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

Thu. Mar 19, 2026 1:00 PM - 3:30 PM JST | Thu. Mar 19, 2026 4:00 AM - 6:30 AM UTC | E1122 (1122, Bldg. 11 [2F])

[E1122-3pm] Oral B

Chair: Tetsuo Iwanaga, Akihito Konishi

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC

[E1122-3pm-01] Environment-Responsive Behavior in a Curved Nanographene

○Jingyun Tan[1], Akimitsu Narita[1] (1. Okinawa Institute of Science and Technology Graduate University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC

[E1122-3pm-02] Functionalization of Dibenzo[*hi*,*st*]ovalene at the "Apex" Positions

○SAURAV RAJ[1], Akimitsu Narita[1] (1. Okinawa Institute of Science and Technology Graduate University)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC

[E1122-3pm-03] Exploring the Optical Properties of Stable Phenalenyl Radicals

○Takuto Kohzuma[1], Takashi Kubo[1,2,3], Weiyi Zhou[1] (1. Graduate School of Science, The Univ. of Osaka, 2. ICS-OTRI, The University of Osaka, 3. SRN-OTRI, The University of Osaka)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC

[E1122-3pm-04] Synthesis and Functional Characterization of π-Cluster with Two Pentacene Units

○Yuta Makihara[1], Tomohiko Nishiuchi[1,2], Takashi Kubo[1,2,3] (1. Graduate School of Science, The University of Osaka, 2. ICS-OTRI, The University of Osaka, 3. SRN-OTRI, The University of Osaka)

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

Break

English
2:30 PM - 2:50 PM JST | 5:30 AM - 5:50 AM UTC

[E1122-3pm-05] Charge Transport Properties of a Tetrabenzoporphyrin Derivatives with the Herringbone Superlattice Structure

○Kazuya Miyazaki[1], Keitaro Yamamoto[2], Mitsuaki Yamauchi[2], Yoshiyuki Mizuhata[2], Hiroko Yamada[2] (1. Grad. Sch. Sci., Kyoto Univ., 2. ICR, Kyoto Univ.)

Japanese
2:50 PM - 3:10 PM JST | 5:50 AM - 6:10 AM UTC

[E1122-3pm-06] Synthesis of Triangular Porphyrin Oligomers toward the Construction of Supramolecular Graphene

○Oto Ooyama[1], Yuki Shibata[3], Ken-ichi Yamashita[1,2], Shohei Saito[1] (1. Graduate School of Science, The University of Osaka, 2. ICS-OTRI, The University of Osaka, 3. Graduate School of Science, Kyoto University)

English
3:10 PM - 3:30 PM JST | 6:10 AM - 6:30 AM UTC

[E1122-3pm-07] Energy Modulation of π-Conjugated System Based on Oxidation Number Changes of Hypervalent Antimony Compounds

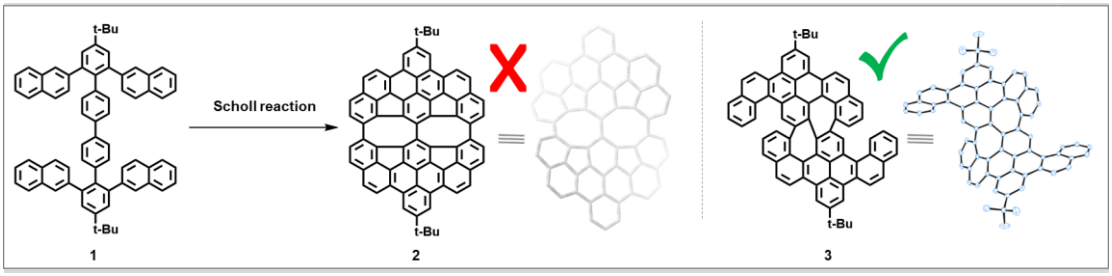
○Masayuki Gon[1], Kazuo Tanaka[1] (1. Kyoto University)

Synthesis of a Curved Nanographene with Environment-responsive Behavior

([1]*Okinawa Institute of Science and Technology*) ○Jingyun Tan,[1] Akimitsu Narita[1]
Keywords: *curved nanographene, environment-responsive emission*

Curved nanographenes that incorporate non-hexagonal rings have attracted increasing attention in view of their distorted π-frameworks with intrinsic strain. These features give access to unconventional conjugated architectures with distinct optical properties and potential for applications in functional materials.[1]

In this study, we report the synthesis and structural characterization of an unexpected curved nanographene that emerged through a rearrangement during the Scholl reaction of precursor **1**. Instead of the anticipated product **2**, the reaction produced heptalene-based nanographene **3** with two incorporated seven-membered rings. Crystallographic analyses confirmed the highly distorted geometry of **3**. Preliminary photophysical investigations have revealed that **3** displays noticeable emission changes upon varying temperature and viscosity. These results underscore the significance of this curved nanographene structure and establish a basis for future development of strained π-systems for environment-sensitive molecular applications.



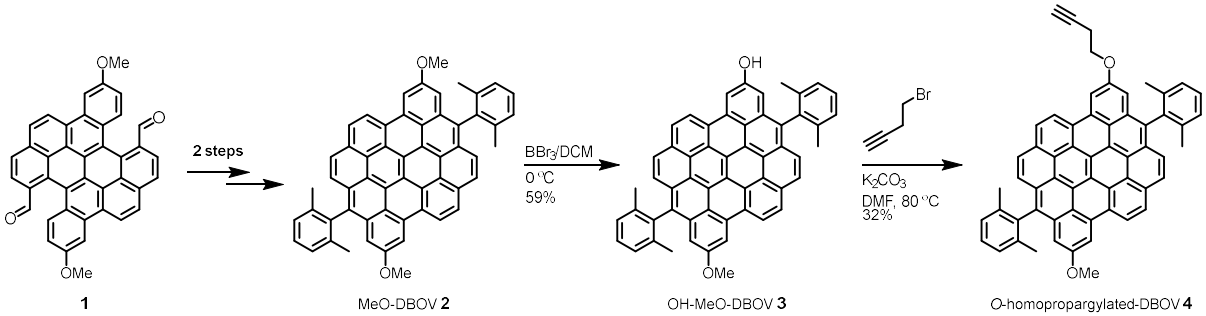
Reference:
(1) (a) Kawasumi, K.; Zhang, Q.; Segawa, Y.; Scott, L.T.; Itami, K. *Nature Chem.* **2013,** *5*, 739-744; (b) Lin, H.-A.; Sato, Y.; Segawa, Y.; Nishihara, T.; Sugimoto, N.; Scott, L.T.; Higashiyama, T.; Itami, K. *Angew. Chem. Int. Ed.* **2018,** *57*, 2874-2878; (c) Qiu, Z.; Asako, S.; Hu, Y.; Ju, C.-W.; Liu, T.; Rondin, L.; Schollmeyer, D.; Lauret, J.-S.; Müllen, K.; Narita, A. *J. Am. Chem. Soc.* **2020,** *142*, 14814-14819; (d) Elbert, S.M.; Paine, O.T.A.; Kirschbaum, T.; Schuldt, M.P.; Weber, L.; Rominger, F.; Mastalerz, M. *J. Am. Chem. Soc.* **2024,** *146*, 27324-27334; (e) Luo, H.; Liu, J. *Angew. Chem. Int. Ed.* **2024,** *63*, e202410759.

Functionalization of Dibenzo[*hi*,*st*]ovalene at the "Apex" Positions

(Okinawa Institute of Science and Technology Graduate University) ○Saurav Raj, Akimitsu Narita

Keywords: Nanographene; Peripheral Functionalization; Hydroxy group; Click reaction

Nanographenes (NGs) are large polycyclic aromatic hydrocarbons (PAHs) that feature defined optical properties dependent on their size, shape, and edge types. Furthermore, functionalization of nanographene provides tunability to its properties. For example, peripheral functionalization is a powerful strategy for tuning the optoelectronic properties, solubility, and intermolecular interactions of nanographene. Our group reported an unprecedented nanographene, dibenzo[*hi*,*st*]ovalene (DBOV), which features zigzag and armchair edges. DBOV displays strong red luminescence, remarkable photostability, and stimulated emission behavior[1]. Furthermore, functionalization of DBOV at the zigzag[2] and bay regions[3] has been established, resulting in DBOV derivatives with various properties. For example, fluoranthene-functionalized DBOV displayed a large Stokes Shift, making it suitable for lasing studies[4]. Azide-functionalized DBOV was used for super-resolution imaging of nascent proteins in neurons using click reaction[5]. Nonetheless, DBOV derivatives functionalized at other peripheral positions have not been investigated. Here we report the "apex" functionalization of DBOV at its 4- and 12-positions. We have previously achieved Cl-DBOV functionalized with chloro groups at its apex positions[6] We also functionalized the "apex" positions with two methoxy groups using its key intermediate **1**[7]. Precursor **1** was further utilized to synthesize MeO-DBOV **2**, which upon controlled BBr_3-mediated demethylation, gave OH-MeO-DBOV **3**. K_2CO_3-DMF mediated etherification of **3** resulted in an *O*-homopropargylated-DBOV **4** as a blue solid. DBOV **4** features an alkyne handle, which is expected to allow its click-chemistry-based fluorescent tagging toward bioimaging applications.



1 MeO-DBOV **2** OH-MeO-DBOV **3** *O*-homopropargylated-DBOV **4**

1) G. M. Paternò, Q. Chen, X.-Y. Wang, J. Liu, S. G. Motti, A. Petrozza, X. Feng, G. Lanzani, K. Müllen, A. Narita and F. Scotognella, *Angew. Chem. Int. Ed.*, **2017**, 56, 6753-6757. 2) Q. Chen, S. Thoms, S. Stöttinger, D. Schollmeyer, K. Müllen, A. Narita and T. Basché, *J. Am. Chem. Soc.*, **2019**, 141, 16439-16449. 3) Q. Chen, D. Wang, M. Baumgarten, D. Schollmeyer, K. Müllen and A. Narita, *Chem. Asian J.*, **2019**, 14, 1703-1707. 4) G. M. Paternò, Q. Chen, R. Muñoz-Mármol, M. Guizzardi, V. Bonal, R. Kabe, A. J. Barker, P. G. Boj, S. Chatterjee, Y. Ie, J. M. Villalvilla, J. A. Quintana, F. Scotognella, K. Müllen, M. A. Díaz-García, A. Narita and G. Lanzani, *Mater. Horiz.*, **2022**, 9, 393-402. 5) X. Zhu, Q. Chen, H. Zhao, Q. Yang, Goudappagouda, M. Gelléri, S. Ritz, D. Ng, K. Koynov, S. H. Parekh, V. K. Chetty, B. K. Thakur, C. Cremer, K. Landfester, K. Müllen, M. Terenzio, M. Bonn, A. Narita and X. Liu, *J. Am. Chem. Soc.*, **2024**, 146, 5195-5203. 6) R. Muñoz-Mármol, S. Raj, M. Russo, G. Serra, H. Zhao, G. Bassi, A. Lucotti, F. Scotognella, G. Cerullo and G. Lanzani, *Small Methods*, **2025**, 2500419. 7) S. Raj, A. Narita, 105th CSJ Meeting, **2025**, [F]2201-1am-13.

Exploring the Optical Properties of Stable Phenalenyl Radicals

([1]*Graduate School of Science, The University of Osaka*, [2]*ICS-OTRI, The University of Osaka,* [3]*SRN-OTRI, The University of Osaka*) ○Takuto Kohzuma,[1] Zhou Weiyi,[1] Takashi Kubo[1,2,3]

Keywords: Phenalenyl radical; Doublet Emission

In recent years, organic radical molecules have attracted increasing attention as novel optoelectronic materials due to their open-shell electronic configurations, which differ fundamentally from those of closed-shell systems. However, the practical utilization of organic radicals has long been hindered by their intrinsic chemical instability, including susceptibility to oxygen and moisture and a strong tendency to form σ-dimers through facile dimerization. The phenalenyl radical possesses a high level of symmetry (D_{3h}) and is the smallest graphene fragments, that consists of solely six-membered rings. With the wide attention phenalenyl chemistry has received over the last 60 years, our understanding of the electronic structure and spectroscopy of the phenalenyl radical has remained sparse.[1,2] Herein, we report 2,5,8-trihalogenatedphenalenyl radical (**X_3-PLY**) as a stable, emissive phenalenyl derivative. **X_3-PLY** shows a monomer–π-dimer equilibrium in solution.

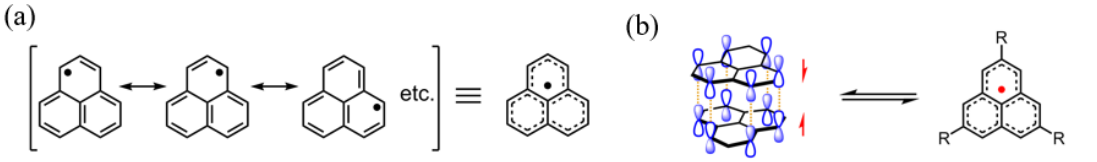


Figure 1. (a) Resonance structures of Phenaleny Radical (b) Equilibrium between π–dimer and monomer

The origin of the luminescence was confirmed by VT-ESR / NMR, and VT-UV-Vis-NIR to be from the monomer. Its high quantum yield, high air stability ($t_{1/2}$ ~ 2 days) and long-lived emission (τ ~ 300 ns) demonstrate the potential of phenalenyl radicals as promising luminescent materials beyond conventional trityl-based systems.[3]

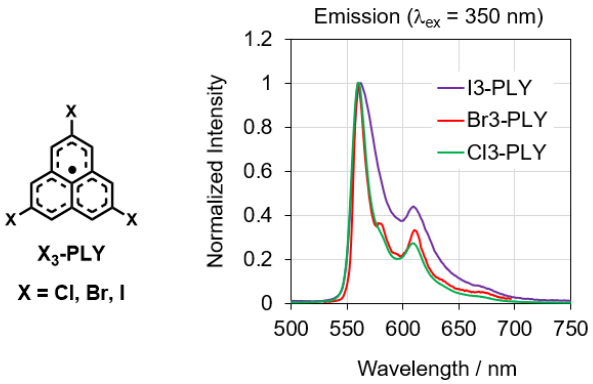


Figure 2. Emission Spectrum of halogenated phenalenyl radicals

1) W. Cofino, S. Van Dam, D. Kamminga, G. Hoornweg, C. Gooijer, C. Maclean, N. Velthorst, *Mol. Phys.* **1984**, *51*, 537. 2) G. D. O'Connor, T. P. Troy, D. A. Roberts, N. Chalyavi, B. Fückel, M. J. Crossley, K. Nauta, J. F. Stanton, T. W. Schmidt, *J. Am. Chem. Soc.* **2011**, *133*, 14554. 3)T. Kohzuma, K. Sugita, Y. Tani, M. Metzelaars, T. Kubo, *Org. Lett.* **2025**, *27*, 6019.

Synthesis and Functional Characterization of π-Clusters with Two Pentacene Units

([1]*Graduate School of Science, The University of Osaka,* [2]*ICS-OTRI, The University of Osaka,* [3]*SRN-OTRI, The University of Osaka*) ○Yuta Makihara[1], Tomohiko Nishiuchi[1,2], Takashi Kubo[1,2,3]

Keywords: *Pentacene, π-cluster, Excimer, Dimer, Through-space interaction*

The molecular orbitals of a π-congested system, in which the distance between two π-planes is less than the sum of the van der Waals radii of carbon atoms (3.40 Å), interact strongly, leading to a reduced HOMO-LUMO energy gap and unique redox and photophysical properties. Previously, we reported a compound in which two anthracene units were introduced at the neighboring positions of a benzene ring, and this showed excimer emission at room temperature and formation of photoisomer that can be reverted by heating or mechanical grinding.[1]

On the other hand, pentacene has attracted attention owing to its narrow HOMO–LUMO gap and unique electronic and optical properties. Therefore, numerous molecules including multiple pentacene units have been reported. Such compounds are important for understanding the interactions between higher acenes. However, only a few molecules have been reported in which pentacene units are placed in proximity.

In this study, we designed and synthesized compound **1** in which two pentacene units are placed at adjacent positions of a benzene ring (Figure 1a). Compound **1** was successfully obtained, and its structure was elucidated by X-ray crystallography (Figure 1b). This revealed that the distance between the C6 carbon atoms of the two pentacene units is exceptionally short (2.96 Å). Interestingly, no excimer emission was observed for compound **1** in contrast to the anthracene dimers. In this presentation, we will discuss the synthesis of compound **1** and the differences in physical properties with related compounds.

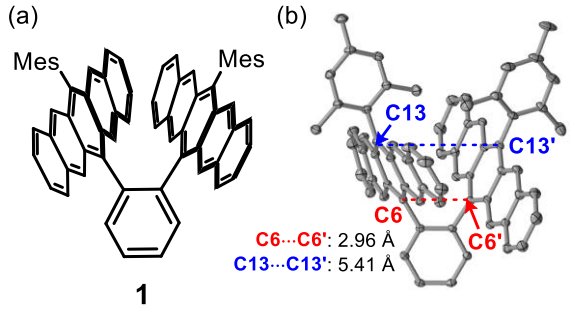


Figure 1. (a)The structure of compound **1** and (b) its crystal structure

1) T. Nishiuchi, S. Uno, Y. Hirao, T. Kubo, *J. Org. Chem.,* **2016**, *81*, 2106-2112.

Charge Transport Properties of a Tetrabenzoporphyrin Derivative with the Superlattice Herringbone Structure

([1]*Institute for Chemical Research, Kyoto University*) ○ Kazuya Miyazaki,[1] Keitaro Yamamoto,[1] Mitsuaki Yamauchi,[1] Yoshiyuki Mizuhata,[1] Hiroko Yamada[1]

Keywords: porphyrins; crystal structure analysis; organic semiconductors

In organic field-effect transistors (OFETs), precise control of crystal packing is essential for realizing two-dimensional charge-transport pathways and achieving high charge-carrier mobility. Among various packing motifs, the herringbone (HB) structure is known to afford efficient lateral transport. We have previously demonstrated that substituent-controlled HB packing in tetrabenzoporphyrins (TBPs) leads to high hole mobilities in OFETs[(1-3)].

In this study, we report the charge-transport properties of a unique superlattice HB structure formed via a solvent-desorption-induced single-crystal-to-single-crystal (SCSC) transformation. 5,15-Bisphenyl-tetrabenzoporphyrin (**Ph-TBP**) forms a cocrystal composed of alternating layers of HB-packed **Ph-TBP** and *o*-dichlorobenzene (*o*-DCB) upon low-temperature recrystallization. Subsequent vacuum heating removes the intercalated *o*-DCB molecules and induces a structural transformation in which alternating **Ph-TBP** layers rotate by 90°, resulting in a superlattice composed of two orthogonally oriented HB packings.

Marcus hopping calculations predict favorable two-dimensional charge transport within both constituent layers of the superlattice. Single-crystal bottom-gate top-contact OFETs fabricated on Si/SiO_2 substrates exhibit anisotropic hole mobilities of 3.8 ± 1.8 $cm^2\ V^{-1}\ s^{-1}$ along the b-axis and 1.5 ± 0.5 $cm^2\ V^{-1}\ s^{-1}$ along the c-axis, with a maximum mobility of 11.3 $cm^2\ V^{-1}\ s^{-1}$, representing the highest value reported for porphyrin-based semiconductors. Detailed crystal structures, device fabrication procedures, and charge-transport characteristics will be presented.

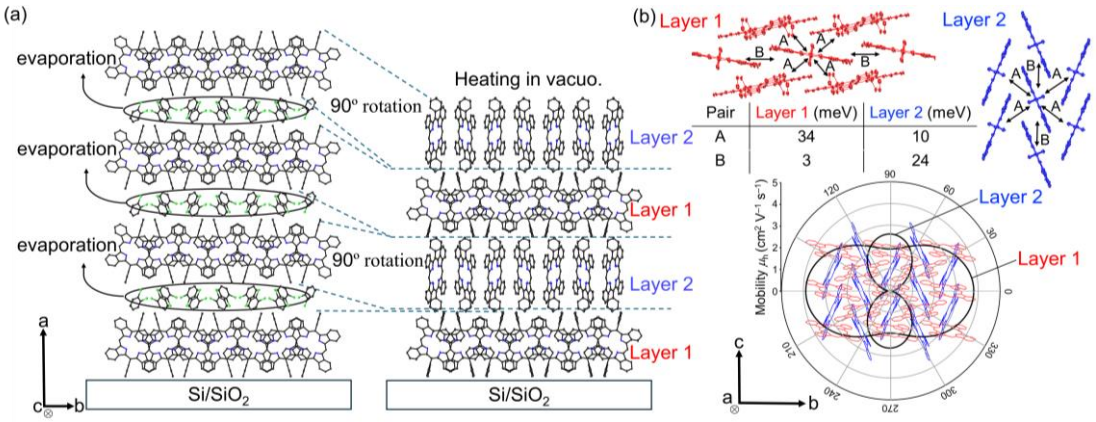


Figure 1. (a) SCSC transformation from the cocrystal of **Ph-TBP** with *o*-DCB to superlattice HB structure formed on a substrate. (b) Calculated charge-transfer integrals and theoretical charge-carrier mobilities calculated using the Marcus hopping model for each layer.

1) K. Miyazaki et al. *Org. Lett.* **2023**, *25*, 7354. 2) K. Miyazaki et al. *Adv. Mater. Interfaces* **2025**, *12*, 2400946. 3) K. Miyazaki et al. *J. Porphyr. Phthalocyanines* **2025**, *29*, 213.

超分子グラフェン構築に向けた 三角形ポルフィリンオリゴマーの合成

（阪大院理[1]・ICS-OTRI[2]・京大院理[3]）○大山 央登[1]・柴田 裕貴[3]・山下 健一[1,2]・齊藤 尚平[1]

Synthesis of Triangular Porphyrin Oligomers toward the Construction of Supramolecular Graphene ([1]*Graduate School of Science, The University of Osaka*, [2]*ICS-OTRI, The University of Osaka,* [3]*Graduate School of Science, Kyoto University*) Oto Ooyama,[1] Yuki Shibata,[3] Ken-ichi Yamashita,[1,2] Shohei Saito[1]

By replacing the sp^2 carbon in graphene as a single triangular molecule and arranging these molecules such that their edges strongly interact, the resulting 2D nanosheet is expected to show an electronic band structure similar to that of graphene. However, with reported triangular molecules designed for edge-to-edge interaction, such sheet-like structures have not yet been realized due to steric hindrance at the vertices. In this study, we designed triangular molecules in which cyclooctatetraene (COT) units are placed at the vertices and porphyrins are incorporated along the edges. Construction of the nanosheet through formation of double-decker complexes based on this triangular molecule has been tried. We will focus on the synthesis of the triangular and polygonal molecules, as well as preliminary investigations into their metal complexation.

Keywords : Macrocycle; Triangle Molecule; Porphyrin; Double-decker complex; COT

グラフェンの sp^2 炭素を一つの三角形分子と見なして辺同士が相互作用するように配列すれば、グラフェンと同様の電子バンド構造をもつシート状化合物が得られると考えられる(**Fig. 1**)。既存の辺同士を相互作用させる三角形分子では頂点部分の立体障害や辺同士がずれて相互作用するなどの理由からシート状化合物は得られていない[1,2]。そこで本研究では頂点部分にシクロオクタテトラエン(COT)、辺部分にポルフィリンを採用し、辺同士でダブルデッカー錯体を形成する三角形分子を設計した。既報のポルフィリンテトラオン体 **1A**[3] とテトラアミノジベンゾ COT **1B**[4]を混合し、加熱撹拌することで目的の三角形分子(n=3)に加えて、対面型二量体から六角形分子(2≦n≦6)の生成が確認された。当日は各化合物の物性・錯化の検討について報告する。

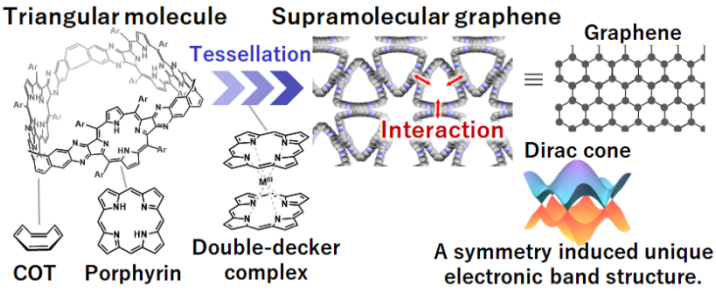
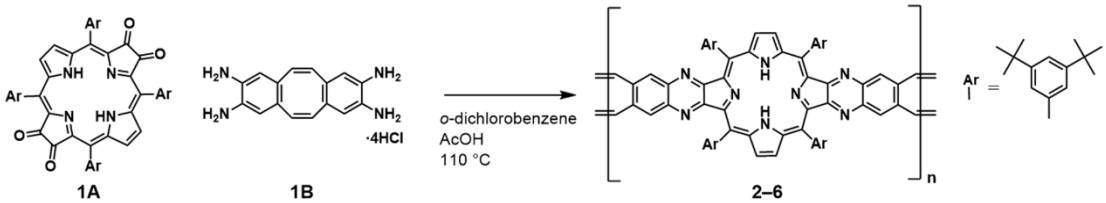


Figure 1. Concept of this work.



1) K. Awaga *et al*., *J. Am. Chem. Soc.* **2015**, *137*, 7612. 2) J. F. Stoddart *et al*., *J. Am. Chem. Soc.* **2019**, *141*, 17783. 3) P. L. Burn *et al*., *J. Chem. Soc*., *Perkin Trans. 1* **2001**, 14. 4) S. Saito *et al*., *Bull. Chem. Soc. Jpn*. **2021**, *94*, 1999.

Energy Modulation of π-Conjugated System Based on Oxidation Number Changes of Hypervalent Antimony Compounds

(*Graduate School of Engineering, Kyoto University*)
○Masayuki Gon, Kazuo Tanaka
Keywords: Antimony; Hypervalent; Luminescence; Chromism; π-Conjugated system

A hypervalent compound is a class of molecules in which a main-group element has more than eight electrons in its valence shell, exceeding the limits of the Lewis octet rule. Recently, we discovered a unique electronic effect of hypervalent bonds on a linked π-conjugated system originating from polarized three-center four-electron (3c-4e) bonds.[1] In addition, we found that the electronic properties of the π-conjugated system can be moderated by the situation of the hypervalent element center, such as coordination numbers and geometry. Herein, we focused on antimony (Sb) in group 15, fifth period. Antimony has different oxidation numbers (+3 and +5), and unique electronic properties are expected to be obtained from hypervalent antinomy compounds depending on the oxidation numbers.

We synthesized the hypervalent antimony compounds **Sb** and **SbN** as the trivalent antimony compounds (Figure 1).[2] **Sb** and **SbN** were oxidized in a reaction with the oxidant, *o*-chloranil. As a result, pentavalent antimony compounds, **Sb-Cl** and **SbN-Cl**, were obtained, respectively. Interestingly, the reaction can proceed with a mechanochemical stimulus and a unique chromism depending on the substituents was observed. In the case of **Sb**, the oxidation reaction to **Sb-Cl** proceeded with hypsochromic shifts in the absorption spectra because of an increase in coordination numbers. In contrast, the oxidation reaction of **SbN** to **SbN-Cl** induced bathochromic shifts in the absorption spectra because of the formation of a donor–acceptor system. These results prove that controlling the oxidation number should be a novel strategy for modulating the energy of π-conjugated systems.

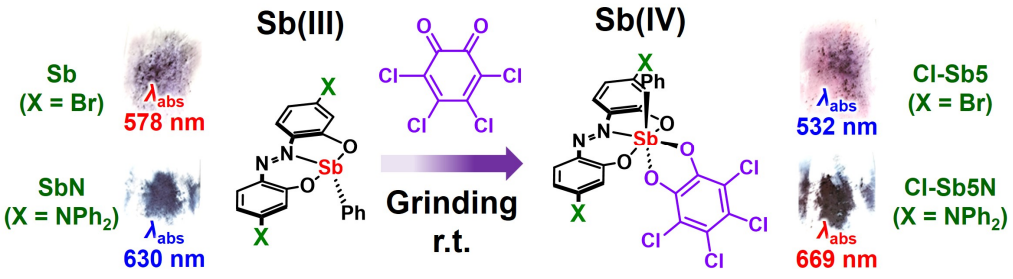


Figure 1. Oxidation reactions from **Sb** and **SbN** to **Cl-Sb5** and **Cl-Sb5N** with *o*-chloranil, respectively, and photographs before and after the reaction with grinding process.

1) Gon, M.; Tanaka, K. *Eur. J. Org. Chem.* **2024**, *27*, e202400738.
2) Tanimura, K.; Gon, M.; Tanaka, K.; Chujo, Y. *Adv. Funct. Mater.* **2025**, *35*, 2418600.