アカデミックプログラム［B講演］｜04. 物理化学—物性：口頭B講演

2025年3月29日(土) 9:30 ~ 10:50 [C]C303(第2学舎 2号館 [3階] C303)

[[C]C303-4am] 04. 物理化学—物性

座長：河合 壯、石川 直人

日本語

9:30 ~ 9:50

[[C]C303-4am-01]

銀クラスターにおける励起状態に依存した円偏光発光特性

〇石井 航[1]、河合 壯[2]、中嶋 琢也[1] (1. 大阪公立大学大学院、2. 奈良先端科学技術大学院大学)

英語

9:50 ~ 10:10

[[C]C303-4am-02]

Defect-Assisted Emission of Hybrid Indium Bromide Single Crystals

〇haichao zhou[1,2,3], Takuya Okamoto[1,3], Kiyonori Takahashi[1,3], Biju Vasudevan Pillai[1,3] (1. Hokkaido university, 2. Graduate School of Environmental Science, 3. Research Insititute of Electronic Science)

英語

10:10 ~ 10:30

[[C]C303-4am-03]

シアノ架橋型Co-W集積体の光電荷移動誘起相転移における超高速ダイナミクス

〇中林 耕二[1]、中村 一輝[1]、Laurent Guérin[2]、Gaël Privault[2]、Marius Hervé[2]、Eric Collet[2]、大越 慎一[1] (1. 東京大学、2. レンヌ大学)

英語

10:30 ~ 10:50

[[C]C303-4am-04]

Ferromagnetic-type Interaction between Two Angular Momenta in π-π* Excited State of Lanthanide(III)-Monoporphyrin Complex

〇Anas Santria[1,2], Naoto Ishikawa[1] (1. Osaka University, 2. National Research and Innovation Agency)

銀クラスターにおける励起状態に依存した円偏光発光特性

（阪公大院理[1]・NAIST[2]）○石井 航[1]・河合 壯[2]・中嶋 琢也[1]
Excited-state dependent circularly polarized luminescence in silver clusters ([1]*Graduate School of Science, Osaka Metropolitan University*, [2]*Division of Materials Science, Nara Institute of Science and Technology*) ○Wataru Ishii,[1] Tsuyoshi Kawai,[2] Takuya Nakashima[1]

Metal nanoclusters (NCs) composed of a defined number of metal atoms and ligands show unique optical properties on the basis of electronic transitions between discrete orbitals. While numerous structures and various properties of nanoclusters (NCs) have been reported, their excited-state dynamics are not fully understood. Meanwhile, circularly polarized luminescence (CPL) spectroscopy is a powerful tool to obtain insights into the chirality in the excited state.

The Ag$_{29}$ NCs capped with 1,3-benzenedithiol ligands exhibit chirality derived from the asymmetric arrangement of surface ligands and show red emission centered at 680 nm.[1,2] Notably, this emission properties can be significantly modulated by metal complex modifications around the NC.[3] In this study, we found that the excited state of Ag$_{29}$ NCs modified with silver complexes (Ag$_{29}$-II NCs) promotes a new structural relaxation process, resulting in a remarkable enhancement of near-infrared CPL intensity. VT-CPL measurements indicated that the structural chirality in the excited state of Ag$_{29}$-II NCs evolves over time.

Keywords : Metal nanocluster; Circularly polarized luminescence; Near infrared emission

一定数の金属原子と配位子から構成される金属ナノクラスター(NC)は、離散的な軌道間の電子遷移に由来する光学特性を示す。過去二十年の間に数多くの NC の構造と諸物性が報告されてきた。しかしながら、NC の励起状態ダイナミクスに関しては未解明な部分が多い。一方、円偏光発光(CPL)測定は励起状態のキラリティについて重要な知見を与えうる。

1,3-ベンゼンジチオール配位子に覆われた Ag$_{29}$ NC は、表面配位子の原子配列構造に由来するキラリティを有し、また 680 nm を中心とする赤色発光を示す[1,2]。この発光特性は NC 周囲への金属錯体修飾によって大きく変調される[3]。本研究では、銀錯体修飾された Ag$_{29}$ NC (Ag$_{29}$-II NC)の励起状態において新たな構造緩和が促進され、イオン対を形成した三重項状態 T$_1$(IP)からの近赤外 CPL が、イオン対形成前の T$_1$ 状態からの CPL に比較して、大きく増強されることを見出した(Fig. 1)。温度可変 CPL 測定結果から、Ag$_{29}$-II NC の励起状態におけるキラリティが時間発展していることが示唆された。

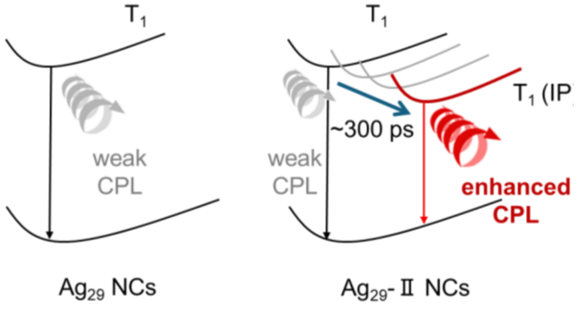


Fig. 1 PL pathways for Ag$_{29}$ and Ag$^+$-complex modified Ag$_{29}$-II NCs.

1) L. G. AbdulHaim et al. *J. Am. Chem. Soc.* **2015**, *137*, 11970. 2) H. Yoshida et al. *Chem. Sci.*, **2020**, *11*, 2394. 3) W. Ishii et al. *J. Am. Chem. Soc*, **2023**, *145*, 11236.

Defect-Assisted Emission from Hybrid Indium Bromide Single Crystals

([1]*Graduate School of Environmental Science, Hokkaido University,* [2]*Research Institute for Electronic Science, Hokkaido University*) ○Haichao Zhou,[1] Takuya Okamoto,[1,2] Kiyonori Takahashi,[1,2] Vasudevanpillai Biju[1,2]

Keywords: Organic-inorganic hybrid halides; Luminescent single crystals; Vacancy-assisted photoluminescence; Dual emission; Delayed emission

Organic-inorganic hybrid metal halides (OIHMH) are non-toxic alternatives to lead halide perovskites.[1] In this regard, indium-based OIHMHs have been studied by many research groups.[2] Although several types of indium-based OIHMHs have been reported, a correlation between their structure, defects, and optical properties is still needed. In this study, we investigate the delayed photoluminescence (PL) from 4-piperidinopiperidine indium bromide $(C_{10}H_{22}N_2)_4In_4Br_{20}$ single crystals prepared by a facile solution processing.[2]

The $(C_{10}H_{22}N_2)_4In_4Br_{20}$ single crystals excited by a 405 nm constant wave laser show green [530 nm, Fig. 1a,b(i)] or yellow [590 nm, Fig. 1a,b(ii)] emission. The PL decays (Fig. 1c) of the crystals are recorded using a time-correlated single-photon counting (TCSPC) system. The PL lifetime of the green- and yellow-emitting crystals are 3.2 and 10.7 ns, respectively. We investigate the role of halogen vacancies on the PL properties of the crystals by breaking the green-emitting crystals following by adding a Br^- solution. The emission color of the broken yellow-emitting crystal changes to green immediately after adding a Br^- solution. Also, the PL lifetime of the crystal decreases by Br vacancy filling, indicating halide vacancy-assisted delayed yellow emission. The PL emission color, intensity, and lifetime of the crystals are correlated with the halide vacancy density.

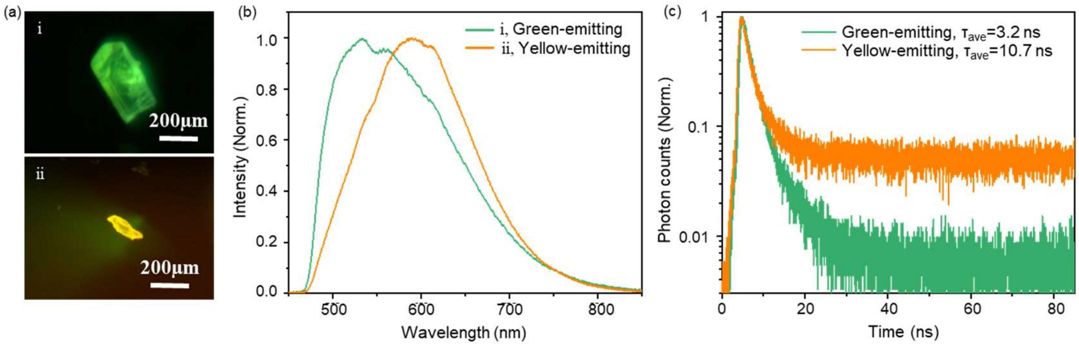


Fig 1. (a) PL images, (b) PL spectra, and (c) PL decays of i) green- and ii) yellow-emitting crystals.

1) Z. Wang, X. Huang, *Chem. Euro. J.* **2022**, *28*, e202200609. 2) N. Sun, J. Lin, S. He, J. Cao, Z. Guo, J. Zhao, Q. Liu, W. Yuan, *Inorg. Chem.* **2023**, *62*, 3018–3025.

Ultrafast dynamics in optically-charge-transfer-induced phase transitions of cyanido-bridged Co-W assemblies

([1]*Graduate School of Science, The University of Tokyo*, [2]*University of Rennes*) ○Koji Nakabayashi,[1] Kazuki Nakamura,[1] Laurent Guérin,[2] Gaël Privault,[2] Marius Hervé,[2] Eric Collet,[2] Shin-ichi Ohkoshi[1]

Keywords: *Photo-induced charge transfer, Femtosecond optical spectroscopy, Phase transition, Cyanido-bridged metal assembly*

Ultrafast photo-responsivity is crucial for advanced photoswitchable materials. Cyanido-bridged metal assemblies have the potential to produce advanced materials with photoswitchable magnetic and optical properties, such as long-range magnetic ordering and THz wave absorption.[1,2] Herein, we report ultrafast dynamics in the cyanido-bridged Co-W assembly, $Cs^{+}_{0.1}(H_5O_2^{+})_{0.9}[Co(4\text{-bromopyridine})_{2.3}\{W(CN)_8\}]$ (**CsCoW**), which shows room temperature bistability and photoinduced ferromagnetism based on the charge-transfer phase transition between low-spin Co^{III}_{LS}-W^{IV} and high-spin Co^{II}_{HS}-W^{V} states.

Time-resolved optical spectroscopy and theoretical studies for the present compound have shown that photoexcitation of the charge-transfer band of Co^{III}_{LS}-W^{IV} state leads to a transient excited state Co^{II}_{LS}-W^{V} state, followed by a spin transition to a Co^{II}_{HS}-W^{V} state within 130 fs. The changes in the electronic state correspond to the decrease and increase of optical density around 600 nm and 700 nm, respectively (Figure 1). The results prove a charge-transfer-induced spin transition (CTIST) process in cyanide-bridged Co-W assemblies. Further experiments in ps time scale revealed that after the fast process a cooperative and thermoelastic process occurs within a few tens of ps near the transition temperature.

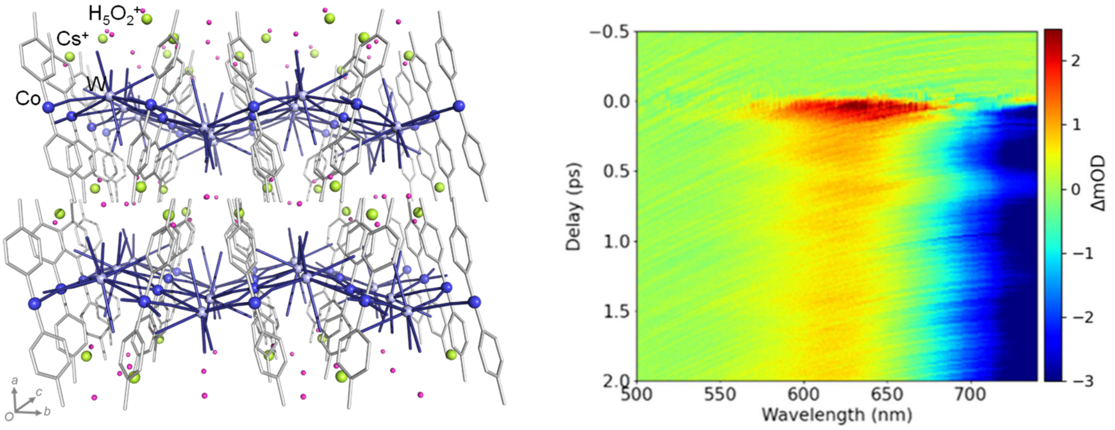


Figure 1. Crystal structure of **CsCoW** with the two-dimensional cyanido-bridged Co-W coordination network (left). Time delay optical density (OD) map of **CsCoW** at room temperature (right).

1) K. Nakamura, K. Nakabayashi, K. Imoto, S. Ohkoshi. **2023**, *10*, 850. 2) T. Yoshida, K. Nakabayashi, H. Tokoro, M. Yoshikiyo, A. Namai, K. Imoto, K. Chiba, S. Ohkoshi, Chem. Sci. **2020**, *11*, 8989.

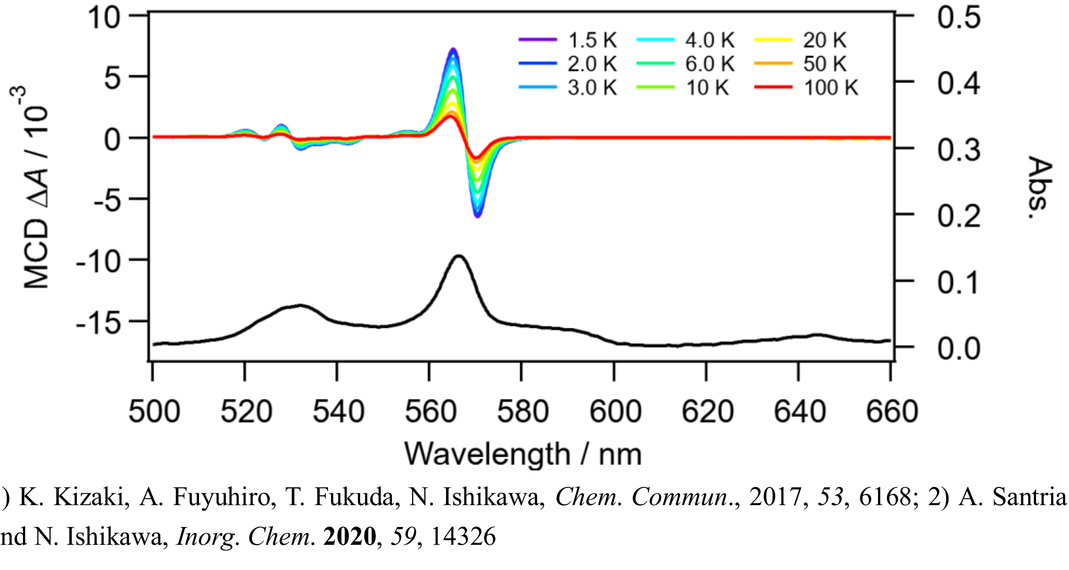
Ferromagnetic-type Interaction between Two Angular Momenta in π-π* Excited State of Lanthanide(III)-Monoporphyrin Complex

([1]*Graduate School of Science, Osaka University*, [2]*Research Center for Chemistry, National Research and Innovation Agency*) ○Anas Santria,[1,2] Naoto Ishikawa,[1]

Keywords: Ferromagnetic; Porphyrin; Excited-State; Lanthanide

This study aims to investigate the electronic interaction in the π–π* excited state of terbium(III) octaethylporphyrinato complex, [Tb(OEP)(cyclen)]Cl (OEP = Octaethylporphyrin; cyclen = 1,4,7,10-tetraazacyclododecane), using magnetic circular dichroism (MCD) spectroscopy. The complex exhibits distinct MCD A-term patterns corresponding to the Soret and Q absorption bands. These patterns show strong temperature dependence and significant non-linearity in the magnetic field dependence, indicating the interaction between two angular momenta: the total angular momentum **J** of 4f-electronic system and the orbital angular momentum **L** of the photoexcited cyclic π–conjugated system.

The coupling between **J** and **L** is parallel, resulting in a ferromagnetic-type interaction. The magnitude of this interaction is estimated by a least-squares fitting to the experimental $\mathcal{A}_1/\mathcal{D}_0$ ratios, with Δ_{JL} and $|L_z|$ as parameters, where $\mathcal{A}_1$ represents A-term intensity and $\mathcal{D}_0$ represents the dipole strength.[1,2] At Q band, the Δ_{JL} matches that of [Tb(TPP)(cyclen)]Cl, while $|L_z|$ value is twice a large. Ab initio calculations support these findings, showing ferromagnetic-type interaction between L_z(f) and L_z(π). Although L_z(π) is larger in [Tb(OEP)(cyclen)]$^+$, the Δ_{JL} remains comparable to that in [Tb(TPP)(cyclen)]$^+$, offering new insights into the magnetic interactions of lanthanide porphyrins.



1) K. Kizaki, A. Fuyuhiro, T. Fukuda, N. Ishikawa, *Chem. Commun.*, 2017, *53*, 6168; 2) A. Santria, and N. Ishikawa, *Inorg. Chem.* **2020**, *59*, 14326