アカデミックプログラム［Ｂ講演］｜09. 錯体化学・有機金属化学：口頭Ｂ講演

2025年3月28日(金) 9:00 ~ 11:40 [B]A301(第2学舎 1号館 [3階] A301)

[[B]A301-3am] 09. 錯体化学・有機金属化学

座長：鈴木 孝義、舩橋 靖博

英語

9:00 ~ 9:20

[[B]A301-3am-01]

コバルト二核錯体における協奏的な二つのレドックスサイトによる電気化学的CO_2還元反応の過電圧の減少

○堂ノ下 将希[1,2]、潘 雲逸[2]、亀谷 陽平[1]、塩田 淑仁[1]、呉 樹旗[1]、佐藤 治[1]、山内 美穂[1,2,3,4,5] (1. 九大先導研、2. 九大院理、3. 九大I2CNER、4. 九大K-NETs、5. 東北大AIMR)

英語

9:20 ~ 9:40

[[B]A301-3am-02]

水からの水素生成を高速駆動するCo-NHC錯体のグラッシーカーボン電極上における電極触媒挙動

○管 昌権[1]、山内 幸正[1]、酒井 健[1] (1. 九大)

英語

9:40 ~ 10:00

[[B]A301-3am-03]

Construction of Porphyrin-Based Framework Catalysts for Small Molecule Conversions

○XIANJUN LI[1], Kento KOSUGI[1], Shigeyuki MASAOKA[2], Mio KONDO[1] (1. Institute of Science Tokyo, 2. The University of Osaka)

英語

10:00 ~ 10:20

[[B]A301-3am-04]

ポリピリジルRu光増感剤修飾TiO_2フォトアノードとCoポルフィリン触媒修飾TiO_2カソードを用いた水中での光電気化学的CO_2還元反応

○合屋 祐輝[1]、酒井 健[1]、小澤 弘宜[1] (1. 九大)

英語

10:20 ~ 10:40

[[B]A301-3am-05]

Synthesis and perchlorate removal properties of cobalt coordination polymers

○Umme Fariha Tasnim[1], Aditya Irfan Witono[1], Xin Zheng[1,2], Shin-ichiro Noro[1,2] (1. Graduate School of Environmental Science, Hokkaido University, 2. Faculty of Environmental Earth Science, Hokkaido University)

日本語

10:40 ~ 11:00

[[B]A301-3am-06]

N_4O_2配位構造を有する非対称型コバルト(II)錯体の合成および物性評価

○菊地 颯人[1]、仲谷 学[1] (1. 城西大院理)

英語

11:00 ~ 11:20

[[B]A301-3am-07]

電子型強誘電体における分極変化の全光制御

〇HUANG YUBO[1]、SHENGQUN SU[1]、SHUQI WU[1]、OSAMU SATO[1] (1. 九大)

🏷 英語

11:20 ~ 11:40

[[B]A301-3am-08]

A solvent-free neutral cobalt complex exhibiting macroscopic polarization switching induced by directional charge transfer

〇Ziqi Zhou[1], Shinji Kanegawa[1], Shuqi Wu[1], Shengqun Su[1], Osamu Sato[1] (1. Institute for Materials Chemistry and Engineering, Kyushu University)

Cooperative Dual Redox Sites in a Dinuclear Cobalt Complex Decrease the Overpotential of CO_2 Electroreduction

([1]*IMCE, Kyushu Univ.*, [2]*Grad. Sch. of Sci., Kyushu Univ.*, [3]*WPI-I*^{2}*CNER, Kyushu Univ.* [4]*K-NETs, Kyushu Univ.*, [5]*WPI-AIMR, Tohoku Univ.*) ○Masaki Donoshita,[1,2] Yunyi Pan,[2] Yohei Kametani,[1] Yoshihito Shiota,[1] Shu-Qi Wu,[1] Osamu Sato,[1] Miho Yamauchi[1,2,3,4,5]

Keywords: CO_2 electroreduction; dinuclear metal complex; redox; DFT calculation

Electrochemical CO_2 reduction (eCO_2R), which provides valuable chemicals from CO_2 using electric power, has attracted growing attentions as a solution to the environmental and energy problems.[1] As eCO_2R catalysts, metal complexes have been widely studied because of their high designability[2], although the overpotential for eCO_2R is still not satisfiable. In this study, we focused on dinuclear complexes, whose multiple redox sites would be advantageous for eCO_2R involving multiple electron reductions. Inspired by the cobalt tetraphenylporphyrin (**Co₁**, **Fig. 1 left**), which is a well-studied catalyst owing to its high selectivity for CO (Faradaic efficiency; >90%),[3] we targeted a dinuclear complex, $[Co^{II}_2(bpypz)_2]^{2+}$ (Hbypz = 3,5-bis(2-pyridyl)pyrazole), which is referred to as **Co₂** (**Fig. 1 right**). Previously, we revealed that **Co₂** exhibits 250 mV more positive onset potential in *N*,*N*-dimethylformamide (DMF) solution compared to that of **Co₁**.[4] In this study, we discuss their catalytic cycles based on the experimental and computational studies in order to reveal the reason for the superior catalytic performance of **Co₂**.

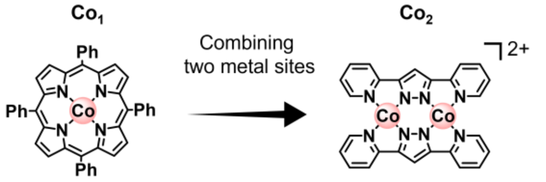


Fig. 1. Molecular structures of **Co₁** (left) and **Co₂** (right).

Chronoamperometry using a microelectrode revealed that **Co₂** exhibits the one-step two-electron reduction, i.e., (Co^{II}, Co^{II})→(Co^{I}, Co^{I}), which is absent in **Co₁**. This behavior affords the difference in the sequence of the electron-transfer steps and CO_2-binding step in the catalytic cycles of **Co₁** and **Co₂**, which was supported by the density functional theory (DFT) calculations. We found that the simultaneous two-electron reduction before the CO_2-binding on **Co₂** circumvents the electron transfer after the CO_2-binding which prevents the catalytic cycle of **Co₁.** Furthermore, DFT calculations suggested the cooperation of the two Co ions in catalytic cycle of **Co₂**, i.e., the metal-to-metal electron transfer and the intermediate with the COOH moiety bridging over the two Co sites (**Fig. 2**). We then concluded that the cooperative functions on the dinuclear complex are the key to the lower overpotential.

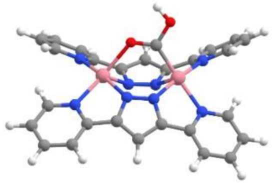


Fig. 2. DFT-optimized structure of an intermediate for eCO_2R on **Co₂**.

1) R. G. Grim *et al.*, *Energy Environ. Sci.* **2020**, *13*, 472. 2) E. Boutin et al., *Chem. Soc. Rev.* **2020**, *49*, 5772. 3) X. Hu *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 6468. 4) Y. Pan *et al.*, *The 104*th *CSJ Annual Meeting* **2024**, F1232-1pm-04.

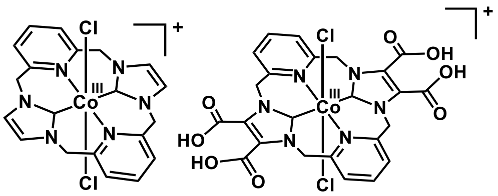
Electrocatalytic Behavior of Co-NHC Complexes over a Glassy Carbon Electrode in Hydrogen Evolution from Neutral Water

([1]*Kyushu Univ.*) ○Masanori Kan,[1] Kosei Yamauchi,[1] Ken Sakai[1]

Keywords: Cobalt complex; Hydrogen evolution reaction (HER); Electrochemistry; Homogeneous electrocatalysis; Tafel analysis

It was previously demonstrated that **Co-NHC1** (**Figure 1a**; NHC = N-heterocyclic carbene)[1] achieves the ultrafast electrocatalytic hydrogen evolution from water with a remarkable turnover frequency (TOF) of 34000000 s^{-1}. In addition, we found that the dip-coated effect of **Co-NHC1** in the presence of some inorganic chloride salts result can be negligible enough to estimate the TOF of **Co-NHC1** under the homogeneous electrocatalysis condition. In this study, the effects of the charge for cobalt-NHC catalysts are investigated by employing **Co-NHC1** and a new bis(NHC)cobalt complex, **Co-NHC-COOH**, which should become anionic at neutral pH. In addition, we also conducted a Tafel analysis for the heterogenized **Co-NHC1** for the hydrogen evolution reaction (HER) to discuss the rate-determining step (RDS).

Importantly, **Co-NHC-COOH** shows the catalytic current of HER at pH 7.0 in the potential domain similar to **Co-NHC1**. On the other hand, **Co-NHC-COOH** passed the rinse and dip tests, indicating the negligible dip-coated effect even in the presence of inorganic chloride salts. McCreery previously reported that there are some oxygen containing functional groups on normally polished glassy carbon (GC) surface.[2] It is thus indicated that the electrostatic interaction between the cationic **Co-NHC1** and GC surface may result in the dip coating of **Co-NHC1** over the GC electrode. Tafel analysis with the GC working electrode heterogenized with a PF_6^- salt of **Co(II)-NHC1** revealed that the electrochemical HER by **Co-NHC1** proceeds via the proton-coupled electron transfer step giving a hydridocobalt(III) species is the RDS.



Co-NHC1 **Co-NHC-COOH**

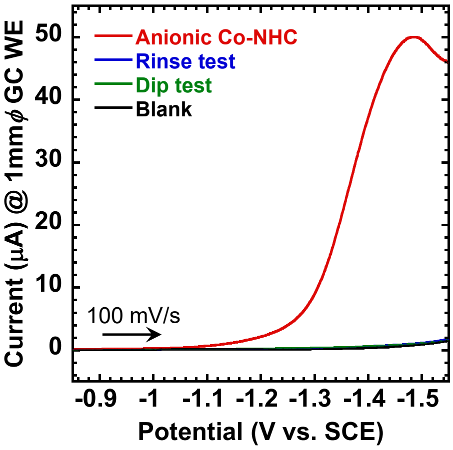


Figure 1. Linear sweep voltammograms (LSVs) measured for aqueous NaPi solutions (pH 7.0; 0.4 M) of **Co-NHC-COOH** (0.1 mM). The LSVs of rinse and dip tests were measured by employing aqueous NaPi solutions (pH 7.0; 0.4 M) without any inorganic salts. WE: GC, CE: GC rod, RE: CE. Under Ar.

1) K. Yamauchi, K. Kawano, K. Yatsuzuka, K. Kawamura, M. Kan, and K. Sakai, *J. Am. Chem. Soc.*, 2025, DOI: 10.1021/jacs.4c10246.

2) P. Chen and R. L. McCreery, *Anal. Chem.*, 1996, **68**, 3958.

Construction of Porphyrin-Based Framework Catalysts for Small Molecule Conversions

([1]*School of Science, Institute of Science Tokyo*, [2]*Graduate School of Engineering, Osaka University*) ○Xianjun Li,[1] Kento Kosugi,[1] Shigeyuki Masaoka,[2] Mio Kondo[1]

Keywords: Small Molecule Conversions, Framework Catalysts, Metal Porphyrins, Heterogeneous Catalysts

Nowadays, our society faces an energy shortage and a global warming problem. Artificial photosynthesis is attractive as it can mimic natural photosynthesis and produce green energy to replace traditional fossil fuels with renewable energy. Artificial photosynthetic reactions consist of two kinds of small molecule reactions (half reactions). To achieve sustainable solar energy conversion system, cooperations of two half reactions are essential. However, in most of the reported works, the catalysts for each half-reaction have been developed separately, and the integration of two distinct catalytic sites and efficient charge transfer without charge recombination is still quite challenging.

Herein, we aimed to construct a molecule-based system in which catalytic oxidation sites and reduction sites are integrated. Our initial study demonstrated that coexisting carboxylate/carboxyl environments for bridging the MOF is a promising strategy to get efficient small molecule conversions due to the following three reasons; i) porosity for the accumulation of substances[1] ii) H-bonding for the capture of substrate[2] and iii) enhancing conductivity[3]. Especially, we successfully synthesized a metal porphyrin-based framework (Figure 1, left) with such coexisting constructions and achieved the photochemical CO_2 reduction with the highest activity among the relevant systems. We also succeeded in the development of a novel MOF in which oxidation and reduction sites are integrated into the framework (Figure 1, right). In the presentation, we will show the structures of framework catalysts and discuss about their catalytic activities.

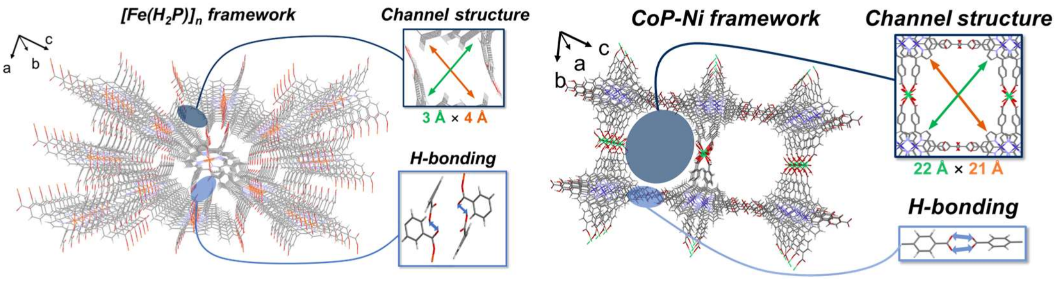


Figure 1. Structure features of **[Fe(H_2P)$_n$]** and **CoP-Ni**.

1) Z. Chen *et al., ACC. Chen. Res.* **2022**, *55*, 579-591
2) C. Wang. *et al., Fuel* **2021**, *287*, 119556.
3) X. X. Xie *et al., Coord. Chem. Rev.* **2020**, *404*, 213100.

Photoelectrochemical CO_2 Reduction in Water with a Co Porphyrin Catalyst Modified TiO_2 Cathode and a Polypyridyl Ru Photosensitizer Modified TiO_2 Photoanode

([1]*Kyushu Univ.*) ○Yuki Goya[1], Ken Sakai[1], Hironobu Ozawa[1]

Keywords: *CO_2 Reduction; TiO_2; Porphyrin; pyridyl anchor; Photoelectrochemical Cell*

Artificial photosynthesis is an ideal reaction for achieving a low-carbon and carbon-recycling society. We have recently reported that the mesoporous TiO_2 cathode modified with a Co porphyrin molecular catalyst having a pyridyl anchor (**FTO/TiO_2/CoP-py**, Figure) can promote electrocatalytic CO_2-to-CO conversion with a relatively higher Faradaic efficiency and selectivity even in aqueous media.[1] In this study, to achieve highly efficient photoelectrocatalytic CO_2-to-CO conversion, the mesoporous TiO_2 electrode modified with a polypyridyl ruthenium photosensitizer (FTO/TiO_2/**Ru-qpy**)[2] has been utilized as a photoanode for the two-electrode configuration molecular-based photoelectrochemical cell (PEC, Figure), and the performance of photoelectrocatalytic CO_2-to-CO conversion has been evaluated in CO_2-saturated $NaHCO_3$ in the presence of an electron donor. This study revealed for the first time that EDTA is the most suitable electron donor for this molecular-based PEC among four kinds of electron donors (TEA, TEOA, EDTA, or hydroquinone) mainly due to the presence of pre-equilibrium between not only EDTA and **Ru-qpy** but also EDTA and TiO_2 surfaces. The total Faradaic efficiency (FE_{total}) and CO selectivity (Sel_{CO}) gradually increase with increasing the applied potential, and seem to almost saturate at around 75% and 70%, respectively, when the applied potential exceeds 0.8 V vs. cathode (Figure). On the other hand, the total external quantum yield (EQY) for CO and H_2 production almost linearly increases even the applied potential exceeds 0.8 V, and reaches to 5.1% at the applied potential of 1.2 V. Although our PEC still utilizes a sacrificial electron donor EDTA, the obtained total EQY is significantly higher than those of molecular-based PECs reported thus far.

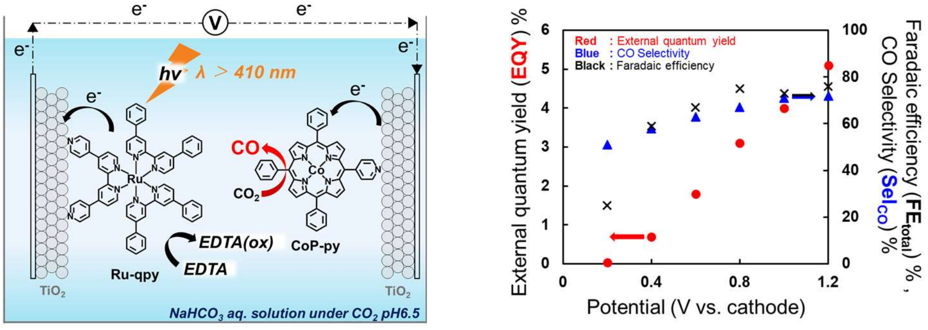


Figure. Schematic representation of a molecular-based photoelectrochemical cell for solar-driven CO_2 reduction (left) and plots of EQY, total FE, and CO selectivity as a function of the applied potential (right).

[1] H. Ozawa, R. Kikunaga, H. Suzuki, R. Abe, K. Sakai, *Sustain. Energy Fuels*, **2023,** *7*, 1627.
[2] K. Morita, K. Sakai, H. Ozawa, *ACS Appl. Energy Mater.,* **2019**, *2*, 987.

Synthesis and perchlorate removal properties of cobalt coordination polymers

([1]*Graduate School of Environmental Science, Hokkaido University*, [2]*Faculty of Environmental Earth Science, Hokkaido University*) ○Umme Fariha Tasnim,[1] Aditya Irfan Witono,[1] Xin Zheng,[1,2] Shin-ichiro Noro[1,2]

Keywords: Perchlorate anion; Coordination polymer; Water purification

Recently, water contamination due to toxic perchlorate anion is a critical environmental concern that demands immediate mitigation. Therefore, developing new materials with adsorption or ion exchange properties is necessary to selectively remove perchlorate from water. Coordination polymers constructed from metal ions and organic bridging ligands can be applied to treat wastewater because of their high structural tunability and diversity. Our study aims to find anion-exchangeable coordination polymers that efficiently remove perchlorate anion from water by anion exchange.

The reaction of $CoCl_2 \cdot 6H_2O$ with hydrophobic bis-benzimidazole-type ligands, 1,3-bis(1*H*-benzo[*d*]imidazol-1-yl)propane (bbip) and 1,4-bis(1*H*-benzo[*d*]imidazol-1-yl)butane (bbib), afforded three Co coordination polymers, one-dimensional $[CoCl_2(bbip)]$ (**1**), two-dimensional $[CoCl_2(bbip)_2]$ (**2**), and three-dimensional $[CoCl_2(bbib)_2]\cdot 4H_2O\cdot 2MeOH$ (**3**). The perchlorate removal capacity of **2** was found to be higher than those of **1** and **3** (Figure 1). **2** showed higher capacity than those of porous $[Zr_6O_4(OH)_4(bdc)_6]$ (**UiO-66**, bdc = 1,4-benzenedicarboxylate) with some Cl^- including defect units[1] and the anion exchange resin purolite A532E and had similar removal capacity with reported $[Cu_3Cl_2(p\text{-bbiteb})_6]\cdot 4Cl$ (**Cu-CP**, *p*-bbiteb = 1,4-bis(benzimidazol-1-yl)-2,3,5,6-tetramethylbenzene)[2] and the resin purolite A530E (Figure 1). The removal of perchlorate anion in these new cobalt coordination polymers likely occurs through an anion-exchange reaction with chloride anion.

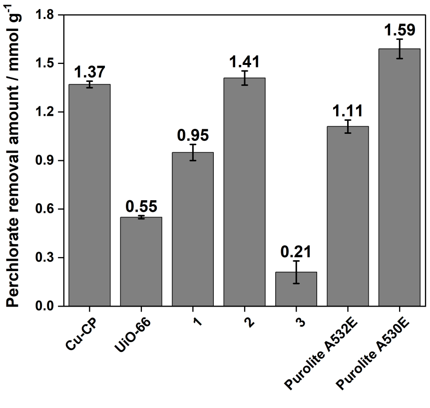


Figure 1. Perchlorate removal performance of Co coordination polymers at 30 °C.

1) A. I. Witono, X. Zheng, Y. Saito, S. Noro, *Chem. Lett.* **2024**, *53*, upae050. 2) E. Sone, M. Sato, K. Yamanishi, C. Kamio, H. Takemoto, M. Kondo, *Dalton Trans.* **2016**, *45*, 894.

N_4O_2配位構造を有する非対称型コバルト(II)錯体の合成及び物性評価

（城西大院理）○菊地 颯人・仲谷 学

Synthesis and physical properties of asymmetric cobalt(II) complexes with N_4O_2 coordination geometry

(*Graduate School of Science, Josai University*) ○Hayato Kikuchi, Manabu Nakaya

Molecular metal complexes with asymmetric coordination geometry or structures have been extensively studied from the aspects of pharmacological activity and reaction catalysis. On the other hand, there are still many unexplored subjects such as functionalities attributed to the electronic and spin based on the asymmetric coordination geometry and mechanical properties derived from the asymmetric structure. We have found that cobalt(II) complexes with an asymmetric N_4O_2 coordination geometry exhibit unique magnetic properties and mechanical response of the crystal. In this study, we systematically investigated the magnetic and mechanical properties of the novel cobalt(II) complexes with various substituents. All the complexes showed SCO phenomena, but the mechanical response was different due to the variety of the molecular assembly.

Keywords：Cobalt(II) complex, Spin Crossover, Magnetic Properties, Soft crystal

非対称配位圏や構造そのものが非対称性を有する分子性金属錯体は、薬理活性や反応触媒としての側面から幅広く研究が行われている[1]。一方で、非対称配位圏による電子やスピン物性、非対称な構造に由来する機械的特性など、まだまだ未開拓な部分も多い。我々は、コバルト(II)イオンが示す磁気特性に関して研究を進めている中で非対称な N_4O_2 配位圏を有するコバルト(II)錯体が特異的な磁気物性、結晶の機械的応答性を示す事を見出した。そこで、非対称配位圏を保ちつつ、分子設計における置換基を様々にすることで、その磁気特性や機械的性質などを系統的に調査することを目的とした。

本研究では、ジピコリン酸(H_2dipic)および π–π 相互作用及び CH–π 相互作用が期待できる種々の置換基を導入したターピリジン(R-terpy; R = phenyl, tolyl, biphenyl)配位子からなる非対称配位圏を有するコバルト(II)錯体 **1**–**3** を合成した。錯体 **1** 及び **2** については温度可変での結晶構造解析に成功した。全ての錯体は水和物で得られ、加熱、冷却による水分子の吸脱着挙動を確認した。全ての錯体は温度変化によってスピン状態が変化する SCO 現象を示した。また、錯体 **1** の結晶は、外部から力を加えると曲がる結晶であり、その最大曲げ歪みから結晶柔軟性を評価したところ、六配位八面体構造の単量体の金属錯体では初めての弾性結晶である事がわかった。その他、詳細な議論は当日述べる予定である。

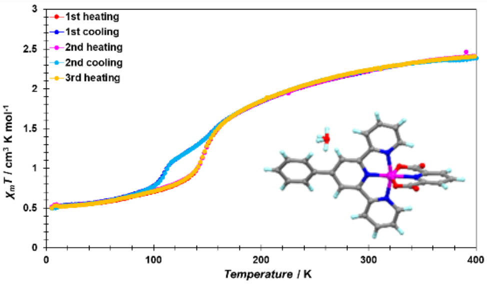


図 1 錯体 **1** の磁化率の温度依存性評価

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1) M. Shionoya *et.al., Nat.Commun.*, **2020**, 11, 6263.

All-optical Control of Polarization Change in Electronic Ferroelectrics

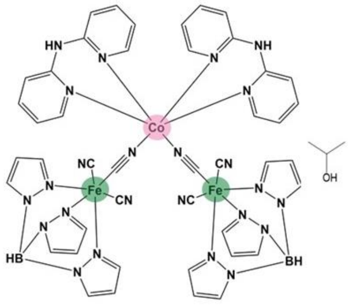
([1]*Graduate School of Science, Kyushu University*) ○Yubo Huang,[1] Shengqun Su,[1] Shuqi Wu,[1] Osamu Sato[1]

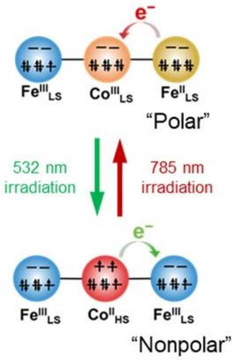
Keywords: Electron Transfer; Spin Transition; Ferroelectrics; Photo Switchable

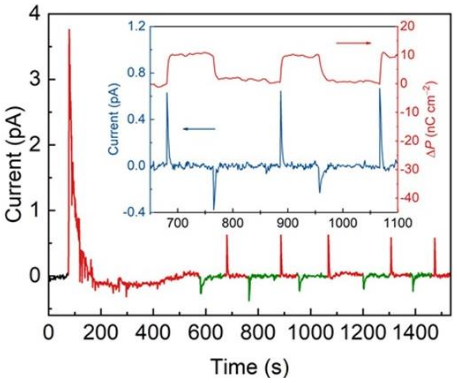
Ferroelectric memory devices are distinguished by their capacity to retain data without continuous power supply, providing significant energy-saving advantages. However, the electrode physically contacts the ferroelectric unit during a typical operation cycle of a FeRAM device, leading to difficulties during device fabrication. In this context, we propose a new approach involving the electron transfer coupled spin transition (ETCST) process in cyanide-bridged [FeCo] bimetallic complexes, which distinguishes from traditional materials by enabling polarization switching in response to light.

Herein, our complex, $[Fe(Tp)(CN)_3]_2(Co(dpa)_2)\cdot 2H_2O\cdot IPA$, exhibits a thermo- and light-induced ETCST associated with a ferroelectric-type phase transition between a nonpolar space group (*C*2/*c*) and a polar one (*Cc*), allowing for the direct observation of polarization switching by conventional pyroelectric measurements.[1] Most impressively, irradiation with a 532 nm laser can convert the nonpolar phase generated by irradiating with a 785 nm laser into the polar phase, producing a clear electric current signal without requiring any external electric field.[2] Such optical cycles provide an optical mimic of the typical operational cycles of FeRAM devices without any electric field.

The successful implementation of thermo- and light-induced polarization switching in a molecular crystal confirm the feasibility of realizing ferroelectricity through the electron transfer mechanism. This finding further validates the feasibility of directional ETCST at the single-crystal level, providing valuable insights to guide the design and synthesis of ferroelectrics via electron transfer.







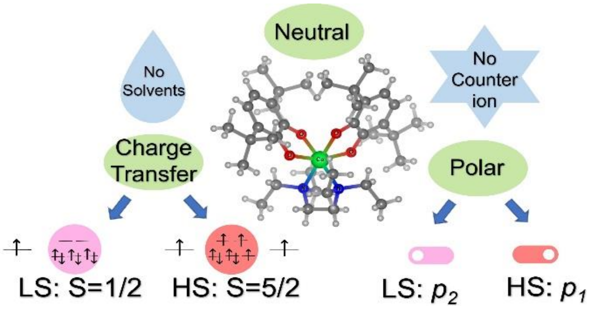
1) Y. B. Huang, *et al.*, *J. Am. Chem. Soc.* **2024**, 146 (1), 201-209. 2) Y. B. Huang, *et al.*, *Angew. Chem. Int. Ed.* **2024**, 63 (38), e202409948.

A Solvent Free Neutral Cobalt Complex Exhibiting Macroscopic Polarization Switching Induced by Directional Charge Transfer

([1]*Institute for Materials Chemistry and Engineering & IRCCS, Kyushu University*,) ○Zi-Qi Zhou,[1] Shu-Qi Wu,[1] Shinji Kanegawa,[1] Sheng-Qun Su,[1] and Osamu Sato[1]

Keywords: Polarization Switching; Solvent Free; Neutral; Charge Transfer; Cobalt Complex

Materials with polarization switching induced by directional charge transfer under the external stimuli are of great interest due to their fast swicthing rate and potential applications. Nonetheless, most of these crystals contain solvents or counter ions, and their effects during measurement or calculations are far from trivial. Therefore, synthesizing a solvent-free and neutral complex exhibiting polarization switching is highly desirable. Herein, we successfully observe directional charge transfer-induced electronic pyroelectricity in a solvent-free neutral cobalt complex, namely Co(teeda)(3,6-dbq)$_2$ (teeda = N,N,N',N'-tetraethylethane-1,2-diamine and 3,6-dbq = 3,6-di-*tert*-butylcatecholate or 3,6-di-*tert*-butylsemiquinonate). The charge transfer property is confirmed by magnetometry, infrared and UV-vis-NIR spectroscopy, and single-crystal X-ray diffraction (SCXRD) measurements. Furthermore, pyroelectric current is observed during the valence tautomerism (VT) process. Theoretical calculations demonstrate that the origin of polarization switching is mainly ascribed to the charge transfer. These results indicate that Co(teeda)(3,6-dbq)$_2$ is a promising candidate for exploring new VT compounds that exhibit polarization switching.



1) O. Sato, *Nat. Chem.*, **2016**, *8*, 644-656. 2) S.-Q. Su, S.-Q. Wu, S. Kanegawa, K. Yamamoto and O. Sato, *Chem. Sci.* **2023**, *14*, 10631-10643. 3) O. Sato, S. Hayami, Z. Z. Gu, K. Takahashi, R. Nakajima and A. Fujishima, *Phase Trans.* **2002**, *75*, 779-785. 4) Z.-Q. Zhou, S.-Q. Wu, Q.-R. Shui, W.-W. Zheng, A. Maeda, X.-P. Zhang, J. Chu, S. Kanegawa, S.-Q. Su and O. Sato, *Inorg. Chem. Front.* **2024**, *11*, 8377.