Academic Program [Oral A] | 11. Organic Chemistry -Structural Organic Chemistry-：Oral A

Thu. Mar 27, 2025 3:55 PM - 5:15 PM JST | Thu. Mar 27, 2025 6:55 AM - 8:15 AM UTC
[F]2201(2201, Bldg. 2, Area 4 [2F])

[[F]2201-2vn] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Yasunori Matsui, Masahiro Ikeshita

Japanese
3:55 PM - 4:05 PM JST | 6:55 AM - 7:05 AM UTC
[[F]2201-2vn-01]

Synthesis and Properties of Bowl-shaped Imine Ligands with π-curved Surfaces

〇Kosuke Ikegami[1], Shigehisa Akine[1,2] (1. Graduate School of Natural Science and Technology, Kanazawa University, 2. Nano Life Science Institute, Kanazawa University)

English
4:05 PM - 4:15 PM JST | 7:05 AM - 7:15 AM UTC
[[F]2201-2vn-02]

Synthesis of Linear Trisilane Compounds and Its Photophysical Properties

〇Liangga Santoso[1], Yoshinori Yamanoi[1], Teppei Yamada[1] (1. Department of Chemistry, School of Science, The University of Tokyo)

English
4:15 PM - 4:25 PM JST | 7:15 AM - 7:25 AM UTC
[[F]2201-2vn-03]

Synthesis and Conjugated Polymerization of Hypervalent Tin Compound Based on Azobenzene Dinuclear Ligand

〇Kento Tanaka[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Kyoto Univ. Grad. Sch. of Eng.)

Japanese
4:25 PM - 4:35 PM JST | 7:25 AM - 7:35 AM UTC
[[F]2201-2vn-04]

Evaluation of Lewis Acidity in Hypervalent Bismuth Compounds with π-Conjugated Molecules

〇Shota Yagi[1], Kazuya Tanimura[2], Masayuki Gon[2], Kazuo Tanaka[2] (1. Kyoto Univ., 2. Grad. Sch. of Eng., Kyoto Univ.)

Japanese
4:35 PM - 4:45 PM JST | 7:35 AM - 7:45 AM UTC
[[F]2201-2vn-05]

Syntheses and Photophysical Properties of Dipyridylmethene Boron Complexes

〇Kohsei Yamada[1], Yuto Aoyama[2], Shunichiro Ito[2], Kazuo Tanaka[2] (1. Kyoto University, 2. Grad. Sch. of Eng., Kyoto Univ.)

English
4:45 PM - 4:55 PM JST | 7:45 AM - 7:55 AM UTC
[[F]2201-2vn-06]

Solid-State Synthesis and Optical Properties of Indium-Fused Azobenzene Complexes from Indium Oxide

〇Chiaki Hotta[1], Masayuki Gon[1], Kazuo Tanaka[1] (1. Kyoto University)

English
4:55 PM - 5:05 PM JST | 7:55 AM - 8:05 AM UTC

[[F]2201-2vn-07]

Control of Optical Properties by Metal Complexation Based on Carborane Derivatives

〇Mei Tokutomi[1], Kazuo Tanaka[1] (1. Graduate School of Engineering, Kyoto University)

Japanese

5:05 PM - 5:15 PM JST | 8:05 AM - 8:15 AM UTC

[[F]2201-2vn-08]

Effects of Coordination-Site Amination on the Optical Properties of Boron Complexes with Seven-Membered Aromatic Ligands

〇Ryusei nakashima[1], Hikari Ogoshi[1], Shunichiro Ito[1], Kazuo Tanaka[1] (1. Grad. Sch. of Eng., Kyoto Univ.)

π曲面を有するお椀型イミン配位子の合成とその物性

（金沢大院自然 [1]・金沢大 NanoLSI[2]）○池上 耕亮 [1]・秋根 茂久 [1,2]

Synthesis and Properties of Bowl-shaped Imine Ligands with π-curved Surfaces

([1]*Graduate School of Natural Science and Technology, Kanazawa University*, [2]*Nano Life Science Institute, Kanazawa University*) ○Kosuke Ikegami,[1] Shigehisa Akine[1,2]

Bowl-shaped imine ligands were synthesized by the cyclization of a dialdehyde with xanthene skeleton **1** and *o*-phenylenediamine. The reaction afforded the trimer $H_6\mathbf{L}^3$ and tetramer $H_8\mathbf{L}^4$, and the formation ratio was controlled by changing the reaction conditions such as solvent and temperature. The X-ray crystallographic analysis revealed that the $H_6\mathbf{L}^3$ and $H_8\mathbf{L}^4$ were deep and shallow bowl-shaped structure, respectively. The NMR measurements suggested that the $H_8\mathbf{L}^4$ quickly undergoes a bowl inversion at room temperature while the $H_6\mathbf{L}^3$ does not invert even at high temperatures.

Keywords : Cyclic Molecule, Dynamic Covalent Bond, Schiff Base, Inversion Barrier, Xanthene

イオンや小分子などを種々の相互作用により認識できるホスト分子の開発は、超分子化学において重要なトピックである。その中でもお椀型のホスト分子は特に盛んに研究されている構造であり、その空孔サイズに応じた選択的なゲスト認識が可能である。イミンなどの配位部位を組み込んだお椀型分子であれば、金属イオンの導入により空孔サイズや曲率の制御ができると予想され、大小様々なゲスト分子の認識に対応できると期待される。本研究では、キサンテン骨格を持つジアルデヒド**1**と*o*-フェニレンジアミンとの縮合を利用してお椀型イミン配位子を合成した。

室温における DMSO-d_6 中での環化反応を ^{1}H NMR により追跡したところ、8.93 ppm のイミンのピークと 0.31 ppm と 0.50 ppm の 2 つに分裂したエチル基のピークが出現し、単一のお椀型構造の形成が示唆された。ESI-MS では m/z = 1195.49 にピークが観測され、主成分として得られた環状化合物は 3 量体 $H_6\mathbf{L}^3$ であることが明らかとなった。環形成時の溶媒や温度等の条件を変えると 4 量体 $H_8\mathbf{L}^4$ も生成し、$H_6\mathbf{L}^3$ と $H_8\mathbf{L}^4$ の生成比は条件によって変化した。それぞれ単結晶を作成し、X 線結晶構造解析を行った結果、$H_6\mathbf{L}^3$ は深いお椀型構造、$H_8\mathbf{L}^4$ は浅いお椀型構造をとることが明らかとなった。反転障壁、分光特性などについても併せて報告する。

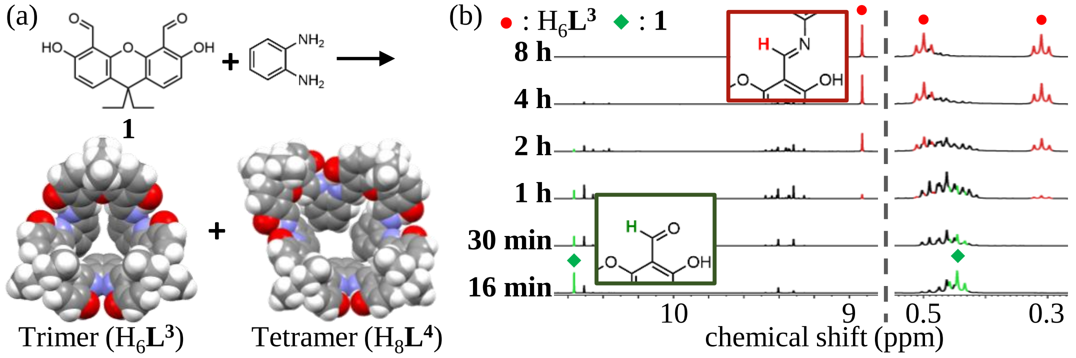


Figure (a) Formation of bowl-shaped imine ligands, $H_6\mathbf{L}^3$ and $H_8\mathbf{L}^4$, and their X-ray crystal structures. (b) ^{1}H NMR spectra showing the formation process of $H_6\mathbf{L}^3$ (600 MHz, DMSO-d_6).

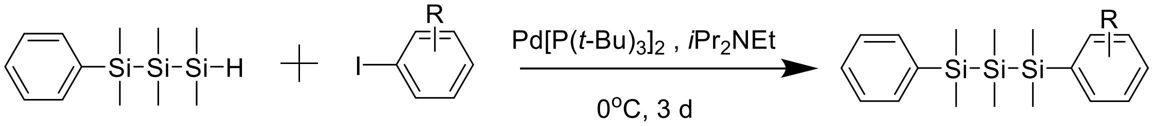
Synthesis of linear Trisilane Compounds and Its Photophysical Properties

Liangga Santoso[1], Yoshinori Yamanoi[1], Teppei Yamada[1]
[*1]Department of Chemistry, School of Science, The University of Tokyo

In recent years, oligosilane conjugated system have received attention because of their σ-π conjugated abilities, resulting in unique optical and electrochemical properties[1]. Many attempts have been made to synthesize diverse oligosilane compounds with Donor(D)-Acceptor(A) system to produce intense fluorescence, enhanced aggregation-induced emission (AIE) properties, and achieved advanced stimuli responsive materials[2]. While many study focused on disilane bridged molecule, trisilane bridged molecule is rarely found due to its synthesis difficulties. Therefore, this study tried to synthesize several linear trisilane compounds through palladium mediated coupling reaction between hydrosilane and aromatic iodides. Synthesized compounds were characterized with ^{1}H-NMR, ^{13}C-NMR, and HRMS. Their photophysical properties were studied using UV-VIS and fluorescence spectroscopy, their quantum yields and fluorescence lifetimes were also measured. DFT/TD-DFT calculations were carried out to investigate their electronic structures.

Keyword: Oligosilane, Trisilane compound, σ-π conjugation, *Photopysical properties, Intramolecular charge transfer*

Synthesis schematic (This study):



1 H. Miyabe, M. Ujita, M. Nishio, T. Nakae, T. Usuki, M. Ikeya, C. Nishimoto, S. Ito, M. Hattori, S. Takeya, S. Hayashi, D. Saito, M. Kato, H. Nishihara, T. Yamada and Y. Yamanoi, *Journal of Organic Chemistry*, 2022, **87**, 8928–8938.

2 Z. Zhou, L. Gai, L.-W. Xu, Z. Guo and H. Lu, *Chem Sci*, 2023, **14**, 10385–10402.

Synthesis and Conjugated Polymerization of Hypervalent Tin Compound Based on Azobenzene Dinuclear Ligand

(*Graduate School of Engineering, Kyoto University*)
○ Kento Tanaka, Masayuki Gon, Kazuo Tanaka

Keywords: Azobenzene; Hypervalent; Tin; Dinuclear Compounds; Conjugated Polymer

π-Conjugated molecules have excellent electronic properties which can be tuned by structural modification, and they have been used in a variety of fields, such as OLEDs and OPVs. Recently, the introduction of heteroatoms into π-conjugated frameworks to impart functionality has attracted attention. Molecules whose electronic states change in response to external stimuli are expected to be applied to sensing materials. Heavy main group elements can form hypervalent state where the number of valence electrons formally exceeds the octet rule, and they can take on a variety of coordination numbers. We have reported on hypervalent tin compounds using azobenzene tridentate ligands[1]. The hypervalent tin compounds can change their electronic states of π-conjugated scaffolds depending on the coordination number of tin atom. In this study, we focused on the two coordination points involved in azobenzene. We synthesized dinuclear hypervalent tin compounds in which two tin atoms are introduced into a single azobenzene ligand and carried out conjugated polymerization using the dinuclear compound as a monomer (Figure 1).

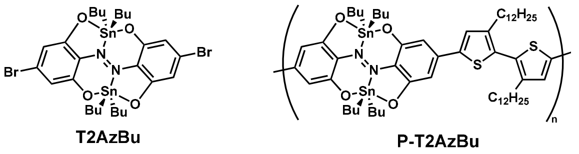


Figure 1. Dinuclear hypervalent tin compound.

Optical measurements showed that the absorption spectra of **T2AzBu** changed in accordance with addition of the coordination solvent, dimethyl sulfoxide (DMSO), as previous research (Figure 2)[1]. The results suggest that two Lewis bases coordinate to the hypervalent tin compound owing to the dinucleation. In this presentation, we will discuss the changes in the electronic states of dinuclear compounds depending on the change in the coordination number.

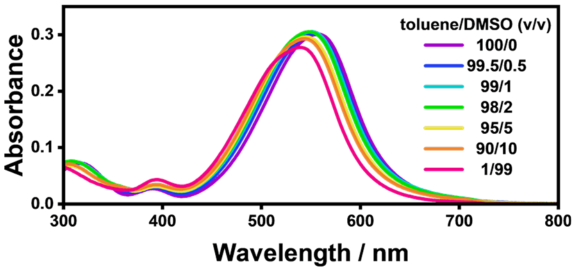


Figure 2. Absorption spectra of **T2AzBu** in each solvent volume ratio (1.0×10^{-5} M).

[1] Gon, M.; Tanaka, K.; Chujo, Y. *Chem. Eur J.* **2021**, *27*, 7561–7571.

π共役系分子を配位子とした超原子価ビスマス化合物の Lewis 酸性評価

（京大工[1]・京大院工[2]）○八木翔大[1]・谷村和哉[2]・権 正行[2]・田中 一生[2]

Evaluation of Lewis Acidity in Hypervalent Bismuth Compounds with π-Conjugated Scaffold

(*Faculty of Engineering, Kyoto University*[1], *Graduate School of Engineering, Kyoto University*[2]) ○Shota Yagi[1], Kazuya Tanimura[2], Masayuki Gon[2], Kazuo Tanaka[2]

Heavy main group elements exhibit the Lewis acidity derived from electrostatic effects and can maintain the Lewis acidity in multi-coordination structures. [1] We have previously reported the synthesis and the Lewis acidity of the hypervalent bismuth compound **BiAz** with the π-conjugated azobenzene tridentate scaffold (Fig. 1). [2] In this research, as the derivative, we synthesized **BiAz-Cl** in which the substituent group on the bismuth atom was altered to the chloride group and evaluated its Lewis acidity by fluoride ion affinity (FIA). [3] As a result, the value of FIA in **BiAz-Cl** (322.7 kJ mol^{-1}) was larger than that in **BiAz** (304.8 kJ mol^{-1}) and we revealed the increase in Lewis acidity. In this presentation, we will discuss the influences on the electronic state by altering the substituent group from the phenyl group to the chloride group, in addition to the detailed evaluation of Lewis acidity.

Keyword: π-Conjugated Molecules; Hypervalent Compounds; Bismuth; Lewis Acidity; Electronic States

高周期主要族元素は、静電的なLewis酸性を示し、多配位構造においてもLewis酸性を維持できる[1]。当研究室では、π共役系アゾベンゼン三座配位子を用いて超原子価ビスマス化合物**BiAz**を合成し、Lewis酸性を示すことを明らかにしている(Fig. 1) [2]。本研究ではさらなるLewis酸性向上のために、ビスマス上の置換基をクロロ基に変更した**BiAz-Cl**を合成し(Fig. 1)、Lewis酸性をFloride ion affinity (FIA)[3]から評価した。その結果FIAの値は、**BiAz** (304.8 kJ mol^{-1})よりも**BiAz-Cl** (322.7 kJ mol^{-1})の方が大きく、Lewis酸性が向上したことを明らかにした。本発表では、Lewis酸性の詳細な評価に加えて、クロロ基が電子状態に与える影響について報告する。

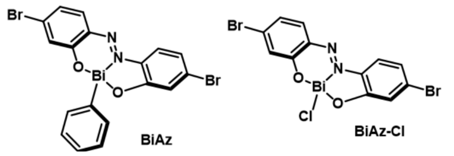


Figure 1. Chemical structures of **BiAz** and **BiAz-Cl**.

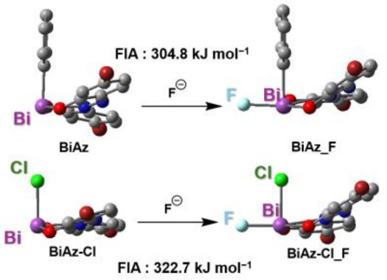


Figure 2. The result of calculated FIA in COF_2/COF_3^- system. The structures of **BiAz**, **BiAz_F**, **BiAz-Cl**, **BiAz-Cl_F** were optimized by DFT at B3LYP-D3BJ/def2qzvpp level. The electronic energies with optimized geometries were calculated by DFT at M062X-D3/def2qzvpp level.

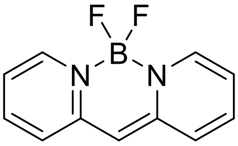
1) Gini, A.; Paraja, M.; Galmes, B.; Besnard, C.; Poblador-Bahamonde, A.; Sakai, N.; Frontera, A.; Matile, S. *Chem. Sci.* **2020**, *11*, 7086–7091.
2) Tanimura, K.; Gon, M.; Tanaka, K. *Inorg. Chem.* **2023***, 62,* 4590−4597.
3) Erdmann, P.; Leitner, J.; Schwarz, J.; Greb, L. *ChemPhysChem* **2020**, *21*, 987–994.

Syntheses and Photophysical Properties of Dipyridylmethene Boron Complexes

(*Graduate School of Engineering, Kyoto University*) ○Kohsei YAMADA, Yuto AOYAMA, Shunichiro ITO, Kazuo TANAKA

Keywords: Group 13 Complex; π-Conjugated Molecule; Emission; Boron

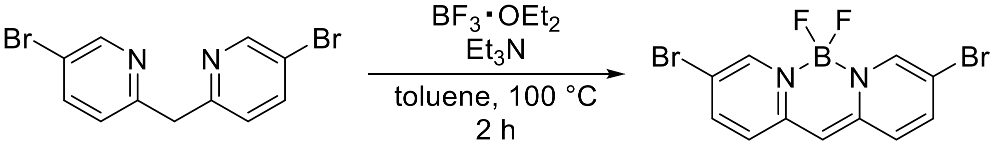
Scheme 1. Chemical structure of dipyridylmethene boron complex



π-Conjugated complexes of group 13 elements have attracted attention because of their unique photophysical properties and variable stimuli-responsiveness. In addition, introducing these complexes into the mainchain of π-conjugated polymers can induce electronic interactions within or between polymer chains. Then, we focused on a dipyridylmethene boron complex, possessing a planar structure and phosphorescent properties (Scheme 1). A pioneering work suggested that their phosphorescent properties are enhanced and depressed depending on the fusing position of the π-system.[1] Therefore, it was envisioned that the introduction of this complex into π-conjugated polymers could lead to changes in both phosphorescent properties and stimuli-responsiveness. Herein, we synthesized a new family of dipyridylmethene boron complexes with various ligand structures (Scheme 2). In the presentation, we will discuss their photophysical properties in detail.

π共役系１３族元素錯体は優れた発光性および種々の刺激応答性を示す有望な骨格である。また、それらをπ共役系高分子鎖中に導入することで、主鎖内あるいは主鎖間での色素間の電子的相互作用を誘起できる。そこで、我々は高い平面性や燐光特性を有するジピリジルメテンホウ素錯体に着目した（Scheme 1）。先行研究ではこの錯体特有の分子軌道に立脚した化学修飾によって燐光特性を制御できることが示唆されている[1]。この錯体の高分子化によって、燐光特性の変調および刺激応答性の発現が期待される。本研究では、高分子化を目指して新規の構造を有するジピリジルメテンホウ素錯体を合成した（Scheme 2）。発表ではそれらの光学特性についても詳述する。

Scheme 2. Synthetic scheme of the dipyridylmethene boron complex



[1] Thompson, M. E. *et al. J. Org. Chem.* **2017**, *82*, 7215−7222.

Solid-State Synthesis of Indium-Fused Azobenzene Complexes from Indium Oxide

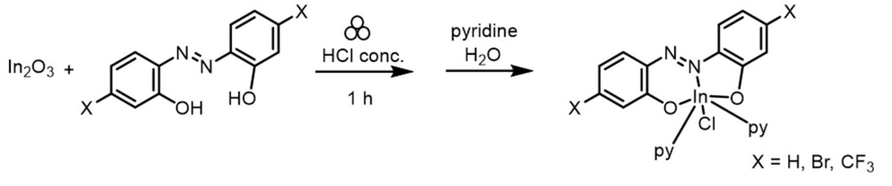
(*Graduate School of Engineering, Kyoto University*) ○Chiaki Hotta, Masayuki Gon, Kazuo Tanaka

Keywords: Indium; Azobenzene; Solid-state synthesis; Luminescence; Hypervalent

Rare metals are indispensable for high-tech industries, whereas their uneven distribution and limited reserves have led to a serious depletion of the resources. Among rare metals, indium is used in many devices as a transparent conducting film (ITO, indium tin oxide), and the recovery of indium from its waste is desired. Conventionally, although various recovery techniques have been proposed[1], simpler and lower-cost recovery methods are required.

From these backgrounds, we focused our attention on solid-state reactions. Solid-state reactions are synthetic methods that minimize the use of solvents, and efficient solvent-free reactions are achieved by the strong mechanical stirring of a ball mill. In fact, Saito *et al.* reported the reduction from ITO to indium metal under a nitrogen atmosphere using Li_3N as a reducing agent.[2] Furthermore, we has designed typical element complexes by combining elements and azobenzene tridentate ligands to create functional luminescent materials. Recently, we reported the creation of functional complexes by solid-state reactions of azobenzene tridentate ligands with organometallic reagents.[3]

In this study, we aimed at simple recovery of indium from ITO and creation of functional compounds by solid-state synthesis. To achieve our goal, indium oxide (In_2O_3) was used as a raw material. As a result, luminescent indium complexes were obtained from In_2O_3 and the azobenzene tridentate ligands by adding a small amount of concd. HCl as a reactant with ball milling for 1 h (Scheme 1). In the presentation, the synthetic conditions and optical properties of the resulting complexes will be discussed in detail.



Scheme 1. Solid-state synthesis of indium-fused azobenzene complexes.

1) Pradhan, D.; Panda, S.; Sukla, L. B. *Miner. Process. Extr. Metall. Rev.* **2018**, *39*, 167–180. 2) Kano, J.; Kobayashi, E.; Tongamp, W.; Miyagi, S.; Saito, F. *J. Alloys Compd.* **2009**, *484*, 422–425. 3) Gon, M.; Kato, T.; Tanimura, K.; Hotta, C.; Tanaka, K. *RSC Mechanochem.* **2024**, *1*, 322–327.

Control of Optical Properties by Metal Complexation Based on Carborane Derivatives

(*Graduate School of Engineering, Kyoto University*) ○Mei Tokutomi, Kazuo Tanaka

Keywords: Carborane; Optical Property; Complexation; Aggregation-Induced Emission; Boron Cluster

Carborane (CB) is a spherical cluster compound consisting of hydrogen, carbon, and boron. It has been revealed that aryl-substituted CB derivatives show intramolecular charge transfer emission and excimer emission in solid state by utilizing intramolecular and intermolecular interaction of CB and π-conjugated systems.[1–3] In this work, we have investigated the effects of metal complexation on optical properties and molecular interactions of aryl-substituted CB derivatives. We especially focus on platinum (II) complexes for exhibiting unique stacking and molecular arrangement behavior in solid state.[4, 5]

We synthesized CB ligands with 2,2'-bipyridyl-substituted at different positions which can coordinate with metal ions (Figure 1). Two CB ligands exhibit similar behavior in absorption and emission to 2,2'-bipyridine. Metal complexation was performed with two ligands (Figure 2). **B4** reacted with $PtCl_2(DMSO)_2$ in acetonitrile solution to afford Pt^{II} complex. **B4** and **B6** reacted with $PtCl_2(DMSO)_2$ in dimethyl sulfoxide solution to afford anionic Pt^{II} complexes with elimination of one boron atom. In this presentation, we will discuss optical properties and the effects of substitute position of CB and metal coordination.

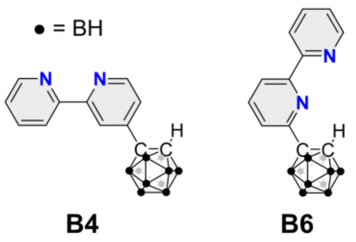


Figure 1. Chemical structures of CB derivatives, **B4** and **B6**.

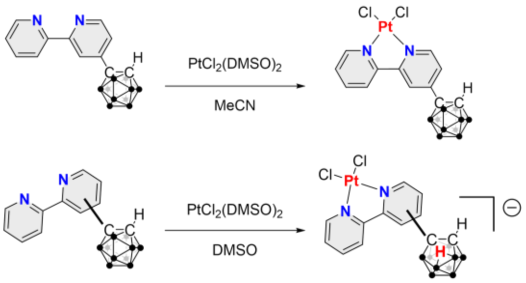


Figure 2. Synthetic scheme of Pt^{II} complexes of CB ligands.

1) Chujo, Y. *et al. Angew. Chem. Int. Ed.* **2017**, *56*, 254.
2) Chujo, Y. *et al. Inorg. Chem.* **2021**, *60,* 8990–8997.
3) Tanaka, Y. *et al. Angew. Chem. Int. Ed.* **2024**, *63*, e202319712.
4) Gray, H. B. *et al. Inorg. Chem.* **1996**, *21*, 6261–6265.
5) Yam, V. W. *et al. Chem. Rev.* **2015**, *15*, 7589–7728.

７員環芳香族配位子からなるホウ素錯体の配位点アミノ化による発光特性への影響

（京大院工）○中島龍星・生越ひかり・伊藤峻一郎・田中一生

Effects of Coordination-Site Amination on the Optical Properties of Boron Complexes with Seven-Membered Aromatic Ligands

(*Graduate School of Engineering, Kyoto University*)
○Ryusei Nakashima, Hikari Ogoshi, Shunichiro Ito, Kazuo Tanaka

Keywords : Aminotropone; Tropolone; Boron Complexes; Optical Properties

Tropolone (**Tp**) shows positively polarized aromaticity derived from the delocalization of 6π-electrons on its seven-membered ring. In our laboratory, it was revealed that **TpB**, the difluoroboron complex of **Tp**, has improved photoluminescence and enhanced aromaticity compared to **Tp**.[1] However, the effect of coordination site structure on the optical and electronic properties is still veiled.

In this work, we focused on the coordination site of **Tp**-based ligand. We converted the hydroxyl group of **Tp** to various amino groups, and synthesized complexes based on the obtained derivatives (Figure 1). DFT calculations of **TpB** and **ATpB-Ph** indicated that **ATpB-Ph** should have longer absorption and photoluminescence wavelengths originating from the smaller energy gap along with the destabilization of the HOMO energy level (Figure 2).

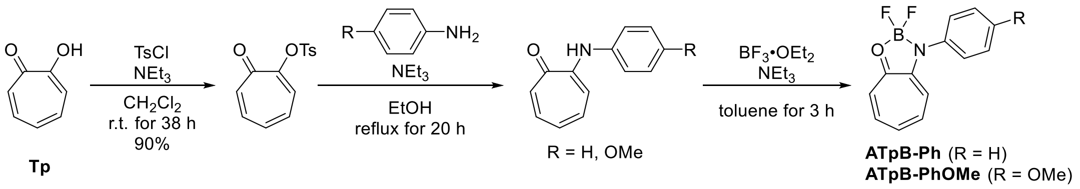


Figure 1. Synthetic scheme of boron complexes investigated in this work.

トロポロン（**Tp**）は７員環上に６π電子が非局在化することで正に分極した芳香族性を示す。当研究室では通常発光しない **Tp** をホウ素錯体化することで発光効率が飛躍的に向上することや芳香族性が増大することを報告してきた[1]。しかし、配位点周辺の構造が光電子物性に与える影響については未開拓である。

そこで、本研究では **Tp** のヒドロキシ基をアミノ基に変換することで、配位点の構造が異なる種々の **Tp** 誘導体を基盤としたホウ素錯体を合成した（Figure１）。**TpB** と **ATpB-Ph** の DFT 計算を行ったところ、アミノ基への変換によって HOMO 準位が大きく上昇し、狭ギャップ化による吸収・発光波長の長波長化を示唆する結果が得られた（Figure 2）。

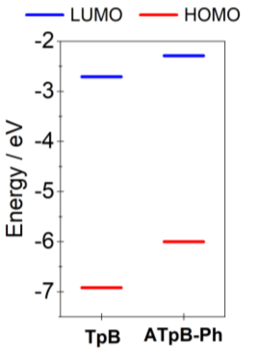


Figure 2. Orbital energy levels of **TpB** and **ATpB-Ph** obtained from DFT calculations.

[1] H. Ogoshi, S. Ito, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2023**, *96*, 452–460.