Academic Program [Oral B] | 09. Coordination Chemistry, Organometallic Chemistry：Oral B

Wed. Mar 26, 2025 1:00 PM - 3:40 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:40 AM UTC
[B]A301(A301, Bldg. 1, Area 2 [3F])

[[B]A301-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Mio Kondo, Shun Ohta

English
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[B]A301-1pm-01]

Vapochromic behavior of a dicationic nickel(II) complex having benzimidazolylmethyl-functionalized NHC ligands induced by organic vapors with low coordinating ability

〇Tatsunari Murakami[1], Atsunobu Masuno[2], Masaaki Okazaki[1], Shun Ohta[1] (1. Grad. Sch. of Sci. and Tech., Hirosaki Univ., 2. Grad. Sch. of Eng., Kyoto Univ.)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[B]A301-1pm-02]

Charge-carrier transport properties in dehydrobenzoannulene-based conductive 2D metal–organic frameworks

〇Enzo Ohkubo[1], Naoya Aizawa[1], Kaoru Ohta[2], Keisuke Tominaga[2], Ken-ichi Nakayama[1], Mitsuharu Suzuki[1] (1. Osaka Univ., 2. Kobe Univ.)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[B]A301-1pm-03]

Electrochemical Properties of a New Water-Soluble Ni-NHC Complex Tethered to Triethylene Glycol Moieties

〇Chen Liao[1], Kosei Yamauchi[1], Ken Sakai[1] (1. Kyushu Univ.)

English
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[B]A301-1pm-04]

Self-Assembled Nickel Catalysts from Simple Building Blocks For Trifluoromethylation and High Oxidation State Stabilization

〇Aleksandr Sorvanov[1], Shubham Deolka[1], Eugene Khaskin[1], Julia Khusnutdinova[1] (1. Okinawa Institute of Science and Technology)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[[B]A301-1pm-05]

Kinetic Activation of the Redox Processes in Dinuclear Nickel Complexes Induced by Structural Distortion

〇Takuya Hirose[1], Yuma Morimoto[1], Makoto Yamashita[1] (1. Institute of Science Tokyo)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[B]A301-1pm-06]

Development of metalloporphyrin-based supramolecular framework catalysts for oxygen atom transfer reactions

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○Akira YONEDA[1], Taito WATANABE[1], Marc Alec Dominic Ong YAU[1], Kento KOSUGI[2], Yutaka SAGA[1], Testuya KAMBE[1], Mio KONDO[2], Shigeyuki MASAOKA[1] (1. Osaka University, 2. Institute of Science Tokyo)

🏷 English

3:00 PM - 3:20 PM JST | 6:00 AM - 6:20 AM UTC

[[B]A301-1pm-07]

Stimuli-Triggered PCET ON-OFF Switching by Metastable Ruthenium Complex

○Masanari Hirahara[1], Yuya Matsuzaki[1], Kanon Taniguchi[1], Yuto Yane[1] (1. Osaka Institute of Technology)

🏷 English

3:20 PM - 3:40 PM JST | 6:20 AM - 6:40 AM UTC

[[B]A301-1pm-08]

Hydrogen-evolving homo-coupling reactions of boronic acids by photoredox cascade catalyst

○Atsushi Kobayashi[1] (1. Hokkaido University)

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Vapochromic behavior of a dicationic nickel(II) complex having benzimidazolylmethyl-functionalized NHC ligands induced by organic vapors with low coordinating ability

([1] *Grad. Sch. of Sci. and Tech., Hirosaki Univ.*, [2] *Grad. Sch. of Eng., Kyoto Univ.*) ○ Tatsunari Murakami,[1] Atsunobu Masuno,[2] Masaaki Okazaki,[1] Shun Ohta[1]

Keywords: Nickel; *N*-Heterocyclic Carbene; Vapochromic Behavior; Single Crystal X-ray Structure Analysis; Volatile Organic Compounds.

Vapochromism, a vapor-induced reversible color change of materials, using 3d transition metal complexes is a useful method for sensing volatile organic compounds (VOCs).[1)] As this vapochromism is usually induced by the coordination of VOC molecules to the metal center, the coordinating ability of VOCs is a key-factor of the vapochromism, and the sensing of VOCs with low coordinating ability by this method is necessarily difficult. This study found that Ni(II) complex **1** (Fig. 1) can exhibit vapochromic behavior toward VOCs with low coordinating abilities.[2)]

Complex **1** was synthesized from **L1·HCl** and $NiCl_2(PPh_3)_2$ via a transmetallation method (Fig. 1). In the solid state, **1** forms a mille-feuille-like packing structure mainly composed of layers of **1** and water (Fig. 2a). The water layer also includes chloride anions. The yellow powder of **1** was reversibly converted to the green solid of **acetone@1** or **CH_2Cl_2@1** by the vapor of acetone or CH_2Cl_2, respectively (Fig. 2b). These reversible color changes were supported by the powder XRD and diffuse reflectance spectroscopic measurements. A comparison of the XANES spectra of the powder of **1** and **acetone@1** suggested that the coordination geometry of the nickel center is maintained to square planar even after an acetone sensing (Fig. 2c). We will also discuss the vaporchromic mechanism based on XAFS measurements and DFT calculation.

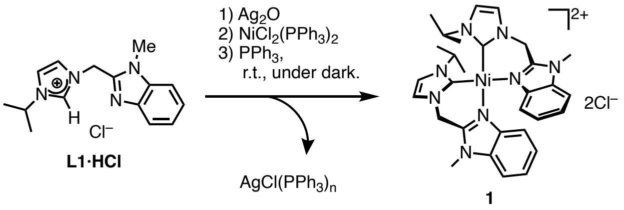

Fig. 1 Synthesis of **1**.

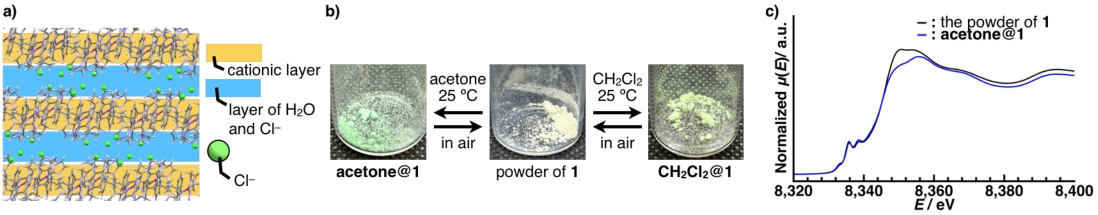

Fig. 2 (a) Packing structure of **1**. (b) Vapochromic behavior of the powder of **1** induced by vapor of acetone or CH_2Cl_2. (c) The Ni K-edge XANES spectra of the powder of **1** and **acetone@1**.

1) Wenger, O. S. *Chem. Rev.* **2013**, *113*, 3686–3733. 2) Alvertz, S. *Chem. Eur. J.*, **2020**, *26*, 4350–4377.

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Charge-Carrier Transport Properties in Dehydrobenzoannulene-Based 2D Conductive Metal–Organic Frameworks

([1]*Graduate School of Engineering, Osaka University*, [2]*Molecular Photoscience Research Center, Kobe University*, [3]*Graduate School of Science, Kobe University*) ○Enzo Ohkubo,[1] Naoya Aizawa,[1] Kaoru Ohta,[2] Keisuke Tominaga,[2, 3] Ken-ichi Nakayama,[1] Mitsuharu Suzuki[1]

Keywords: Metal–Organic Frameworks; Dehydrobenzoannulenes; Porous Materials; Two-Dimensional Polymers; Charge-Carrier Mobility

Conductive 2D metal–organic frameworks (2D c-MOFs) are layered, sheet-like coordination polymers renowned for their crystallinity, porosity, and electrical conductivity. These properties make them promising for various applications such as sensing.[1] Currently, we are exploring the construction and functional development of 2D c-MOFs comprising dehydrobenzoannulenes (DBAs) as ligands, and previously reported two novel DBA-based 2D c-MOFs, Ni-HA12 and Ni-HA18 (Fig. 1a, c).[2] These MOFs achieve BET surface areas of up to 1720 $m^2\ g^{-1}$, surpassing the previously reported maximum.

In this work, we investigated the charge-carrier transport properties of these DBA-MOFs. Band diagrams from DFT calculations revealed that the band dispersions along the intraplane direction were comparable to those of conventional sp^2-carbon-based 2D c-MOFs, suggesting that the DBA-MOFs may exhibit excellent charge-carrier transport capabilities (Fig. 1b, d). This presentation will discuss the charge-carrier transport characteristics of these MOFs, estimated from the band calculations and time-resolved terahertz spectroscopy.

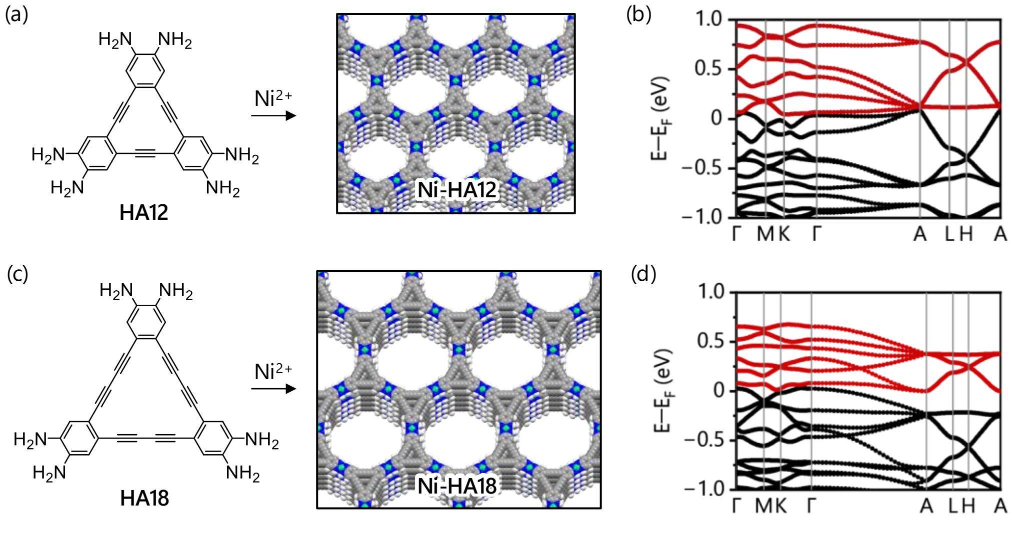

Fig. 1 Expected structures and calculated band diagrams of Ni-HA12 (a, b) and Ni-HA18 (c, d). Black and red lines in b and d indicate the valence and conduction bands, respectively.

(1) Liu, W. et al. *Chem. Eur. J.* **2024**, *30*, e202402747. (2) Ohkubo, E. et al. The 104th CSJ Annual Meeting, F1233-1pm (**2024**).

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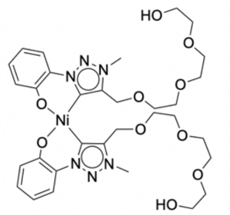
Electrochemical Properties of a New Water-Soluble Ni-NHC Complex Tethered to Triethylene Glycol Moieties

([1]*Department of Chemistry, Kyushu University*) ○Chen Liao,[1] Kosei Yamauchi,[1] Ken Sakai[1]

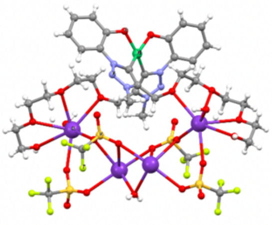
Keywords: Water-Soluble Ni-NHC; Electrocatalysis; CO_2 Reduction; Homogeneous.

The reduction of CO_2 to formic acid represents a critical pathway for converting this pervasive greenhouse gas into valuable industrial products, such as synthetic materials and hydrogen storage solutions. While carbon monoxide production often dominates CO_2 reduction efforts using earth-abundant metal catalysts, *cis*-Ni-NHC complexes have shown promise for selective formate production.[1] Building on previous studies by Albrecht and co-workers[1] and our own work on the mechanisms of formate production via Ni-NHC complexes,[2] this study introduces a novel water-soluble Ni-NHC complex tethered to triethylene glycol (TEG), synthesized using a microwave-assisted reactor with its structure confirmed by single-crystal X-ray diffraction (see figures on the right). The inclusion of K^+ and triflate anions demonstrates the intricate balance of ionic and coordination interactions essential for its crystalline structure.



Schematic structure: $Ni(NHC)_2$

The complex's water solubility and stability in both organic and aqueous solutions allow for broader application potentials. Electrochemical analyses identified a reduction peak of $Ni^{(II/I)}$ at -1.98 V vs SCE in MeCN (**Figure 1a**). Furthermore, under CO_2 atmosphere and with water as a proton source, the complex exhibits catalytic reactivity, indicating its efficacy in CO_2 reduction (**Figure 1b**).



Crystal structure: $Ni(NHC)_2{\cdot}4CF_3SO_3K{\cdot}3H_2O$

These features not only augment our understanding of Ni-NHC complexes in electrochemical CO_2 reduction but also illuminate the potential of water-soluble catalysts in promoting sustainable chemical processes like water splitting. In this context, the discussion will delve into the synthesis, structure, and electrochemical properties of this complex, offering detailed insights into its potential applications and advantages in sustainable chemistry.

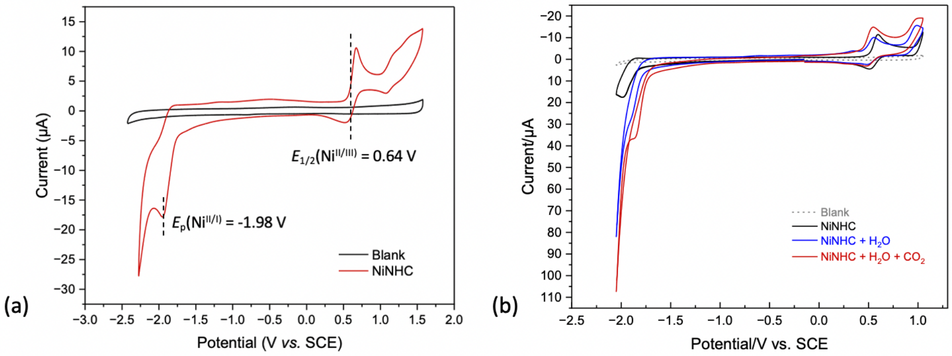


Figure 1. (a) CV of 0.5 mM Ni-NHC in MeCN with 0.1 M $(Bu_4N)PF_6$ as supporting electrolyte; (b) CVs of 0.5 mM Ni-NHC in MeCN under different conditions.

1. S. Bertini, M. Rahaman, A. Dutta, P. Schollhammer, A. Rudnev, F. Gloaguen, P. Broekmann and M. Albrecht, *Green Chem.*, **2021**, *23*, 3365-3373.
2. C. Liao, K. Yamauchi and K. Sakai, *ACS Catal.*, **2024**, *14*, 11131−11137.

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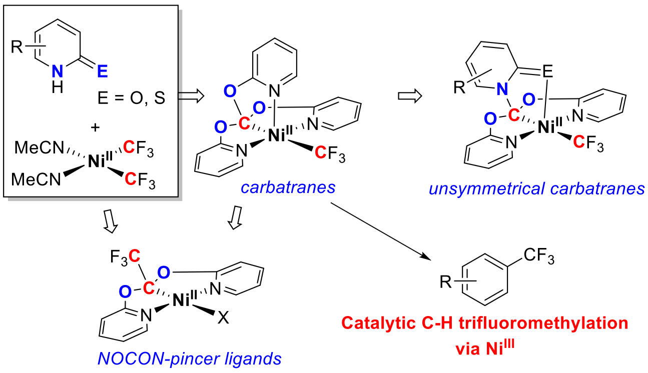
Self-Assembled Nickel Catalysts from Simple Building Blocks For Trifluoromethylation and High Oxidation State Stabilization

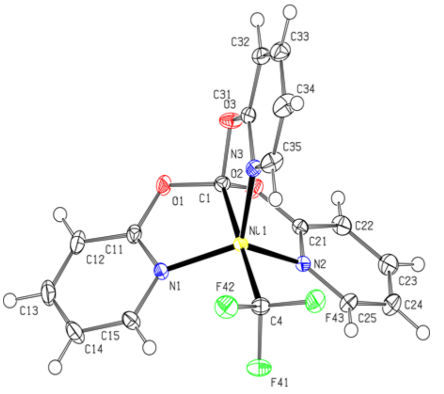
([1]*Okinawa Institute of Science and Technology Graduate University*) ○Aleksandr Sorvanov,[1] Shubham Deolka,[1,] Eugene Khaskin,[1] Julia Khusnutdinova[1]

Keywords: C-F bond activation; Carbatranes; Nickel; Trifluoromethylation; High-Valent **【5 words at most】**

2-Pyridonate is a versatile ligand possessing diverse coordination modes, which have been widely utilized in organometallic chemistry for a long time. It gained a particular prominence due to the presence in the Fe-hydrogenase active site facilitating hydrogen activation, which was widely adopted in bioinspired systems for metal-ligand cooperative bond activation.[1] On the other hand, its application in coordination chemistry of fluoroalkyl complexes is scarce.[2]

In this light, we aimed to test the reactivity of this ligand family towards nickel perfluoroalkyl complexes. Treatment of a simple nickel trifluoromethyl precursor $(MeCN)_2Ni(CF_3)_2$ with 2-pyridone in THF at room temperature resulted in the formation of a self-assembled pentacoordinated Ni^{II} carbatrane complex **2** via C-F bonds activation and subsequent C-O coupling.[3] Furthermore, the scorpionate ligand in **2** could be easily *in complex* modified by 2-thio-N-heterocycles providing a convenient synthetic route to the previously unknown unsymmetrical carbatranes or converted into a novel class of NOCON-pincer complexes. All the complexes were isolated and fully characterized. We also demonstrated the reactivity differences of the synthesized complexes in arene and heteroarene C-H trifluoromethylation. A number of nickel(III) and nickel(IV) complexes have been isolated and/or structurally characterized. **【ref. This body consists of 272 words.】**





sc-XRD of **2**

1) J. R. Khusnutdinova, D. Milstein *Angew. Chem. Int. Ed.* **2015**, 54, 12236-12273. 2) Martínez-Salvador, S.; Menjón, B.; Forniés, J.; Martín, A.; Usón, I. *Angew. Chem. Int. Ed.* **2010**, 49, 4286-4289

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構造歪の導入による二核ニッケル錯体の酸化還元過程の速度論的活性化

（科学大理）○廣瀬拓也・森本祐麻・山下 誠

Kinetic Activation of the Redox Processes in Dinuclear Nickel Complexes Induced by Structural Distortion

(*School of Science, Institute of Science Tokyo*) ○Takuya Hirose, Yuma Morimoto, Makoto Yamashita

The metal active centers of metalloenzymes in biological systems often adopt distorted structures, enabling to accelerate catalytic reactions efficiently. In our previous work, we observed structural changes between di(μ-OH)dinickel(II) complex (**H**) and di(μ-O)dinickel(III) complex (**O**) under the same ligand framework.[1] To reduce the activation barrier of the redox process involving the dinuclear nickel complex, we introduced a linker moiety into the ligand to impose distortion at the metal centers. The newly synthesized system generated **O** from **H** and H_2O_2 with more than 100 times faster rate than that of the original complex without the linker. Furthermore, the oxidation reactivity of **O** with the linker toward external substrates was enhanced by 148-fold compared to the original complex.

Keywords : Dinuclear Complex, Structural Distortion, Hydrogen Peroxide, Hydrogen Atom Transfer

酸化還元に伴う遷移金属錯体の配位構造の変化は、その再配向エネルギーを大きくし、反応速度低下の要因となる。一方で金属酵素は様々な酸化状態における最適構造の中間的な構造を中心金属に与えることで触媒サイクルにおける構造変化を小さくして反応を高速化している。我々はジ(μ-ヒドロキシド)二核Ni(II)錯体(**H**)とジ(μ-オキシド)二核 Ni(III)錯体(**O**)が酸化状態に応じて異なる構造をとることを明らかにしている [1]。そこで我々は、この二核 Ni 錯体に構造歪みを導入することで、酸化還元の両過程を促進できると考えた。

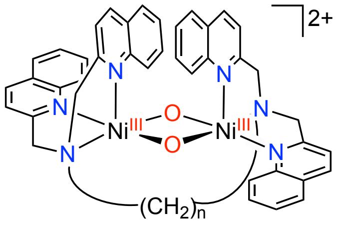

Figure 1. Structure of **O**^{n} (n = 4–7)

ビスキノリルメチルアミン三座配位子(**L0**)を長さの異なるアルキレン架橋基で連結した配位子(**L4–7**)を合成した。これらと過塩素酸 Ni(II)より一連の二核 Ni(II)錯体(**OH**^{n}, n = 0, 4–7)を調製した。–80 °C において過剰モル量の H_2O_2 を加えると **O** は一次の速度式に従って生成した。これにより擬一次反応速度定数(k_{obs}, s^{-1})を決定した[>0.2 (**OH**^{4}), >0.2 (**OH**^{5}), 0.10 (**OH**^{6}), 0.24 (**OH**^{7})]。この条件では架橋基のない **OH**^{0} 錯体は **O** を生成しなかったことから、架橋基の導入はジ(μ-O)活性種の生成効率を著しく向上することが分かった。続いて 9,10-ジヒドロアントラセン(DHA)を基質としてこれらの錯体の反応性を速度論的に検討し、–60 °C における二次反応速度定数を決定した。**O**^{4} による DHA の酸化反応の速度定数[$k = (1.3 \pm 0.1) \times 10\ M^{-1}s^{-1}$]を、**O**^{0} のもの [$k = (8.8 \pm 1.0) \times 10^{-3}\ M^{-1}s^{-1}$]と比較すると、$C_4$ 架橋基の導入により反応が 148 倍加速されることが分かった。

1) Y. Takagi, Y. Morimoto, S. Itoh, CSJ Annual Conference 2018.

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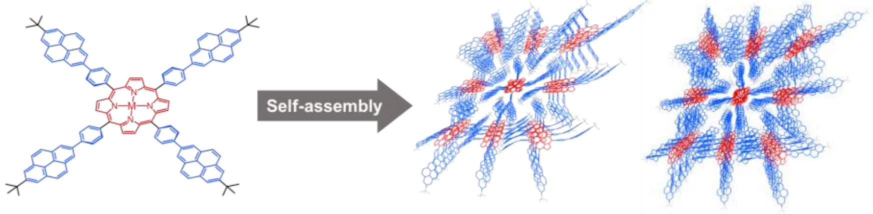
Development of metalloporphyrin-based supramolecular framework catalysts for oxygen atom transfer reactions

([1]*Graduate School of Engineering, Osaka University*, [2]*School of Science, Institute of Science Tokyo*) ○Akira Yoneda,[1] Taito Watanabe,[1] Yau Marc Alec Dominic Ong,[1] Kento Kosugi,[2] Yutaka Saga,[1] Testuya Kambe,[1] Mio Kondo,[2] Shigeyuki Masaoka[1]

Keywords: Supramolecular framework, Self-assembly, Porphyrin, Oxygen atom transfer reaction, Porous material

Catalysts for oxygen atom transfer (OAT) reactions have recently gained significant attention in both synthetic and biological systems. The systems of oxo-metalloporphyrin have been utilized for OAT reactions due to their high reactivity. However, the catalytic deactivation is caused by dimerization or disproportionation. The heterogenization of metalloporphyrin could improve their catalytic performance. To date, there are many reports on the synthesis of molecule-based heterogeneous-framework catalysts by the self-assembly of metal complexes through coordination bonds (forming metal–organic frameworks (MOFs))[1] or intermolecular interactions.[2] These framework catalysts generally show unique features derived from the catalytic centers immobilized in their structures and a heterogeneous porous nature. Thus, catalytic materials enabling the accumulation of substrates, a high reaction selectivity and recyclable properties can be synthesized. However, the literature contains few reports on molecule-based heterogeneous framework catalysts with intermolecular interactions.

Herein, we report the development of a new Ru-porphyrin-based supramolecular-framework catalysts containing intermolecular interactions for styrene epoxidation.[3] A Ru(II)-porphyrin complex with pyrenylphenyl moieties at the *meso*-position, aquacarbonyl {5,10,15,20-tetrakis(4-(7-tert-butyl)-pyrene-2-yl)phenyl)porphyrinato}ruthenium(II) (**RuBPPy**), was used as the building unit of the catalyst. **RuBPPy** contains two key features: a Ru-based catalytic center for the OAT reaction and pyrenylphenyl moieties as intermolecular interaction sites. The self-assembly of **RuBPPy** *via* intermolecular interactions results in the supramolecular framework catalyst, [**RuBPPy**]$_{\mathrm{FC}}$. These recyclable catalysts facilitate OAT reactions more efficiently than homogeneous Ru-porphyrin catalytic systems. The results of the investigation into the [**MnBPPy**]$_{\mathrm{FC}}$ system for OAT reactions will also be presented.



MBPPy (M = Ru, Mn) [**RuBPPy**]$_{\mathrm{FC}}$ [**MnBPPy**]$_{\mathrm{FC}}$

1) J. T. Hupp *et al.*, *Chem. Soc. Rev.*, **2022**, *51*, 1045. 2) K. Kosugi *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 10451. 3) A. Yoneda *et al.*, *Chem. Commun*. **2024**, *60*, 13939.

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Stimuli-Triggered PCET ON-OFF Switching by Metastable Ruthenium Complex

(Osaka Institute of Technology) ○Masanari Hirahara, Yuya Matsuzaki, Kanon Taniguchi, Yuto Yane

Keywords: PCET; Photochemistry; Ruthenium; Electrochemistry; Bistability

Stimuli-responsive ruthenium complexes have been widely applied in catalysis[1] and metallodrugs.[2] In this work, stimuli-responsive proton coupled electron transfer (PCET) ON-OFF complexes were investigated. A ruthenium complex in which carboxy moiety is ligated (**1(Ru^{II})**) are thermally stable and did not show thermal substitution reaction with water. Light irradiation to the aqueous solution of **1(Ru^{II})** gave **2(Ru^{II}-OH$_2$)** in neutral condition and **2(Ru^{II}-OH)** in strong basic conditions (Figure 1, left). The key of the structural change is intramolecular hydrogen bonding between the aqua ligand and pendant naphthyridine moiety . Meta-stable polypyridyl ruthenium aqua complex **2(Ru^{II}-OH$_2$)** displayed PCET to ruthenium oxo complex **2(Ru^{IV}=O)** via **2(Ru^{III}-OH)**. In neutral and weak acidic conditions, the oxidation current diminished as increasing the scan cycles (Figure 1, right). Simulation of the voltammogram indicated structural change from **2(Ru^{III}-OH)** to **1(Ru^{III})**. The rate constants for the structural change were highly dependent on the pH. The results indicate that redox potential of both complexes are highly correlated with the electrochemical structural change. At pH 9 or 10, the redox of **1(Ru^{II})** /**1(Ru^{III})** and **2(Ru^{II}-OH$_2$)/ 2(Ru^{III}-OH)/ 2(Ru^{IV}=O)** is far different (> 0.5 V) which decrease the rate of structural change to **1(Ru^{III})**. On one hand, at weak acidic pH (< pH 5) the difference is less than 0.1V, which allow the fast transformation to **2(Ru^{III}-OH)**.

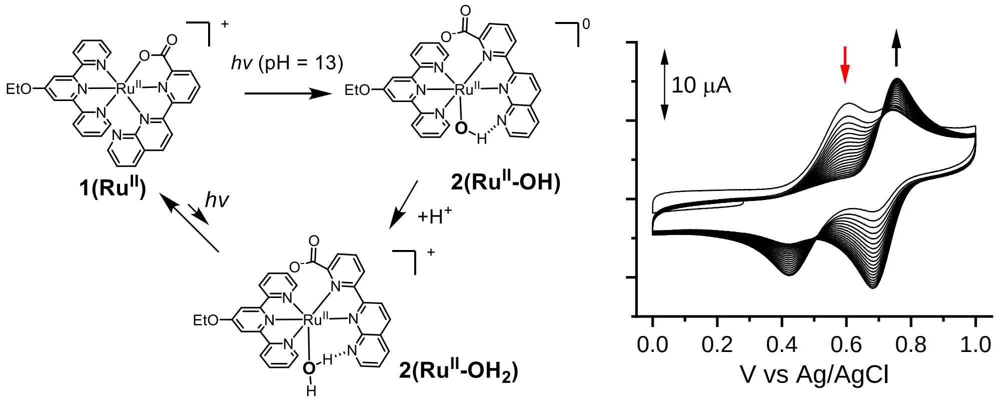

Figure 1. Left: Interconversion among **1(Ru^{II})**, **2(Ru^{II}-OH$_2$)**, and **2(Ru^{II}-OH)**. Right: CVs of **2(Ru^{II}-OH$_2$)** in 40% TFE and 60% 0.1 M phosphate buffer (pH7) at 1 V s^{-1}.

[1] M. Hirahara, H. Goto, M. Yagi and Y. Umemura, *Chemical Communications* **2020**, *56*, 12825-12828.

[2] S. Bonnet, *Journal of the American Chemical Society* **2023**, *145*, 23397-23415.

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Hydrogen-evolving Homo-coupling Reactions of Boronic Acids by Photoredox Cascade Catalyst

(*Faculty of Science, Hokkaido University*) ○Atsushi Kobayashi

Keywords: Photocatalysis; Hydrogen Production; Boronic Acid; Coupling Reaction

Solar water splitting reaction has been attracted considerable attention as a means of building a sustainable *hydrogen* society. However, water splitting reaction cannot provide valuable organic chemicals. To overcome this issue, we have constructed a photo-redox cascade catalyst (**PRCC**) consisting of dual-Ru(II)-dye sensitized Pt-TiO_2 photocatalyst (**DDSP**) and molecular oxidation catalysts, which generates hydrogen photocatalytically not only from redox-reversible electron donors[1] but also primary -OH or allylic C-H group containing organic substrates.[2-3] In this work, to extend this strategy further, a new **PRCC** system was fabricated by combining $Pd(OAc)_2$ (AcO^- = acetate) complex as an molecular catalyst to promote the oxidative homo-coupling reaction of boronic acids, TEMPO (2,2,6,6,-tetramethylpiperidine 1-oxyl) as an electron mediator, and **DDSP** (Figure 1, right). H_2 photocatalytically evolved by blue light irradiation to the reaction mixture containing **DDSP**, $[Pd(OAc)_2]$, TEMPO and 4-methylphenylboronic acid (Figure 1a), and the evolved amount depended on the $[Pd(OAc)_2]$ concentration, indicating a crucial role of $[Pd(OAc)_2]$ complex. ^1H NMR spectra of reaction solutions clearly indicate the generation of 4,4'-dimethylbiphenyl because of the Pd-catalyzed oxidative homocoupling reaction (Figure 1b). Details will be discussed.

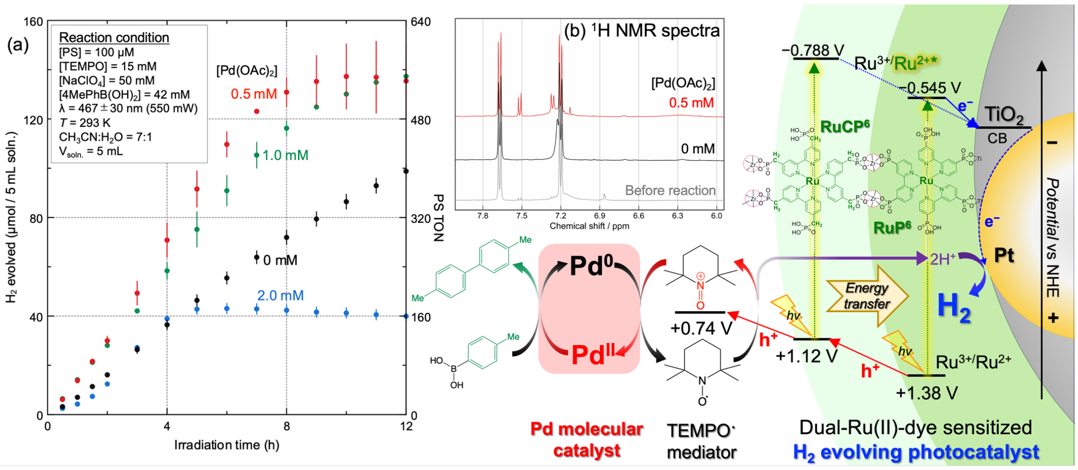

Figure 1. (left, a) Photocatalytic H_2 production with Pd-catalyzed homo-coupling of boronic acid, (center, b) ^1H NMR spectra of the reaction supernatants and (right) schematic energy diagram of this **PRCC** system.

1) N. Yoshimura, M. Yoshida, A. Kobayashi, *J. Am. Chem. Soc.* **2023**, *145*, 6035. 2) A. Kobayashi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202313014. 3) A. Kobayashi, *Catal. Sci. Technol.* **2024**, *14*, 3893.

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