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

2024年3月19日(火) 15:55 ~ 17:15 F1233(12号館 [3階] 1233)

[F1233-2vn] 09. 錯体化学・有機金属化学

座長：小林 洋一、堀内 新之介

英語

15:55 ~ 16:15

[F1233-2vn-01]

キラルベンジルアミン配位子修飾シリカ表面への固定化による発光性Tb錯体のキラリティー誘起

○白井 そら[1]、松井 久宜[2]、邨次 智[1]、中井 英隆[2]、唯 美津木[1,3] (1. 名大院理、2. 近畿大院総理工、3. 名大物国セ)

英語

16:15 ~ 16:35

[F1233-2vn-02]

四角酸と硝酸エルビウムから合成された3種の錯体における構造と磁気特性

○高野 莉奈[1]、益田 晃希[2]、北河 康隆[2]、石田 尚行[1] (1. 電気通信大学、2. 大阪大学)

日本語

16:35 ~ 16:55

[F1233-2vn-03]

β-ジケトナート配位子の光分解過程の理解と希土類錯体の光耐久性の向上

○岡安 祥徳[1]、小林 洋一[1,2] (1. 立命館大学、2. JST さきがけ)

日本語

16:55 ~ 17:15

[F1233-2vn-04]

新規ペンタキス（*β*-ジケトン）型コラニュレン配位子による多核Eu(III)錯体形成

○山田 美穂子[1]、松本 大河[1]、加納 春華[1]、河合 壮[1] (1. 奈良先端科学技術大学院大学)

Chirality Induction of Luminous Tb Complexes on Silica Surface Functionalized with Chiral Benzylamine Ligands

([1]*Dept. Chem. Grad. Sch. Sci., Nagoya Univ.*, [2]*Dept. Energy Mater. Grad. Sch. Sci. Eng., Kindai Univ.* [3]*RCMS, Nagoya Univ.*)
○Sora Shirai,[1] Hisaki Matsui,[2] Satoshi Muratsugu,[1] Hidetaka Nakai,[2] Mizuki Tada[1,3]

Keywords: Terbium Complex; Chirality; Chiral Ligand; Silica Surface; Circularly Polarized Luminescence

Immobilization of chiral metal complexes on solid surfaces produces chiral metal complexes on solid materials, which are applied to chiral sensors and heterogeneous asymmetric catalysts etc. The preparation of new chiral molecular structures on SiO_2 surface was investigated by the attachment of an achiral Tb complex on a SiO_2 surface modified with chiral moieties and the chirality induction of an achiral Tb complex ($^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$) on a SiO_2 surface with chiral benzylamine ligands (**$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$**) was successfully achieved.

A chiral ligand (**$\mathbf{L_{NHBoc}}$(*R*/*S*)**), whose amine moiety was protected with a *t*-butoxycarbonyl (Boc) group, was newly synthesized and characterized by ^{1}H NMR, FT-IR, and ESI-MS. **$\mathbf{L_{NHBoc}}$(*R*/*S*)** was attached to a SiO_2 surface, and the Boc group was finally deprotected to prepare **$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$** (Figure 1). Solid-state CD spectra of **$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$** showed inverted CD peaks derived from the surface-attached chiral benzylamine moieties, suggesting the formation of a homo-chiral SiO_2 surface with chiral benzylamine.

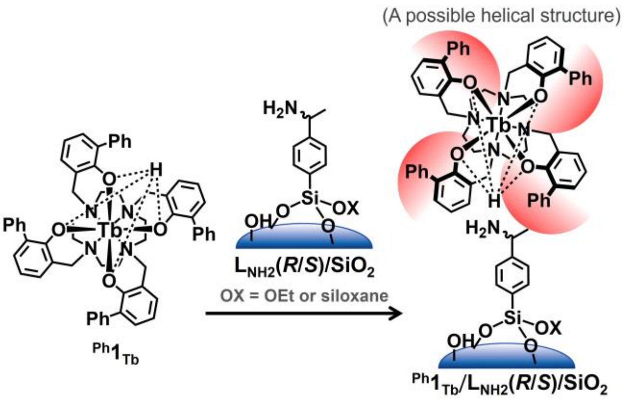


Figure 1. Preparation of **$^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$/$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$**.

An achiral Tb complex with a tetraazacyclododecane-based tetrakis-(2-phenylphenoxide) ligand ($^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$) was immobilized on **$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$** (Figure 1). Tb L_{III}-edge EXAFS of **$^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$/$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$** were similar to that of $^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$, indicating that the coordination structure of the precursor $^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$ was maintained on the SiO_2 surface (Figure 2). Solid-state CPL spectra of **$^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$/$\mathbf{L_{NH2}}$(*R*/*S*)/$\mathbf{SiO_2}$** showed inverted CPL peaks derived from f-f emissions of $^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$, strongly suggesting that the chirality of $^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$ was successfully induced on the attached SiO_2 surface with the chiral benzylamine ligands.

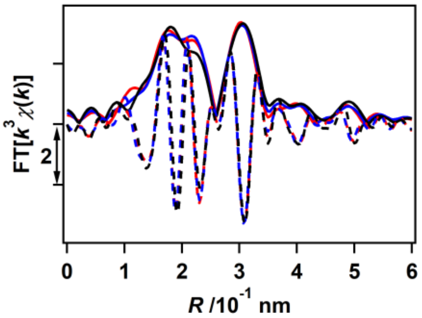


Figure 2. k^3-weighted Tb L_{III}-edge EXAFS Fourier transforms (k = 30－105 nm^{-1}) of $^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$ (black), **$^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$/$\mathbf{L_{NH2}}$(*R*)/$\mathbf{SiO_2}$** (blue), and **$^{\mathbf{Ph}}\mathbf{1}_{\mathbf{Tb}}$/$\mathbf{L_{NH2}}$(*S*)/$\mathbf{SiO_2}$** (red) (at 20 K). Solid lines: magnitude; dotted lines: imaginary parts.

Structures and Magnetic Properties of Three Types of Complexes Prepared from Squarate and Erbium Nitrate

([1]*The University of Electro-Communications*, [2]*Osaka University*) ○Rina Takano,[1] Koki Masuda,[2] Yasutaka Kitagawa,[2] Takayuki Ishida[1]

Keywords: Heavy Lanthanide Ions; Multi Nuclear Complexes; Magnetic Properties; Computation Chemistry

Single ion magnets are expected to show high-performance magnetic properties. To develop such magnets, it is necessary to characterize the properties of each single ion, such as the crystal field and electronic environment. Squaric acid (H_2sq) is well known as a versatile ligand to produce several types of complexes from mononuclear to polymer[1-4)]. We obtained three types of structures from erbium(III) nitrate and squaric acid by means of hydrothermal synthesis. Oxalate (ox^{2-}) appeared as a decomposed product from squarate. The structures of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$, $[Er_2(sq)_3(H_2O)_8]_n$,[1)] $[Er_2(sq)_2(ox)\ (H_2O)_4]_n$ were confirmed to be discrete mononuclear (Fig. (a)), double-layer two-dimensional polynuclear, and three-dimensional polynuclear (Fig. (b)), respectively.

DC magnetic results indicate negligible magnetic interaction among lanthanide ions. In the AC magnetic measurements, all the compounds showed frequency dependence when a bias-field was applied. From the Arrhenius plots, the magnetization relaxation barriers were determined as 27(2), 14(1), and 20.6(9) K for $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$ (Fig. (c)), $[Er_2(sq)_3(H_2O)_8]_n$, and $[Er_2(sq)_2(ox)(H_2O)_4]_n$, respectively. The CASSCF calculations are ongoing by using the crystal structures determined. The relationship between magnetic properties and crystal structure will be discussed.

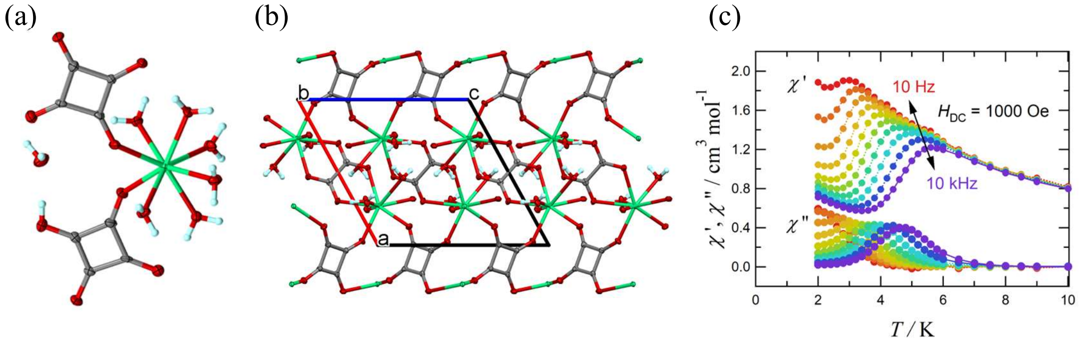


Fig. (a) Crystal structures of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$ and (b) $[Er_2(sq)_2(ox)(H_2O)_4]_n$ viewed along the *b* axis. (c)AC magnetic susceptibility result of $[Er(sq)(Hsq)(H_2O)_6]\cdot(H_2O)$.

Ref. 1) R. Takano et al., *Dalton Trans*. **2023**, *52*, 8873. 2) J. F. Petit et al, *Inorg. Chim. Acta* **1990**, *167*, 51. 3) S. Biswas et al., *Inorg. Chem*. **2013**, *53*, 3926. 4) L. Wang et al., *Aust. J. Chem*. **2011**, *64*, 1373.

β-ジケトナート配位子の光分解過程の理解と希土類錯体の光耐久性の向上

（立命館大生命科学 [1]・JST さきがけ [2]）岡安 祥徳 [1]・小林 洋一 [1,2]

Understanding of photodecomposition mechanisms of β-diketonate ligand and improving the photodurability of lanthanide complexes

([1]*College of Life Sciences, Ritsumeikan Univ.*, [2]*PRESTO JST*)○Yoshinori Okayasu,[1] Yoichi Kobayashi[1,2]

Suppression of photodegradation is important for applications in sensors and organic light-emitting devices. Although energy transfer processes from ligands to lanthanide ions have been extensively studied in recent years, more detailed investigations of the excited-state dynamics are necessary for unveiling the photodegradation mechanism. In this study, we synthesized mono- and dinuclear Eu(III) complexes with β-diketonate ligands (Eu(PhDK)$_3$ and Eu$_2$(BTP)$_3$) and investigated the excited state dynamics in detail using femtosecond to millisecond time-resolved spectroscopic measurements.

The sub-millisecond transient absorption spectra of Eu(PhDK)$_3$ in acetonitrile show a positive signal at 320 nm immediately after the excitation. This signal was not observed for Y(PhDK)$_3$, suggesting that it originated from electron transfer from the ligand to the Eu(III) ion. Eu(PhDK)$_3$ is more decomposed than Y(PhDK)$_3$, and the electron transfer process promotes photodecomposition.

Keywords: *Lanthanide complex; β-diketonate ligand; Photostability; Photodegradation; Time-resolved spectroscopy*

特徴的な光学特性を示す希土類錯体は、配位子から希土類イオンへのエネルギー移動過程が詳細に研究されている一方、光分解過程においては未解明な部分が多く、光耐久性の高い分子設計は確立されていない。光分解過程の詳細な理解は分解の抑制につながり、その知見は希土類錯体を用いたセンサーや発光デバイスにおいて重要である。

本研究では、β-ジケトナート配位子を有する単核および二核Eu(III)錯体 (Eu(PhDK)$_3$, Eu$_2$(BTP)$_3$)を合成し(Fig. 1a)、フェムト秒からミリ秒の時間分解分光測定を行い、分解メカニズムを詳細に検討したので報告する。

窒素雰囲気下、Eu(PhDK)$_3$ のアセトニトリル溶液に 355 nm のナノ秒レーザーを照射すると、励起直後から 320 nm に正のシグナルが観測された(Fig.1b)。このシグナルは電子移動の起こらない Y(PhDK)$_3$ では観測されず、配位子から Eu(III)イオンへの電子移動に由来することが示唆された。また、Eu(PhDK)$_3$の方が Y(PhDK)$_3$よりも分解反応が進行するため、電子移動過程が分解を促進することがわかった。

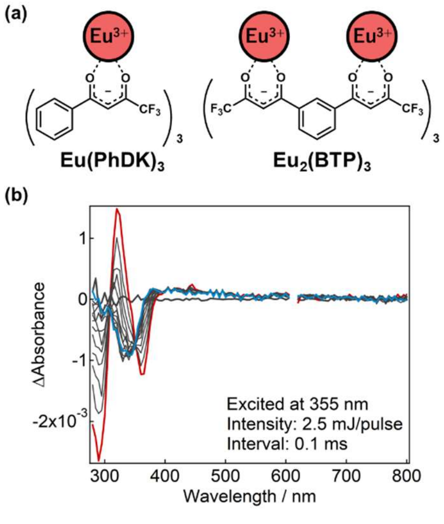


Fig.1 (a) Chemical structure of the Eu(III) complexes. (b) Transient absorption spectra of Eu(PhDK)$_3$ in acetonitrile (10 μM) on sub-millisecond timescales with a 355 nm nanosecond laser pulse (2.5 mJ pulse^{-1}) under a nitrogen atmosphere at room temperature.

新規ペンタキス(*β*-ジケトン)型コラニュレン配位子による多核Eu(III)錯体形成

（奈良先端大物質 [1]）○山田 美穂子 [1]・松本 大河 [1]・加納 春華 [1]・河合 壯 [1]

Formation of Multinuclear Europium(III) Complexes with a New Pentakis(*β*-diketone)-Type Corannulene Ligand

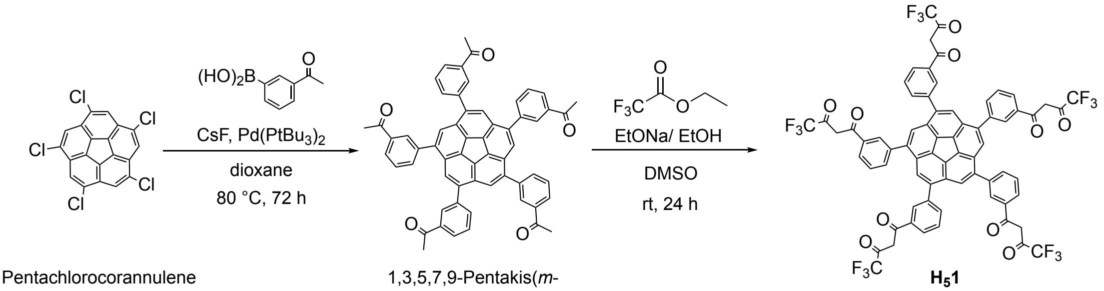
([1]*Division of Materials Science, Nara Institute of Science and Technology*)
○Mihoko Yamada,[1] Taiga Matsumoto,[1] Haruka Kano,[1] Tsuyoshi Kawai[1]

Emission of Eu complex is enhanced by the antenna effect of the ligands having large absorption coefficient. C_5-Symmetric curved aromatic corannulene with a large absorption coefficient is a promising motif for enhancement of emission of Eu(III) complexes. It has been found that Eu(III) complex, which has a large diversity of coordination geometries, is effectively stabilized by forming the closed structure. In this work, focusing on the stability of the closed structure and the charge balance, we studied formation behavior of multinuclear Eu(III) complexes with a new pentakis(*β*-diketone)-type ligand having a corannulene skeleton.

Keywords : Europium Complex; Corannulene; Multinuclear Complex; Closed Structure; Emission

Eu(III)錯体はシャープな発光特性を示すことから、発光材料への応用のために、発光強度や効率向上を目指した研究が行われてきた。C_5 対称の湾曲状芳香族コラニュレンは大きなモル吸光係数を有し、光アンテナ効果による Eu(III)錯体の発光増強が期待できる。近年、柔軟性の高い Eu(III)錯体の配位構造制御に向けて閉殻かご状構造の適用が検討されている [1]。本研究では、発光効率向上と錯体の多核化による機能制御を目指し、新規ペンタキス（*β*-ジケトン）型コラニュレン配位子の多核 Eu(III)錯体形成挙動を検討した。

まず、ペンタクロロコラニュレンから 2 段階で、5 つの *β*-ジケトン配位部位とコラニュレン骨格を有する新規配位子 $\mathbf{H_5 1}$ を合成した。得られた $\mathbf{H_5 1}$ を DMSO 中で過剰量の Eu(III)と反応させたところ、613 nm に Eu(III)錯体に特徴的な発光バンドが観測され、Eu(III)錯体の形成が示唆された。この発光は顕著な O_2 消光効果を示したことから、配位子の T_1 準位を経由するものと推定された。配位子 $\mathbf{H_5 1}$ と Eu(III)による滴定実験の分光測定と ESI-MS 測定から、Eu(III):$\mathbf{1}^{5-}$=4:2 錯体が安定に得られることが示唆された。当日は、閉殻構造と電荷バランスに注目し、錯体の構造についても議論する。



Pentachlorocorannulene

1,3,5,7,9-Pentakis(*m*-acetylphenyl)corannulene

$\mathbf{H_5 1}$

1) Y. B. Tan, *et al.*, *J. Am. Chem. Soc.* **2020**, *142*, 17653–17661.