および二価の陰イオンの存在を明らかにし、さらに化学的に還元した三核錯体の紫外-可視-赤外光吸収により 3つの金属原子間の電気的な相互作用の存在を明らかにした。

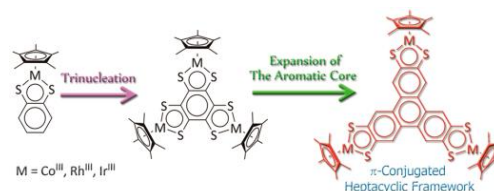


図2 π 共役系メタラジチオレン三核錯体の構造
1.(1)-7) *Inorg. Chem.*, **52**, 7411-7416 (2013)

(3) トリアリールアミン部位を有するビス(ジピリナト)亜鉛(II)錯体の光・電気化学物性

ジピリンとその金属錯体は優れた光物性を示すことが知られており、色素部位として機能する。一方、トリアリールアミン部位を付加した分子は吸収強度の増大や分子内電荷移動等の物性が付与される事が知られている。当研究室では、この知見をもとにトリアリールアミン部位を有するビス(ジピリナト)亜鉛(II)錯体を合成し、その物性を調べた。

ジピリンのメソ位にトリアリールアミンを有する錯体 **1, 2** を合成した (図 3(a))。X線結晶構造解析により、ジピリン部位は亜鉛中心に正四面体配位する事が分かった。したがって、隣接するトリアリールアミン部位、ジピリン部位同士はそれぞれ直交している。それぞれの錯体の紫外可視吸収スペクトルはトリアリールアミン部位とジピリン部位の吸収の単純な重ねあわせで分かった。一方、錯体 **1, 2** のサイクリックボルタモグラムは複雑な酸化還元波を示した (図 3(b))。以上の結果から、トリアリールアミン部位をジピリン部位間には相互作用が存在する事が分かった。

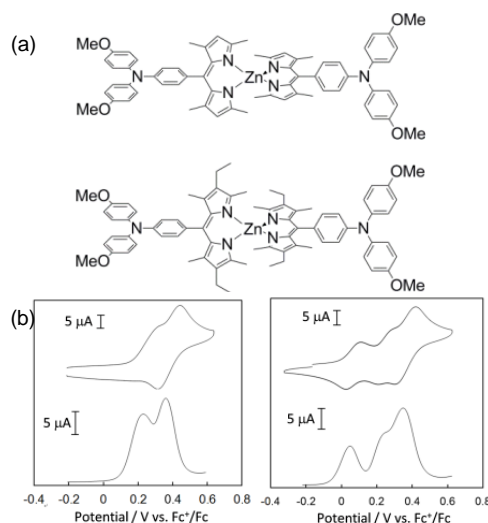


図3 錯体 **1, 2** の構造式(a)とサイクリックボルタモグラム(b), 走査速度: 0.1 Vs⁻¹, 電解質/溶媒: 0.1 M *n*-Bu₄ClO₄/dichloromethane, 濃度: ca. 0.5 mM)

- 1.(1)-19) *Chem. Asian J.*, **8**, 723-727 (2013)
- 1.(1)-20) *Electrochemistry*, **81**, 337-339 (2013)

1. 原著論文

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- 11) "Orthogonal bis(terpyridine)-Fe(II) metal complex wires on a tripod scaffold: Rapid electron transport", Ryota Sakamoto, Yuuki Ohirabaru, Ryota Matsuoka, Hiroaki Maeda, Shunsuke Katagiri, Hiroshi Nishihara, *Chem. Commun.*, **49**, 7108-7110 (2013).
- 12) "Metal Complex Oligomer and Polymer Wires on Electrodes: Tactical Constructions and Versatile Functionalities", Hiroaki Maeda, Ryota Sakamoto, Hiroshi Nishihara, *Polymer*, **54**, 4383-4403 (2013).
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- 21) "Solvated-Ion-Pairing-Sensitive Molecular Bistability Based on Copper(I)-Coordinated Pyrimidine Ring Rotation", Michihiro Nishikawa, Kuniharu Nomoto, Shoko Kume, Hiroshi Nishihara, *Inorg. Chem.*, **52**, 369-380 (2013).
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2. 総説・解説

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