

# Polymorphism-based luminescence of lanthanide complexes with a deuterated 1,10-phenanthroline



S. Ogata, A. Ishii, C.L. Lu, T. Kondo, N. Yajima, M. Hasegawa\*

College of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagami-hara, Kanagawa 252-5258, Japan

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## ABSTRACT

Deuteration and/or polymorphism effects on the ff emission of lanthanide complexes were discussed by using phenanthroline (phen) and deuterated phenanthroline (phen- $d_8$ ) complexes with Eu, Tb, Gd and Tm ion as a center metal. Lanthanide complexes with phen or phen- $d_8$  form polymorphism such as phase **IIa** and **I**. The ratio of polymorphism **IIa** to **I** of Gd or Tm complexes with phen was newly estimated by a synchrotron XRPD. From the measurement of luminescence spectra, lifetimes and absolute quantum yields at room temperature and 77 K, it was found that the ff emissions of above lanthanide complexes were explained by their energy relaxation process through intermolecular energy transfer and the polymorphism effects. Luminescence of Eu was intensified by the deuteration of phen, due to deactivation with the overtones of C-H/D vibrations, and each luminescence quantum yield of two phase was theoretically estimated. Tb had no influence clearly by the deuteration in phen, but did by the polymorphism formation. Blue luminescence of Tm was observed in both phen/phen- $d_8$  complexes. Furthermore, the luminescence component ratios of lanthanide complexes with phen corresponded to the ratios from the observation of XRD.

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## 1. Introduction

Luminescent materials of lanthanide complexes have been widely synthesized, since their stable luminescence wavelengths under various environments are applicable to sensors [1] or electric devices [2]. The ff emission of lanthanide complexes is basically sensitized by the photo-excitation of the organic ligand via the intramolecular energy transfer. Each lanthanide has unique energy acceptor levels and luminescence wavelengths and an appropriate molecular design will accelerate the ff emission. There are some approaches to increasing the luminescence intensity of lanthanide complexes. For instance, the efficient energy transfer system through the intramolecular energy transfer, prediction of intramolecular or medium's vibration and chelate effect to keep the stable coordination environment even in solutions have been reported [3].

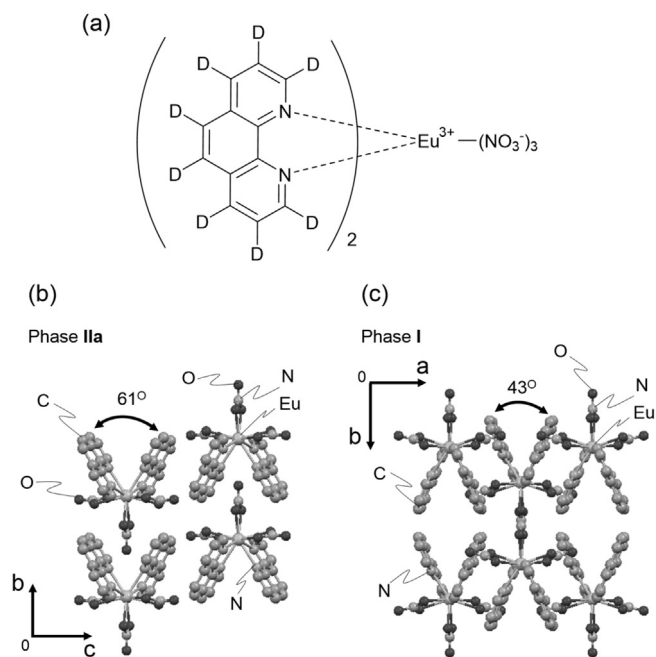
Deuterated organic ligands will become a key to controlling the lanthanide luminescence originating from ff transitions. This luminescence is normally weakened by the resonance effect of intramolecular vibrations between carbon and hydrogen (C—H) bonds [4]. Hemmilä and co-workers reported the above effect on

Eu<sup>III</sup> and Tb<sup>III</sup> complexes with analogous seven-dentate and nine-dentate EDTA ligands in aqueous solutions [5]. In the literature, for instance, Eu<sup>III</sup> luminescence was strengthened by the replacement of C—H bonds with C—D bonds in the ligands, whereas the effect for Tb<sup>III</sup> was negligibly small. Seitz, et al. explained the nonradiative deactivation mechanism of lanthanide excited states by the multiphonon relaxation based on aromatic C—H and C—D oscillator overtones [6].

1,10-phenanthroline (abbreviated to phen) is one of the most useful ligand moiety to coordinating metal ions. Actually, various metal complexes with phen have been reported due to being stable compounds with chelate rings [7]. The Pr complexes with phen and its analogous were reported to elucidate the energy transfer pathway and the rate constant of intramolecular energy transfer from phen to Pr by using picosecond time resolved luminescence spectra [8]. The excitation triplet state of phen acted as an energy donor of a Pr ion through the energy transfer in  $3.3 \times 10^9 \text{ s}^{-1}$  of the constant. The ligand shape is quite stable to form the chelate ring with a series of lanthanide, and is useful to sensitize the ff emission of a series of lanthanide ion such as Eu and Tb [9]. We previously evaluated the deuteration effect on the structure of Eu and Tb complexes with deuterated phen (abbreviated to phen- $d_8$ ) from synchrotron X-ray powder diffraction (XRPD) measurements [10]. For instance, Euphen forms a single crystalline phase as phase **IIa**,

\* Corresponding author.

E-mail address: [hasemiki@chem.aoyama.ac.jp](mailto:hasemiki@chem.aoyama.ac.jp) (M. Hasegawa).



**Fig. 1.** Molecular structure of Euphen- $d_8$  (or Euphen) (a) and their packing structure of phase **IIa** (b) and **I** (c) referred from previous paper [10]. Hydrogen atoms are omitted to clarity.

while Euphen- $d_8$  has two phases; phase **IIa** and **I** (Fig. 1). The dihedral angles between the two phen moieties coordinating  $\text{Eu}^{\text{III}}$  in the phase **IIa** and **I** of Euphen- $d_8$  were  $61^\circ$  (existence ratio: 74.8%) and  $43^\circ$  (25.2%), respectively. In Tb complexes, phases **IIa** and **I** exist in the ratio of 90.8% and 9.2% for the undeuterated species and 78.3% and 21.7% for deuterated one.

In this study, we will describe the quantitative luminescence mechanisms of phen- $d_8$  complexes with lanthanide ions such as  $\text{Eu}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$  and  $\text{Tm}^{\text{III}}$  in the solid state. Here, the deuteration effects on the luminescence of Euphen- $d_8$ , Tbphen- $d_8$  and Tmphen- $d_8$  are discussed based on measurements of electronic spectra, luminescence lifetimes and quantum yields. Undeuterated phen complexes with  $\text{Eu}^{\text{III}}$ ,  $\text{Gd}^{\text{III}}$ ,  $\text{Tb}^{\text{III}}$  and  $\text{Tm}^{\text{III}}$  were also used for comparison of the energy relaxation processes. The radiative and nonradiative constants and energy transfer efficiencies were calculated by theoretical supporting of the luminescence behaviour of these complexes. Structural assignments of Gd and Tm complexes were evaluated by the measurement of synchrotron XRPD.

## 2. Experimental

### 2.1. Preparation of lanthanide complexes

A series of lanthanide complexes was prepared by the previous literature [10]. Gd and Tm complexes with phen- $d_8$  (98 Atom% D, ISOTECH) were newly synthesized with yields in 83% and 89%, respectively. Elemental analysis for  $\text{Gd}(\text{phen})_2(\text{NO}_3)_3$ ; calcd.: C 40.97, H 2.29, N 13.93; found: C 40.59, H 2.41, N 13.80, and for  $\text{Tm}(\text{phen})_2(\text{NO}_3)_3$ ; calcd.: C 40.30, H 2.25, N 13.71; found: C 40.04, H 2.53, N 13.52.

### 2.2. Apparatus

Attenuated Total Reflectance FT-IR spectra were measured by Nicolet iS5 (Thermo Scientific). From the measurements of synchrotron XRPD (Beam line BL02B2 at SPring-8) of a series of complexes, their patterns were assigned with the comparison of

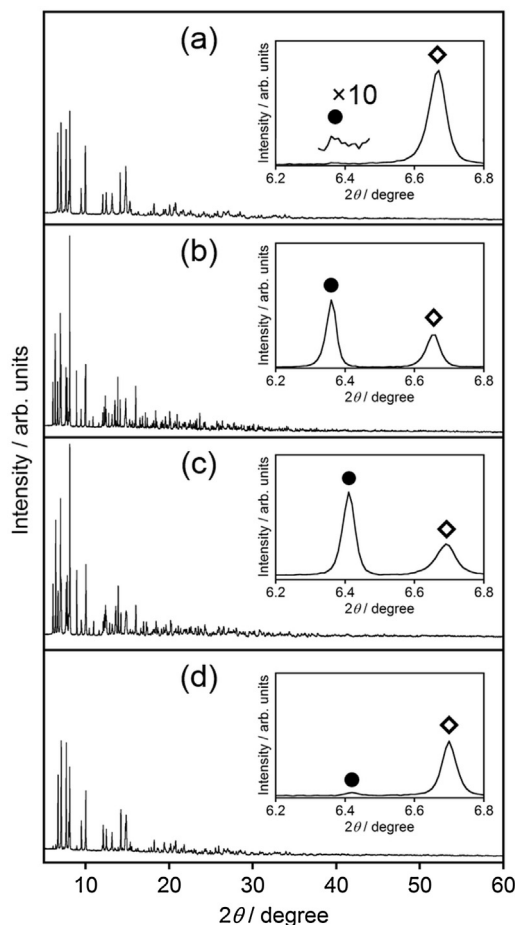
those of Euphen or Euphen- $d_8$  [10]. Electronic absorption spectra were obtained from the diffused reflection method with conversion of the y-axis by UV-3600S (Shimadzu). Luminescence and excitation spectra were recorded on Fluorolog 3–22 (Horiba Jobin Yvon). Absolute luminescence quantum yields and luminescence lifetimes were determined by an Absolute Luminescence Quantum Yields Spectrometer C9920-02 (Hamamatsu Photonics K. K.) and Quantaaurus-Tau C11367-12 (Hamamatsu Photonics K. K.) with the pulsed excitation light source.

## 3. Results and discussion

### 3.1. Structural analyses of lanthanide complexes with phen

#### 3.1.1. Synchrotron XRD of Gdphen/phen- $d_8$ and Tmphen/phen- $d_8$

Powder XRD patterns are useful to precisely know the polymorphism such as phen complexes with Eu or Tb in the previous report [10]. Fig. 2 shows synchrotron XRPD patterns of Gd and Tm complexes with phen and phen- $d_8$  to evaluate the component ratios of phases **IIa** and **I**. From the previous report [10], characteristic peaks assigned to phases **IIa** and **I** will appear at  $2\theta = 6.7^\circ$  and  $\sim 6.3^\circ$ , respectively, and their peak intensities enhance the component ratios. In this study, Gd and Tm complexes also showed these XRD peaks at same position. Thus, these complexes have polymorphism, and their existence ratios were calculated in **IIa** and **I** as 97%: 3% for Gdphen- $d_8$ , 48%: 52% for Gdphen, 48%: 52% for Tmphen- $d_8$ , and 91%: 9% for Tmphen.



**Fig. 2.** Synchrotron XRPD patterns of Gdphen- $d_8$  (a), Gdphen (b), Tmphen- $d_8$  (c) and Tmphen (d). Insets show extended figures. Filled-circles and open-diamonds are peaks assigned to the phases **I** and **IIa**, respectively.  $\lambda = 0.998852 \text{ \AA}$ .

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