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

Wed. Mar 26, 2025 1:00 PM - 3:20 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:20 AM UTC
[B]A503(A503, Bldg. 1, Area 2 [5F])

[[B]A503-1pm] 09. Coordination Chemistry, Organometallic Chemistry

Chair: Miki Hasegawa, Junpey Yuasa

Japanese
1:00 PM - 1:20 PM JST | 4:00 AM - 4:20 AM UTC
[[B]A503-1pm-01]

Low-energy excitation of near-infrared-emitting lanthanide ions using β-thioxoketone

〇Michiko Suzuki[1], Eiko Mieda[1], Hiroyuki Miyake[1], Satoshi Shinoda[1] (1. Osaka Metoropolitan University)

English
1:20 PM - 1:40 PM JST | 4:20 AM - 4:40 AM UTC
[[B]A503-1pm-02]

Europium(III)-based nanotubular assemblies with photooxidative ability

〇Kotaro Yakuwa[1], Junpei Yuasa[1] (1. Tokyo University of Science)

English
1:40 PM - 2:00 PM JST | 4:40 AM - 5:00 AM UTC
[[B]A503-1pm-03]

Crystallin morphological control of Eu(III) coordination polymer with phosphineoxide linker

〇Masaki Enokido[1], Mengfei Wnag[2,3], Yuichi Kitagawa[2,3], Yasuchika Hasegawa[2,3] (1. Grad. Sch. Chem. Sci. Eng., Hokkaido Univ., 2. Fac. Eng., Hokkaido Univ., 3. WPI-ICReDD, Hokkaido Univ.)

Japanese
2:00 PM - 2:20 PM JST | 5:00 AM - 5:20 AM UTC
[[B]A503-1pm-04]

Luminescence Properties of Eu(III)-Tb(III) Mixed Complexes Based on Corona-Discharge

〇Kota Inage[1], Yuichi Hirai[2], Takayuki Nakanishi[2], Mengfei Wang[3,4], Yasuchika Hasegawa[3,4], Yuichi Kitagawa[3,4] (1. Grad. Sch. of Chem. Sci. Eng., Hokkaido Univ., 2. NIMS, 3. Fac. of Eng., Hokkaido Univ., 4. WPI-ICReDD, Hokkaido Univ.)

Japanese
2:20 PM - 2:40 PM JST | 5:20 AM - 5:40 AM UTC
[[B]A503-1pm-05]

Photostability of Eu(III) complexes composed of phosphine oxide ligands with bulky functional group

〇Masanori Yamamoto[1,2], Keisuke Araki[1], Hiroya Honda[1], Naoyuki Koiso[2], Ryo Nakagame[2], Kohei Iwanaga[2] (1. SCRI, 2. TOSOH CORPORATION)

English
2:40 PM - 3:00 PM JST | 5:40 AM - 6:00 AM UTC
[[B]A503-1pm-06]

Structural and dual luminescence aspects of tetranuclear lanthanide complexes coordinating isonicotinic acid

〇Shun Fujii[1], Miki Hasegawa[1] (1. Coll, Sci. & Eng., Aoyama Gakuin Univ)

English

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

[[B]A503-1pm-07]

The Counter Anion and π-electronic Systems Elongation-enhancement for Triboluminescence of a Series of Chiral Lanthanide Complexes

〇Reo Ohno[1], Daisuke Hayauchi[1], Miki Hasegawa[1] (1. Coll. Sci. & Eng., Aoyama Gakuin University)

β-チオキソケトンを用いた近赤外発光ランタノイドイオンの低エネルギー励起

（阪公大院理）○鈴木 理子・三枝 栄子・三宅 弘之・篠田 哲史

Low-energy excitation of near-infrared-emitting lanthanide ions using *β*-thioxoketone

(*Department of Chemistry, Graduate School of Science, Osaka Metropolitan University*)
○Michiko Suzuki, Eiko Mieda, Hiroyuki Miyake, Satoshi Shinoda

Lanthanide ions coordinated by organic ligands are known to produce strong, pure-color luminescence. In this study, we attempted to synthesize lanthanide complexes with diphenyl-*β*-thioxoketone ligands that use the soft element sulfur as a coordination site, and confirmed their luminescent behavior. We attempted to synthesize complexes with Yb^{3+}, Nd^{3+}, and Er^{3+} as the central metal by heating lanthanide salts and 3eq. *β*-thioxoketone with 1eq. 1,10-phenanthroline in ethanol under basic conditions for 5 minutes. The near-infrared emission spectra of the resulting solids were measured, and characteristic near-infrared emissions corresponding to the central metal were detected. The excitation spectra all had maxima in the visible light region, and excitation in the low-energy region was observed compared to conventional complexes with dioxo type ligands. We will also report on our investigations into structural analysis using various measurements.

Keywords: Lanthanide Complex; β-thioxoketone; Near-infrared emission; Low-energy excitation

ランタノイドイオンは適切な有機配位子を配位させることにより、強く色純度の高い発光が得られることが知られている。ランタノイドイオンがハードな酸であることから、ソフトな塩基をドナーとする錯体についての報告例は少ない。本研究では、ソフトな元素である硫黄を配位サイトとする、ジフェニル-*β*-チオキソケトン配位子を有したランタノイド錯体の合成を試み、発光挙動を調査した。既報にある類似の錯体合成方法[1]を参考に、ランタノイド塩（Yb^{3+}, Nd^{3+}, Er^{3+}）に対して3当量の*β*-チオキソケトンとともに1当量の1,10-フェナントロリンを塩基性条件下エタノール中で5分間 加熱することにより、錯体の合成を行った。生成した固体の近赤外発光スペクトルを測定した結果、中心金属に応じた特徴的な近赤外発光が観測された（Fig.1)。励起スペクトルはいずれも可視光領域にも極大を持ち、従来のジオキソ型配位子をもつ錯体と比較して低エネルギーでの光励起が可能であった。また各種スペクトルによる構造解析の検討についても報告する。

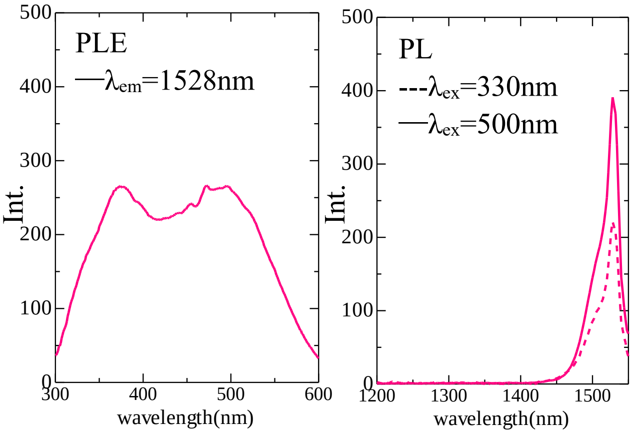

Fig. 1. NIR PEL・PL spectra of　Er^{3+} complex
Solid state(slit : em:5nm, ex=5nm)

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[1] A.I. Voloshin et al., *Journal of Luminescence*, **2001**, 93, 115–118.

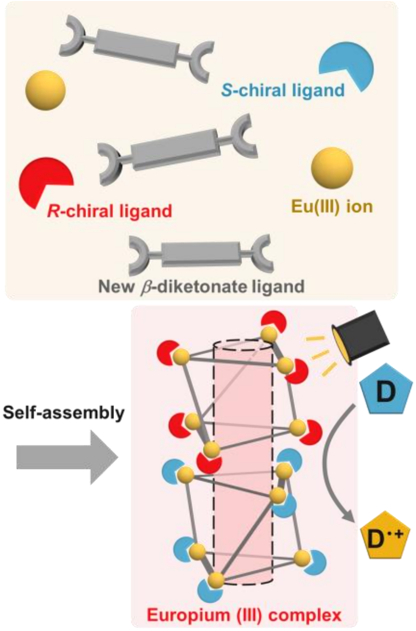
Europium (III)-based nanotubular assemblies with photooxidative ability

(*Grad. Sch. Sci., TUS*) ○Kotaro Yakuwa, Junpei Yuasa

Keywords: Europium complex, *β*-diketonate ligand, Host-guest chemistry

Nanotube with one dimensional porous cavity is an attractive material for material transport and scaffolds of catalytic reactions, but rational construction of one-dimensional nanoporous structures remain difficult. Among the synthetic nanoporous structures, one dimensional metal-organic frameworks (1D MOFs) and stacked macrocyclic assemblies are the most accessible materials. However, the synthetic nanoporous structures reported so far have fixed coordinate bond angles or fixed angularity of covalent bonds, making it difficult to create smooth concentric one-dimensional cavities. In contrast, nanotube structures in natural, such as tobacco mosaic virus, form smooth, concentric, one-dimensional cavities by stacking proteins at periodic angles(1). In this work, we synthesized Europium (III) complex having smooth concentric one-dimensional cavities and studied photooxidative ability of it (**Scheme 1**).

We synthesized new *β*-diketonate ligand, and Europium (III) complex using it and chiral ligands. In result of X-ray diffraction of Europium (III) complex crystal, it constructed nanotube structure having smooth concentric one-dimensional cavities (**Figure 1a, b**). Next, we irradiated UV light to pyrrole in Europium (III) complex crystal after crystal sponge. In this result, crystal' yellow was deeper after UV light irradiation (**Figure 1c, d**).



Scheme 1. The concept of this work.

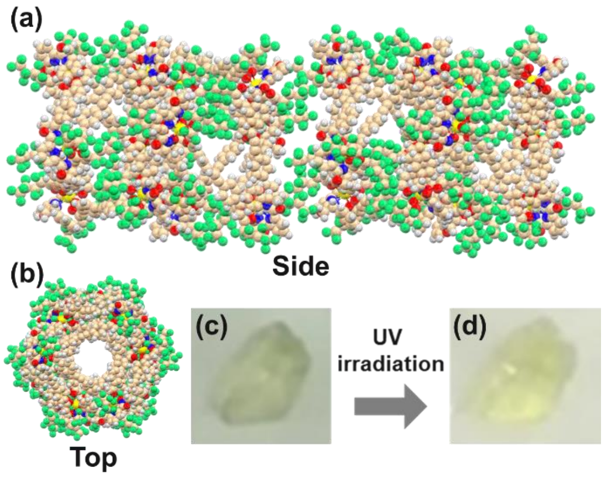


Figure 1. (a, b) Crystal structure of Europium (III) complexes. (c, d) Crystal color of pyrrole in Europium (III) complex before(c) and after (d) UV irradiation.

1) Klug, A. *Philosophical Transactions of the Royal Society of London B.* **1999**, *354*, 531–535.

Crystalline Morphological Control of Eu(III) Coordination Polymer with Phosphine Oxide Linker

([1]*Grad. Sch. Chem. Sci. Eng., Hokkaido Univ.,* [2]*Fac. Eng., Hokkaido Univ.,* [3]*WPI-ICReDD, Hokkaido Univ.*) ○Masaki Enokido[1], Mengfei Wang[2,3], Yuichi Kitagawa[2,3], Yasuchika Hasegawa[2,3]

Keywords: Crystal Morphology; Trivalent Europium; Lanthanide Coordination Polymer; Luminescent Complexes; Micro-crystal

Photophysical properties of coordination polymers depend on the composition and the coordination geometry. Recently, the effect of crystal morphology on photophysical properties have also been investigated. We reported that the emission lifetime of Eu(III) coordination polymers with phosphine oxide linkers is affected by their crystal morphology.[1] To study the correlation between their crystal morphology and photophysical properties, crystal morphological control method is required. Eu(III) coordination polymer crystals with different morphology have been previously synthesized by controlling the amount of phosphine oxide ligands to Eu(III) units.[2] In this study, the morphological control of one-dimensional lanthanide coordination polymers using surfactants is demonstrated.

A solution of $[Eu(hfa)_3(H_2O)_2]$ (hfa; hexafluoroacetylacetonate) in diethyl ether (DEE) was add dropwise anionic surfactant (sodium dodecyl sulfate) solution. Another solution was prepared by dissolving cationic surfactant (cetyltrimethylammonium, lauryl-trimethylammonium, or octyltrimethylammonium bromide) and adding a dichloromethane (DCM) solution of *m*-dpb phosphine oxide ligand (1,3-bis(diphenyl- phosphoryl)benzene) dropwise. The $[Eu(hfa)_3(m\text{-dpb})]_n$ was synthesized by mixing the two solutions (Fig. 1)

The crystal morphologies of $[Eu(hfa)_3(m\text{-dpb})]_n$ dependent on the kind of the cationic surfactant were observed in SEM images. This result suggests that the hydrocarbon chains of cationic surfactants affect the intermolecular interaction between coordination polymer chains. The details of crystal morphological control and photophysical properties are reported in this presentation.

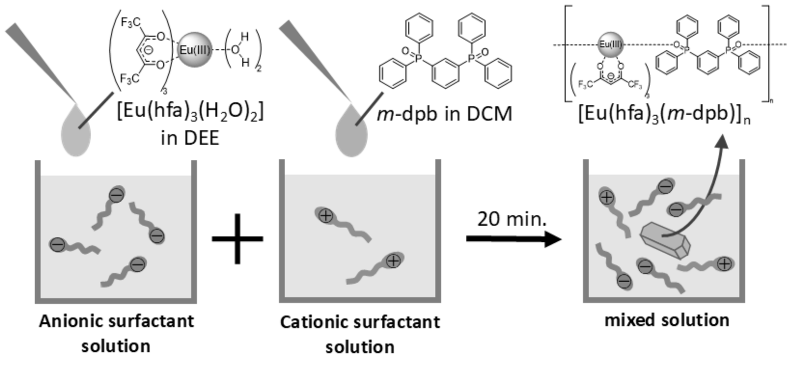


Fig. 1 Synthesis of $[Eu(hfa)_3(m\text{-dpb})]_n$ crystal.

1) M. Enokido et al., *J. Phys. Chem. C* **2023**, 49, 23785. 2) T. Nakanishi et al., *Sci. Technol. Adv. Mater.* **2023**, 24, 2183711.

コロナ放電に基づく Eu(III)-Tb(III)混合錯体の発光機能創出

（北大院総化 [1]・NIMS[2]・北大院工 [3]・北大 WPI-ICReDD[4]）○稲毛 康太 [1]・平井 悠一 [2]・中西 貴之 [2]・ワン メンフィ [3,4]・長谷川 靖哉 [3,4]・北川 裕一 [3,4]

Luminescence Properties of Eu(III)-Tb(III) Mixed Complexes Based on Corona-Discharge

([1]*Grad. Sch. of Chem. Sci. Eng., Hokkaido Univ.*, [2]*NIMS*, [3]*Fac. of Eng., Hokkaido Univ.*, [4]*WPI-ICReDD, Hokkaido Univ.*) ○Kota Inage,[1] Yuichi Hirai,[2] Takayuki Nakanishi,[2] Mengfei Wang,[3,4] Yasuchika Hasegawa,[3,4] Yuichi Kitagawa[3,4]

Color-changeable luminescent molecules have attracted attention as sensors and security inks.1) Their color changes are based on molecular structural transformation induced by external stimuli. The exploration of novel external stimuli is important for advancing luminescence technology and developing methods for transforming molecular structures. In this study, we demonstrate the luminescence color change of a Eu(III)-Tb(III) mixed complex induced by corona-discharge (Fig. 1).

A Corona-charging gun (Green Techno, GC-90N) was used as the corona discharge source. The Eu(III)-Tb(III) mixed complex exhibited luminescence upon corona discharge. In addition, its color changed depending on discharge time. This is the first demonstration of luminescence color change induced by corona discharge.

Keywords : Luminescence; Corona Discharge; Europium; Terbium; 4f-4f Transition

外部刺激による分子構造変化に基づいて発光色を変化させる分子材料はセンサーやセキュリティインクとして注目を集めている 1)。発光色変化を誘起する外部刺激の探索は、新しい光科学技術の構築だけでなく分子構造の制御法開拓にもつながる重要な研究課題である。本研究では、外部刺激としてコロナ放電を用いた Eu(III)-Tb(III)混合結晶の発光色変化について検討を行った(Fig. 1)。

コロナ帯電ガン(GC-90N)を用いて混合結晶を帯電させたところ、Eu(III)および Tb(III)に由来する発光を示した。さらに帯電させ続けたところ、発光色が経時変化した。これはコロナ放電を用いた発光色変化に関する初めての実証例である。

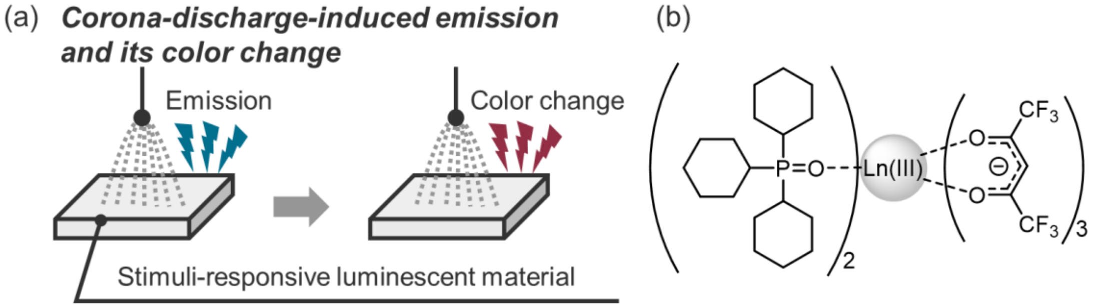


Fig. 1. (a) Conceptual design of this work. (b) Chemical structure of a Eu(III)-Tb(III) mixed complex.

1) (a) Y.-C. Chang *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 9848–9851. (b) A. Abdollahi *et al.*, *ACS Nano* **2020**, *14*, 14417–14492.

嵩高いホスフィンオキシド配位子を用いたEu(III)錯体の光耐久性評価

（相模中研[1]・東ソー（株）[2]）○山本 昌紀[1,2]・荒木 啓介[1]・本田 寛哉[1]・小礒 尚之[2]・仲亀 良[2]・岩永 宏平[2]

Photostability of Eu(III) complexes composed of phosphine oxide ligands with bulky functional group

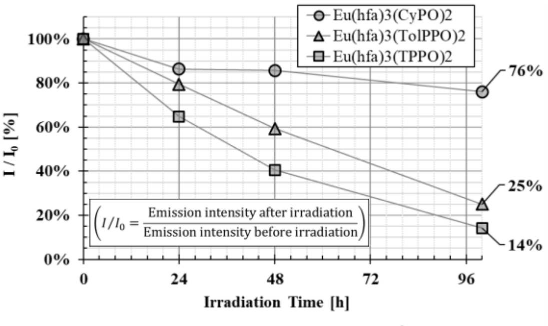
([1]*SCRI*, [2]*TOSOH CORPORATION*) ○ Masanori Yamamoto,[1,2] Keisuke Araki,[1] Hiroya Honda,[1] Naoyuki Koiso,[2] Ryo Nakagame,[2] Kohei Iwanaga[2]

Eu(III) complexes exhibit a large Stokes shift and high-color-purity red luminescence. Among the existing β-diketonate-type Eu(III) complexes, $[\mathrm{Eu(hfa)_3(TPPO)_2}]$ is known to exhibit high emission quantum yield and strong luminescence. However, its photostability is low. To overcome this problem, we synthesized novel Eu(III) complexes composed of phosphine oxide ligands with bulky functional groups, and evaluated their photostability.

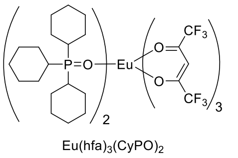
Keywords : Lanthanide complex; Europium complex; Photostability; Luminescent material; Phosphine oxide ligand

Eu(III)錯体はストークスシフトが大きく、色純度の高い赤色発光を示すことから、様々な光学材料への応用が期待される1)。既存のβジケトナト型Eu（III）錯体として、$[\mathrm{Eu(hfa)_3(TPPO)_2}]$が高効率な発光を示すこと知られているが、低耐光性であることが課題である。そこで我々は、高耐光性Eu(III)錯体の開発を目的として、立体的に嵩高いホスフィンオキシド配位子に置き換えたEu(III)錯体を種々合成し、それらの耐光性評価を実施した2,3)。立体的に嵩高い有機配位子を導入することで、酸素や水分子がEu(III)イオンに接近することを防ぎ、光劣化の抑制を期待した。

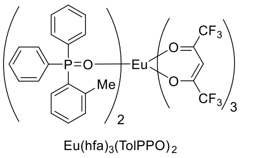
耐光性評価は、粉体、及び1.0wt%PMMA薄膜試料を促進耐候性試験機（キセノンウェザーメーター）内で任意の時間、一定の照度で光照射し、光照射前後の発光強度比（I/I_0）より評価した。1.0wt%PMMA薄膜において、光照射100 h（屋外光1.7か月相当）後のI/I_0は、各々、$[\mathrm{Eu(hfa)_3(CyPO)_2}]$: 76%、$[\mathrm{Eu(hfa)_3(TolPPO)_2}]$: 25%、$[\mathrm{Eu(hfa)_3(TPPO)_2}]$: 14%となり、$[\mathrm{Eu(hfa)_3(CyPO)_2}]$が最も優れた耐光性を示した。



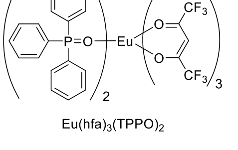
1.0wt% PMMA Film | **Light source** : 300-400 nm / TUV , 120 W/m² | **Condition** : Air, 63°C



$\mathrm{Eu(hfa)_3(CyPO)_2}$



$\mathrm{Eu(hfa)_3(TolPPO)_2}$



$\mathrm{Eu(hfa)_3(TPPO)_2}$

1）Y. Kitagawa, F. Suzue, T. Nakanishi, K. Fushimi, T. Seki, H. Ito, Y. Hasegawa, *Commun. Chem.* **2020**, *3*, Article number 3. 2）東ソー株式会社, 公益財団法人相模中央化学研究所, ユウロピウム錯体及びその用途, 特開 2019-94332, 2019-06-20. 3）東ソー株式会社, 公益財団法人相模中央化学研究所, ユウロピウム錯体, 特開 2020-90475, 2020-06-11.

Structural and Dual Luminescence Aspects of Tetranuclear Lanthanide Complexes Coordinating Isonicotinic Acid

(*Coll, Sci. & Eng., Aoyama Gakuin Univ.*) ○Shun Fujii, Miki Hasegawa

Keywords: *Lanthanide Complex, Luminescence Spectrum, Multiple Luminescence, Single Crystal Structure Analysis, Tetranuclear Clusters*

2,2'-Bipyridine skeletons and their derivatives are well known as efficient photo-antennae to enhance the luminescence of Eu complexes[1,2]. While, quantitative discussions on the monopyridine derivative as energy acceptors in Ln complexes are limited. Since the energy levels of the donor species, the π-electronic system of monopyridine, are at higher than that of the acceptor, it may be a challenge to luminesce Eu ions via the intramolecular energy transfer. In this study, we successfully obtain new luminescent Ln complexes with a very small π-electronic system, NA (isonicotinic acid), as a photo-antenna, resulting in **LnNA** (Ln = Eu, Gd, and Tb) complexes. Resemblances of **LnNA** were reported[3], for example, the complex forms octanuclear clusters as a discrete, not MOF, and the magnetic properties of the Dy complex were evaluated. The octanuclear Eu complex in the literature also luminesces at the typical band positions originated from ff transitions of Eu ions.

From the single crystal structural analysis of **EuNA**, four Eu forms the tetranuclear cluster coordinating four NA species. These NA can be classified into two; as a bridge between two Eu ions by carboxylate-oxygen and nitrogen atoms of a NA, and as a terminal to a Eu ion via its oxygen atoms. The space group of **EuNA**, as well as **GdNA** and **TbNA**, was *Im*-3. Under 270 nm excitation, **EuNA** shows ff emissions. Interestingly, if the excitation wavelength was changed at 340 nm, **EuNA** exhibited both ff and ligand-centered luminescence bands. Thus, **EuNA** is a multi-emissive compound with excitation wavelength dependences. The photo-antenna species having absorption bands at 270 and 340 nm are assigned to the bridged and capped NA, respectively. The luminescence of **GdNA** also supported their assignments. **TbNA** will be also reported here.

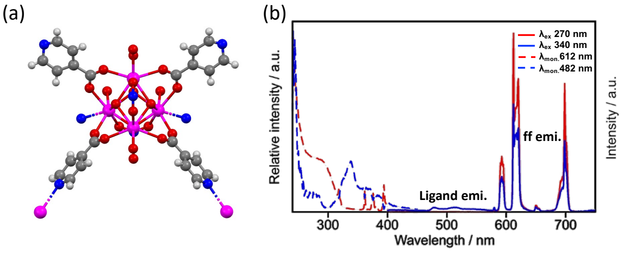


Fig. 1 (a) Crystal structure of **EuNA**. Color code: Eu, Magenta; C, Gray; N, Blue; O, Red; H, White. (b) Luminescence and excitation spectra of **EuNA**.

1) S. V. Eliseevaa and J. G. Büzli, *Chem. Soc. Rev.* 2010, **39**, 189 – 227.
2) M. Hasegawa, *et al.*, *Handbook on the Physics and Chemistry of Rare Earths*. 2024, **66**, 173 – 230.
3) J. F. Li, *et al.*, *Dalton Trans.* 2021, **50**, 13925 – 13931.

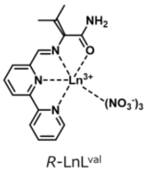
The Counter Anion and π-electronic Systems Elongation-enhancement for Triboluminescence of a Series of Chiral Lanthanide Complexes

([1]*Coll. Sci. & Eng., Aoyama Gakuin University*) ○Reo Ohno,[1] Daisuke Hayauchi,[1] Miki Hasegawa[1]

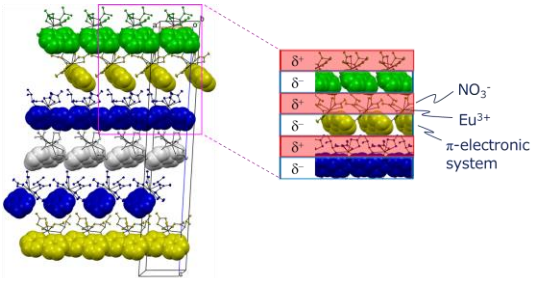
Keywords: Lanthanide Complex; Triboluminescence; Drop Tower System; Chiral Tetradentate Ligand

Triboluminescence (TL) is one of the luminescence phenomena occurring by fracturing molecular crystals with mechanical stimuli.[1] The mechanism of TL has been reported to include the contribution of atmospheric N_2 gas [2] and direct excitation by piezoelectric currents during crystal fracturing [3], however, it is still unclear on many sides. Hitherto, we have focused on the TL of lanthanide (Ln) complexes coordinating a chiral tetradentate ligand with the amino acid skeleton chiral-LnL^{val} [4] using the Drop Tower System (DTS). In this study, we succeed in obtaining new aspects for the appearance mechanism and manipulation of TL in unknown fields of Ln complexes, from the viewpoint of combination between the atmosphere-gas progressing TL, counter anions, and various π electronic systems.

The space group of *R*-LnL^{val} is $P6_5$ (hexagonal). Six molecules of *R*-LnL^{val} are helically forwarded to the *c*-axis. These molecules were classified into four types according to the symmetric operation, and each of them periodically arranged in pillar along the *ab*- plane. The pillars alternate between electron-rich bipyridine layers and electron-poor nitrate ions one. It suggests that the electric polarization state at the inter-pillar interface drives the TL. Here, the TL of *R*-Eu/TbL^{val} (Eu:Tb = 1:10) corresponded to its luminescence spectrum. Furthermore, the fluorescence of the ligand was observed in the TL of *R*-GdL^{val}. It means that the excitation process of *R*-LnL^{val} is similar to the photo-antenna effect, which is the emission mechanism of the Ln complex. While, *R*-EuL^{val}Cl, which has chloride ions, exhibits no TL because the space group is $P2_12_12_1$ (orthorhombic). Furthermore, we also discuss the case of extended π-electronic systems.



R-LnL^{val}



1) A. J. Walton, *Adv. Phys.*, **1977**, *26*, 887-948. 2) G. L. Sharipov, A. A. Tukhbatullin, *J. Lumin.*, **2019**, *215*, 116691. 3) L. M. Sweeting, *Chem. Matter.*, **2001**, *13*, 854-870. 4) M. Hasegawa, H. Ohmagari, M. Iwamura, K. Nozaki, *et al.*, *ChemPlusChem*, **2020**, *85*, 294–300.