

# 無機化学研究室

## 研究ハイライト

### (1) ビス(ジチオラト)白金錯体ナノシートの合成方法の開発

金属イオンと配位子からなる配位ナノシート (Coordination Nanosheet; CONASH) の一つであるビス(ジチオラト)ニッケル錯体ナノシート NiDT はトポロジカル絶縁体(物質内部は絶縁体だが表面やエッジ部分は電気を通すという特殊な物質)の候補物質であると、計算科学で予測されている。トポロジカル絶縁性を実験的に観測することは重要な課題であるが、NiDT のトポロジカル絶縁性の発現に関わるバンドギャップは小さく、観測が困難である。このバンドギャップは、より重い元素が入っている物質の方が大きくなる。本年度、我々はニッケルよりも重い元素である白金を中心金属とするビス(ジチオラト)白金錯体ナノシート PtDT を合成した。PtDT を合成するにあたり問題となるのは白金イオンが容易に還元されて白金ナノ粒子を形成してしまう点である。この還元反応を抑制するため、配位子のベンゼンヘキサチオール(BHT)を修飾した SnBHT を配位子に用いて、トランスメタル化による錯形成過程を組み込んだ(図1)。この手法により合成した PtDT の構造を粉末 X 線回折を用いて求め、その構造を用いてバンド構造を求めると、NiDT よりもバンドギャップが大きく、室温でもトポロジカル絶縁性を観測できると期待されるほどに開いていることが示唆された。

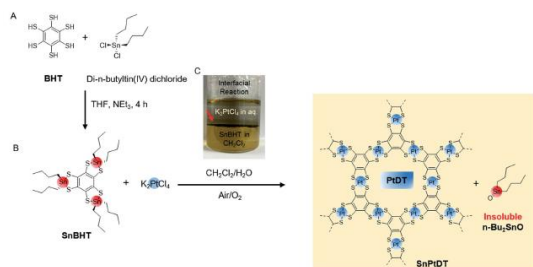


図 1. トランスメタル化を利用した PtDT の液液二相界面合成。

### (2) CONASH の有機 LED への応用

従来の有機 LED(OLED)のホール輸送層としては PEDOT/PSS が使われていたが、PSS は強酸性で水分を取り込みやすく変質しやすい、また強酸性で電極にダメージを与えてしまうという問題があった。今回、導電性の高い NiDT をホール輸送層として、Super-Yellow を発光層として用いた OLED 素子を構築し、素子特性の評価を行った。電流注入により、セル全面から均一に発光していることが確認された。PEDOT/PSS を用いた従来素子との比較において、NiDT を用いた素子は電流量や発光特性はほぼ同程度であったが、負荷特性が優れており、さらに素子耐久性は約 2 倍に向上していた。これらの特性は NiDT のホール伝導特性の高さや、Super-Yellow とのエネルギー準位の関係、電極へのダメージの少なさなどに起因していると考えられる。

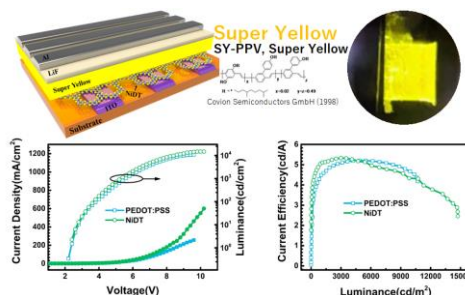


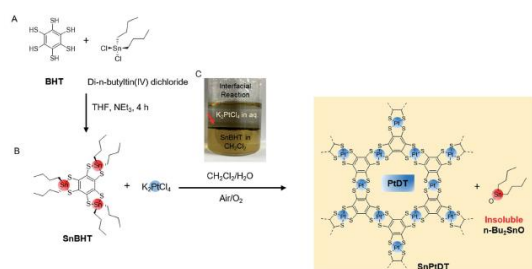
図 2. Super-Yellow を発光層として、NiDT をホール輸送層とした OLED 素子。電流特性等で、PEDOT/PSS と同等もしくは同等以上の特性向上が得られている。

# Inorganic Chemistry

## Annual Research Highlights

### (1) “Development of Synthesis Method for Bis(dithiolato)platinum Complex Nanosheet”

Bis(dithiolato)nickel complex nanosheet NiDT, one of the coordination nanosheets (CONASH) consisting of metal ions and ligands, is predicted by computational science to be a candidate material for topological insulators (a special material in which the inside of the material is insulating but the surface and edges conduct electricity). Computational science predicts that NiDT is a candidate for topological insulators. Experimental observation of topological insulating properties is an important issue, but is difficult because the band gap associated with the development of topological insulating properties in NiDT is small. This band gap is larger for materials containing heavier elements. In this year, we have synthesized bis(dithiolato)platinum complex nanosheets PtDTs with platinum as the central metal, which is heavier than nickel. To suppress this reduction reaction, the complexation process by transmetalation was incorporated by using SnBHT modified with benzene hexathiol (BHT) as a ligand (Fig. 1). The structure of PtDT synthesized by this method was determined using powder X-ray diffraction, and the band structure obtained from the structure suggests that the band gap is larger than that of NiDT, and is open enough to be expected that topological insulating properties can be

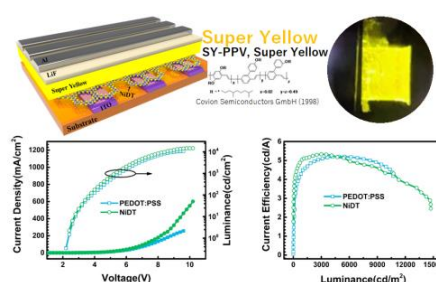


**Fig 1.** Liquid-liquid two-phase interfacial synthesis of PtDT using transmetalation.

observed even at room temperature.

### (2) “Application of CONASH to organic LEDs”

PEDOT/PSS has been used as the hole transport layer in conventional organic LEDs (OLEDs), but PSS is strongly acidic and easily takes up moisture and easily deteriorates, and also damages the electrodes due to its strong acidity. In this study, we constructed an OLED device using highly conductive NiDT as the hole transport layer and Super-Yellow as the emission layer, and evaluated the device characteristics. In comparison with the conventional device using PEDOT/PSS, the NiDT-based device showed almost the same amount of current and luminescence characteristics, but the load characteristics were superior and the device durability was improved by a factor of two. These properties were attributed to the high hole conduction properties of NiDT, the energy level relationship with Super-Yellow, and the low damage to the electrodes.



**Fig 2.** OLED device using Super-Yellow as the light emitting layer and NiDT as the hole transport layer. The current and other characteristics are equivalent to or better than those of PEDOT/PSS.

## 1. 原著論文

### (1) Refereed Journals

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- 2) Tetsuro Kusamoto, Hiroshi Nishihara, "Zero-, one- and two-dimensional bis(dithiolato)metal complexes with unique physical and chemical properties", *Coord. Chem. Rev.*, **380**, 419-439 (2019).
- 3) Ken Kato, Shun Kimura, Tetsuro Kusamoto, Hiroshi Nishihara, Yoshio Teki, "Luminescent Radical-Excimer: Excited-State Dynamics of Luminescent Radicals in Doped Host Crystals", *Angew. Chem. Int. Ed.*, **58**, 2606-2611 (2019).
- 4) Akira Tanushi, Shun Kimura, Tetsuro Kusamoto, Moe Tominaga, Yasutaka Kitagawa, Masayoshi Nakano, Hiroshi Nishihara, "NIR Emission and Acid-Induced Intramolecular Electron Transfer Derived from a SOMO-HOMO Converted Non-Aufbau Electronic Structure", *J. Phys. Chem. C.*, **123**, 4417-4423 (2019).
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- 6) Tsukasa Usuki, Kenichiro Omoto, Masaki Shimada, Yoshinori Yamanoi, Hidetaka Kasai, Eiji Nishibori, Hiroshi Nishihara, "Effects of Substituents on the Blue Luminescence of Disilane-Linked Donor-Acceptor-Donor Triads", *Molecules*, **24**, 521 (2019).
- 7) Truong Giang Do, Emanuel Hupf, Enno Lork, Julius F. Kogel, Fabian Mohr, Alex Brown, Ryojun Toyoda, Ryota Sakamoto, Hiroshi Nishihara, Stefan Mebs, Jens Beckmann, "Aurophilicity and Photoluminescence of (6-Diphenylpicenogenoacenaphth-5-yl)gold Compounds", *Eur. J. Inorg. Chem.*, 647-659 (2019).
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- 10) Daiki Nishiori, Wenchao Zhu, Raphael Salles, Mariko Miyachi, Yoshinori Yamanoi, Takashi Ikuta, Kenzo Maehashi, Tatsuya Tomo, Hiroshi Nishihara, "Photosensing System Using Photosystem I and Gold Nanoparticle on Graphene Field-Effect Transistor", *ACS Al. Mater. Interfaces*, **11**, 42773-42779 (2019).
- 11) Yoshinori Yamanoi, Tsukasa Usuki, Kenichiro Omoto, Masaki Shimada, Hikaru Koike, Munetaka Iwamura, Koichi Nozaki, Daisuke Saito, Masako Kato, Hiroshi Nishihara, "Dioxacyclophanes as a Scaffold for Silicon-based Circularly Polarized Luminescent Materials", *Tetrahedron Lett.*, **60**, 1108-1112 (2019).
- 12) Yurong Liu, Ryota Sakamoto, Cheuk-Lam Ho, Hiroshi Nishihara, Wai-Yeung Wong, "Electrochromic triphenylamine-based cobalt(II) complex nanosheets", *J. Mater. Chem. C*, **7**, 9159-9166 (2019).
- 13) Tsukasa Usuki, Hikaru Uchida, Kenichiro Omoto, Yoshinori Yamanoi, Ayano Yamada, Munetaka Iwamura, Koichi Nozaki, Hiroshi Nishihara, "Enhancement of the Photofunction of Phosphorescent Pt(II) Cyclometalated Complexes Driven by Substituents: Solid-State Luminescence and Circularly Polarized Luminescence", *J. Org. Chem.*, **84**, 10749-10756 (2019).

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## 2. 解説・総説

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## 3. 著書

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## 4. その他

レフェリー付プロシーディングス

(1) K.Niitsu, T. Sakabe, M. Miyachi, Y. Yamanoi, H. Nishihara, T. Tomo, K. Nakazato, “2D Optical Imaging Using Photosystem I Photosensor Platform with 32x32 CMOS Biosensor Array”, *24TH ASIA AND SOUTH PACIFIC DESIGN AUTOMATION CONFERENCE*, 7-8 (2019).