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学位論文内容の要約

博士の専攻分野の名称　博士（工学）　氏名　和田　智志

学位論文題目

Study on External Field-induced Photophysical Properties of Chiral Lanthanide Complexes

（キラル希土類錯体の外場に誘起された光物性に関する研究）

An incorporation of lanthanide (Ln) with designed organic molecules is a useful method to control photophysical properties of Ln(III) ions. Ln(III) complexes exhibit unique luminescence properties deriving from the 4f electrons. Among the organic-inorganic hybrid lanthanide compounds, Ln(III) complexes coordinated with chiral organic molecules have attracted attention for their characteristic (natural) optical activities. Chiral molecules exhibit selective electronic transitions of left- and right-handed circularly polarized light with absorption (circular dichroism: CD) or emission (circularly polarized luminescence: CPL) according to the molecular chirality. Generally, chiral Ln(III) complex displays higher CPL performance than that of typical chiral organic molecules or transition metal complexes. The high performance of Ln(III) complex has been attracted attention for various field such as bioimaging, 3D display, security tag, and data storage. Polarization response such as optical activity in the electronic transition is not limited to the chiral compounds. Lanthanides also exhibit high performance for magneto-optical activities deriving from the 4f electrons by applying external magnetic field. The Faraday rotation and magnetic circular dichroism (MCD) are representatives of magneto-optical activities. The Faraday effect of lanthanide compounds has been applied to optical isolators employed in optical communication systems. These polarization responses of Ln(III) complexes are governed by steric and electronic structures of Ln(III) complexes depending on external environment.

The objective of this study is to develop chiral Ln(III) complexes for applying to CPL materials and clarifying the mechanism of optical- and magneto-optical activities depending on external environment. Optical- and magneto-optical activities of chiral Ln(III) complexes originate from the electronic transition of 4f electrons. The photophysical properties of Ln(III)

complexes are strongly affected by the electronic state of Ln(III) ion, where mixing of wavefunctions by configuration- and/or *J*-mixing is occurred based on the external environments such as electric (crystal) field of coordinated ligands and/or external magnetic field. The optical- and magneto-optical activities of chiral Ln(III) complexes should be affected by the external environment. Clarifying the effect of electronic state (or configuration) mixing under external environments on optical activities of chiral Ln(III) complexes is required for controlling the optical- and magneto-optical activities and developing photo-functional chiral Ln(III) complexes. In this research, the effect of the electronic state (or configuration) mixing to polarized light response, i.e. optical- and magneto-optical activities, of chiral Ln(III) complexes is focused on. Several kinds of chiral Ln(III) complexes are synthesized and the optical- and magneto-optical activities are investigated.

In Chapter 1, photophysical properties and polarization response of Ln(III) compounds depending on external environment are overviewed. The objective of this research is described in relation to the electronic state and chirality of Ln(III) complexes under surrounding environment.

In Chapter 2, a chiral Eu(III) complex with large dissymmetry factor of CPL (g_{CPL}) in film state is explored for the application to transparent materials with CPL property. Red luminescent non-crystalline chiral Eu(III) complex was successfully prepared by co-grinding of Eu(III) complex with camphor derivative ligand and achiral phosphine oxide molecule without any solvents. The camphor Eu(III) complexes were also obtained by general solution synthesis as a transparent film. The Eu(III) complex in film state exhibited extra-large CPL performance (g_{CPL} = -1.5) and high emission efficiency (Φ_L = 11%) by tuning the amount of phosphine oxide molecules. The g_{CPL} value is as large as previously reported maximum g_{CPL} value (g_{CPL} = -1.45) of chiral Eu(III) complex. Furthermore, the Φ_L was more than ten times as large as that of the Eu(III) complex with the maximum g_{CPL} value. The high performances were attributed to the weak interaction between the camphor Eu(III) complex and bulky phosphine oxide molecule. The film was applied to a simple model of CPL security ink. The difference in CPL intensity of the film was easily detected to the naked eye with simple setup of CPL determination, which is potentially applicable to security ink. The results provide a novel strategy for designing the Eu(III) complex with large CPL performance and high emission intensity, leading to a new application for CPL materials such as security ink, bioimaging, and 3D display.

In Chapter 3, the detail CPL mechanism of chiral Ln(III) complexes is evaluated by measuring CPL of Eu(III) complexes in solution, where the effect of electronic state mixing is discussed. Previously reported chiral Eu(III) complexes with camphor derivative ligands and

phosphine oxide ligands were synthesized. A novel mechanism for chiroptical activity inversion based on the electronic structure of metal complexes without Λ- or Δ-type structure change was demonstrated spectroscopically and theoretically. The steric and electronic structures of the Eu(III) complex were adjusted by additional achiral phosphine oxide and coordinating acetone molecules. CPL sign inversion, which was independent of Λ- or Δ-type structure changes from the spectroscopic viewpoint, and a drastic g_{CPL} change from +0.013 to -1.0 were observed depending on the external achiral molecules around Eu(III) ion. These phenomena provide the first clarification of optical activity change associated with electronic structure rather than chiral coordination structure-type (Λ or Δ) under external environments. The CPL phenomena were attributed to the chiral electronic structure depending on the transition electric dipole moment ($\vec{\mu}$) under *J*-mixing. The results provide a novel aspect for the optical activity of metal complexes and for molecular design of chiral lanthanide complex for maximizing the g_{CPL} value.

In Chapter 4, electronic state mixing of chiral Ln(III) complex is applied to magneto-optical activity, in an attempt to develop a new field of polarization response induced by chirality and magnetic field. The chiroptical and magneto-optical properties of novel four types of chiral nonanuclear Tb(III) clusters, which are composed of nine Tb(III) ions and sixteen chiral salicylate ligands, were assessed. The CD signals in the ππ* transition of the Tb(III) clusters were dependent on the coordination structures induced by the ester groups of the salicylate ligands. The chiral Tb(III) clusters exhibited CPL signals corresponding to the 4f-4f transitions, which indicated that the chirality of ligands was reflected to the Tb(III) core in the clusters. Furthermore, the Faraday rotation was affected by the chirality of the Tb(III) clusters. These results provide significant new insight regarding the interrelation between chirality and the Faraday effect.

In Chapter 5, finally, summary and outlook of the research are described. Optical activities of chiral compounds potentially include numerous information on the light. Ln(III) complexes under chiral environment are hopeful candidate for next generation photo-functional materials with polarized light response that cannot be achieved by chiral organic molecules or other metal complexes. In this study, the chirality of Ln(III) complex was clarified from the viewpoint of the electronic state depending on the external field. The results lead to the possibility of generating novel CPL materials and new magneto-optical phenomenon of chiral Ln(III) complex controlled by external environment.