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

Tue. Mar 19, 2024 3:55 PM - 5:15 PM JST | Tue. Mar 19, 2024 6:55 AM - 8:15 AM UTC E1121(1121, Bldg. 11 [2F])

[E1121-2vn] 11. Organic Chemistry -Structural Organic Chemistry-

Chair: Tomohisa Sawada, Yohei Haketa

Japanese
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[E1121-2vn-01]

Direct evidence for a carbon•carbon one-electron σ-bond and its nature

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English
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[E1121-2vn-02]

Predicting Solid Mixing Ratios Using Image-based Machine Learning and Application to Chemical Reaction Analysis

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English
4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC
[E1121-2vn-03]

A Coordination Cage as a Crystalline Sponge

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Japanese
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[E1121-2vn-04]

Regioselective coordination toward metal ion and regioselective metal ions exchange by Pentakis(armed-cyclen)s: Molecular Othello

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炭素·炭素一電子結合：存在の実証とその性質

（北大院理[1]・北大創成研究機構[2]・北大理[3]）○島尻 拓哉[1,2]・川口 聡貴[3]・鈴木 孝紀[1]・石垣 侑祐[1]

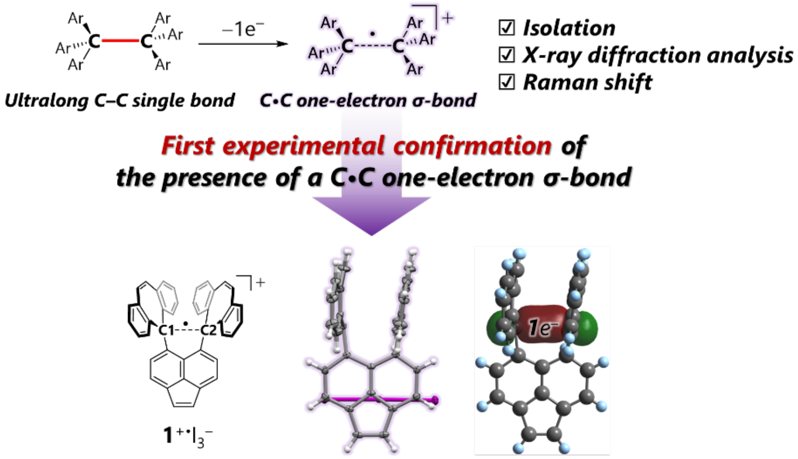
Direct evidence for a carbon•carbon one-electron σ-bond and its nature

([1,3]*Faculty of Science, Hokkaido University*, [2]*Creative Research Institution, Hokkaido University*) ○ Takuya Shimajiri,[1,2] Soki Kawaguchi,[3] Takanori Suzuki,[1] Yusuke Ishigaki[1]

As early as 1931, Pauling postulated the existence of one-electron bonds.[1] However, in striking contrast to the large body of work on electron-pair bonds, the paucity of examples with one-electron bonds is remarkable,[2-4] which is most likely due to their intrinsic weakness. In this work, we disclose the synthesis and isolation of radical cation salt with a carbon•carbon one-electron σ-bond (2.921(3) Å at 100 K). The presence of the bond was demonstrated by experimental and theoretical investigations. Such a carbon•carbon one-electron bond can induce near-infrared-absorbing properties even with just one σ-bond in contrast to common organic near-infrared-absorbing materials.

Keywords : One-electron bond; X-ray analysis; Raman spectroscopy; Near-infrared absorption

Pauling が一電子結合を提案して以来[1]、その存在について多くの調査がなされてきた。一方で、現在まで X 線構造解析によりその存在が実証された例は極めて少なく[2-4]、中でも炭素原子間ではおよそ百年にわたって報告例がない。本研究では、炭化水素 **1** の一電子酸化により、炭素•炭素一電子結合を有するラジカルカチオン $\mathbf{1}^{\bullet+}\mathrm{I}_3^{-}$の合成、X 線構造解析に成功した。$\mathbf{1}^{\bullet+}\mathrm{I}_3^{-}$は 2.921(3) Å の近接した炭素原子間距離を有しており、ラマン測定によって C–C 対称伸縮振動に対応するラマンシフトが観測されたことから、炭素原子間における一電子結合を直接的に初めて実証した。また、この一電子結合の小さな軌道の分裂に基づいて、$\mathbf{1}^{\bullet+}\mathrm{I}_3^{-}$は近赤外光吸収特性を示したので、その詳細を報告する。



1) L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225.; 2) G. Bertrand *et al., Science* **1998**, *279*, 2080.; 3) J. C. Peters *et al., J. Am. Chem. Soc.* **2013**, *135*, 3792.; 4) M. Wagner *et al., Angew. Chem. Int. Ed.* **2014**, *53*, 4832.

Predicting Solid Mixing Ratios Using Image-based Machine Learning and Application to Chemical Reaction Analysis

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○Hayato Shirakura,[1] Taichi Sano,[1] Yuki Ide,[2] Sheng Hu,[2] Ichigaku Takigawa,[2,3] Yasuhide Inokuma[1,2]

Keywords: Machine Learning; Enantiomer Ratio; Mixing Ratio Prediction; Reaction Yield Prediction; Organic Crystal

Machine learning is recently used as a powerful tool for discovering relationships between complex chemical parameters, and enabling predictions in chemical reactions and molecular design. Our laboratory recently reported machine learning systems that instantly predicts mixing ratios of sugar and dietary salt from their images[1]. Image-based prediction has potentials to analyze objects that are difficult to identify with human eyes. In this research, we explored the practical applicability of this machine learning system for chemical research.

Crystal polymorphs are defined as different crystal structures of the same compound, and instrumental analysis methods are limited to the solid state. It was assumed that glycine with different crystalline polymorphs of α- and γ-from can be visually distinguished. Machine learning model built from 300 images of 200 mg α- and γ-glycine mixtures and their mixing ratios (training data) can predict mixing ratios from images with an error of 4.0% (**Figure 1a**). Prediction of the enantiomeric ratio of D-/L-tartaric acid was also possible, although the difference between the crystals was more difficult to distinguish with naked eyes. Furthermore, yield prediction was conducted as an application to chemical reaction. Reaction yield prediction of *m*-aminophenol obtained by solid-state decarboxylation for *p*-aminosalicylic acid was achieved with an error of 5.7% by using sample images and ^{1}H NMR yields (**Figure 1b**). As an example of more practical systems in chemical research, we attempted to predict the mixing ratios using sample solutions. The enantiomeric ratio was predicted from evaporated solid-state images of solutions containing (*R*)- or (*S*)-1,1'-binaphthyl with an error of 6.8% (**Figure 1c**).

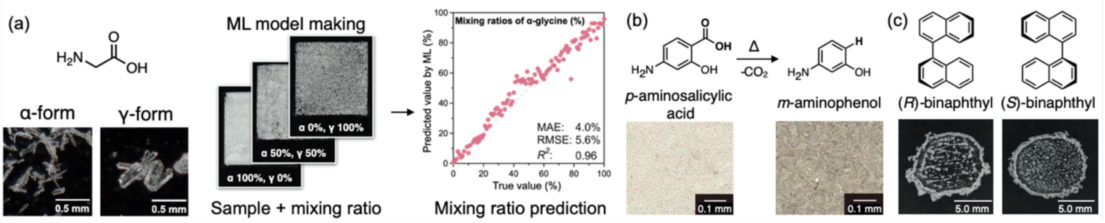

Figure 1. (a) Crystal polymorph mixing ratio prediction results from α- and γ-glycine crystal images. (b) Yield prediction using solid-state reaction images. (c) Enantiomeric ratio prediction using droplet drying images.

1) Y. Ide, H. Shirakura, T. Sano, M. Murugavel, Y. Inaba, S. Hu, I. Takigawa, Y. Inokuma, *Ind. Eng. Chem. Res.* **2023**, *62*, 13790.

A Coordination Cage as a Crystalline Sponge

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○Wei He,[1] Hiroki Takezawa,[1] Makoto Fujita[1,2,3]

Keywords: Coordination Cage, Molecular Recognition, Crystalline Sponge

The crystalline sponge (CS) method has emerged as an innovative X-ray technique for single-crystal diffraction analysis, eliminating the need for the traditional crystallization of analytes.[1] However, certain limitations persist, including constraints on the molecular size and polarity of analytes. In this study, we employ an M_6L_4 cage, a self-assembled molecular host with well-established host-guest chemistry,[2] as an enhanced CS to address the limitations of the original method. Large aromatic polysulfonates, or "*sticker*" anions, significantly facilitate the crystallization of the cage and circumvent the issue of static guest disorder encountered in crystallographic analysis by producing crystals in a low space group symmetry (typically, *P*-1). Benefiting from the large cavity of the cage coupled with its strong guest-binding properties, the enhanced CS allows for the analysis of a broader spectrum of analytes, including rare synthetic molecules, water-soluble molecules, and large amphiphilic molecules with a molecular weight up to ~1200.

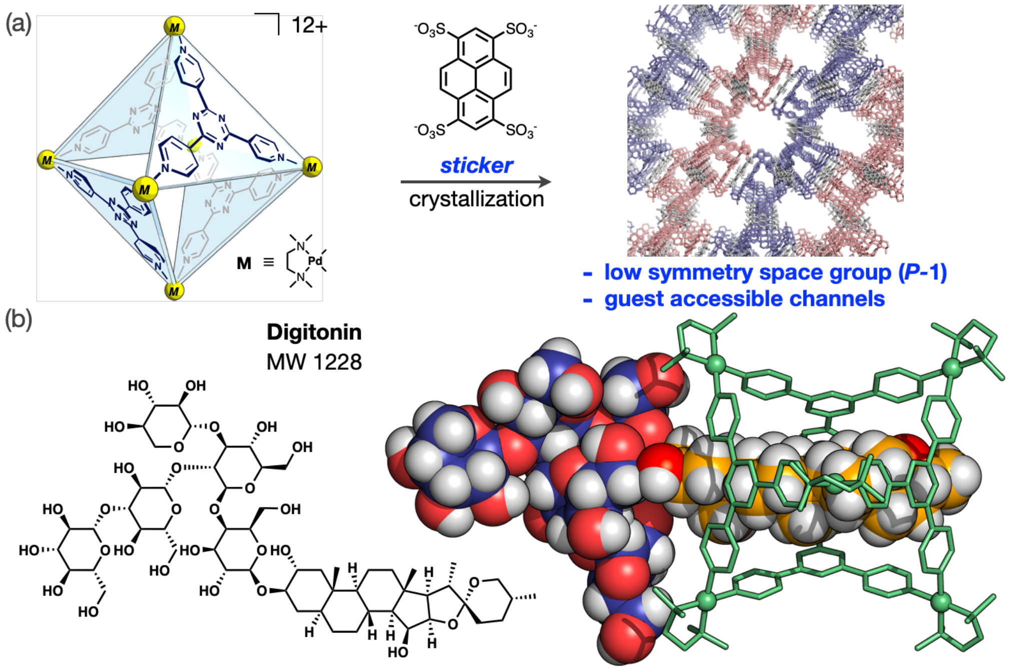

Fig.1. (a) Crystallization of an M_6L_4 cage into a potent crystalline sponge. (b) Crystal structures of guests were determined using an M_6L_4 cage as a crystalline sponge.

1) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen, M. Fujita, *Nature*. **2013**, *496*, 461. 2) H. Takezawa, M. Fujita, *Bull. Chem. Soc. Jpn*. **2021**, *94*, 2351.

ペンタキス（アームドサイクレン）による金属イオンに対する位置選択的な配位と位置選択的な金属イオン置換：分子オセロ

（東邦大理 [1]・東邦大複合物性研究セ [2]・千葉工大工 [3]）○堀田拓希 [1]・池田茉莉 [3]・桑原俊介 [1,2]・幅田揚一 [1,2]

Regioselective coordination toward metal ion and regioselective metal ions exchange by Pentakis(armed-cyclen)s: Molecular Othello

([1]*Department of Chemistry and* [2]*Research Center for Materials with Integrated Properties, Toho University,* [3]*Department of Chemistry, Education Center, Chiba Institute of Technology*) ○Hiroki Horita,[1] Mari Ikeda,[3] Shunsuke Kuwahara,[1,2] Yoichi Habata[1,2]

L1 (**Fig. 1**), which consists of three tetra-armed cyclens, coordinates regioselectively to Ag$^+$ by the electron density of the aromatic side arms.[1] In this study, we designed **L2** (**Fig. 1**) which has more cyclen moieties, and aimed to develop a molecule that exhibits unprecedented complexation behavior by regioselective coordination to Ag$^+$ and metal ions exchange.

We added metal ions to **L2** and confirmed the complexation behavior by ^{1}H and ^{19}F NMR. When Ag$^+$ was added, the central three cyclens with MeO groups formed complexes with Ag$^+$ by regioselective coordination. When Hg^{2+} was added, the cyclens at both ends that had not formed complexes coordinated to Hg^{2+} first, and metal ions exchange (Ag$^+$→Hg^{2+}) occurred in the three cyclens in the center after adding more Hg^{2+}. This behavior is similar to that of a disk's front and back sides in an Othello game, indicating that **L2** behaves as a "Molecular Othello".

Keywords: Cyclen; Regioselective Coordination; Electron Density; Silver Ion; Metal Ions Exchange

テトラアームドサイクレンを 3 個連結した配位子 **L1**（**Fig. 1**）は芳香環側鎖の電子密度を変えることで Ag$^+$に対して位置選択的に配位する．[1] 本研究では，さらに多くのサイクレンを連結した配位子 **L2**（**Fig. 1**）を設計し，Ag$^+$に対する位置選択的な配位と他の金属イオンを用いた金属イオン交換によって，これまでにない錯形成挙動を示す分子の開発を目的とした．

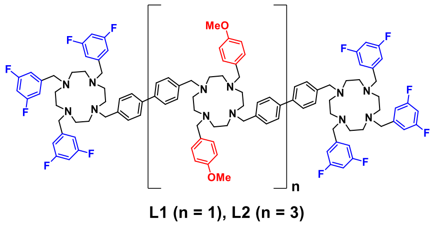

Figure 1. 配位子の構造.

L2 に金属イオンを添加し，^{1}H と ^{19}F NMR で錯形成挙動を確認した．まず Ag$^+$を添加すると位置選択的な配位により，4-メトキシベンジル基を持つ中央の 3 個のサイクレンが Ag$^+$と錯体を形成した．そこに Hg^{2+}を添加していくと，錯形成していない両端のサイクレンが先に Hg^{2+}と錯体を形成し，さらに加えると中央の 3 個のサイクレンで金属イオン置換（Ag$^+$→Hg^{2+}）が起こった．これはオセロゲームにおいてディスクの表と裏が入れ替わるような挙動であり，**L2** が「分子オセロ」として振る舞うことがわかった．

[1] H. Horita *et al. Inorg. Chem.*, **2023**, *62 (31)*, 12272–12282.