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# 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 平井 悠一

## 学 位 論 文 題 名

Study on Assembled Structures and Physical Properties of Luminescent Lanthanide(III)  
Complexes

（発光性希土類錯体の集積形態と物理特性に関する研究）

Significant efforts have been focused on exploring the luminescent materials composed of inorganic, organic, or coordination compounds. Among these materials, lanthanide (Ln(III)) coordination compounds are highly attractive due to their versatile photophysical properties arising from characteristic 4f-4f transitions. These compounds are generally known to show line-like emission and long-lived emission lifetimes that make them useful in applications such as lighting devices, displays, and bio-probes.

In this study, the author focused on the relationships between assembled structures of Ln(III)-hexafluoroacetylacetonate (hfa) compounds and their physical properties.

In Chapter 1, the history and importance of Ln(III) coordination compounds are reviewed. The general theoretical background for strong luminescence and the objectives of this study are also described.

In Chapter 2, the strategy for strong luminescence by antenna-excitation of Eu(III) coordination polymers is reported. Novel Eu(III) coordination polymers with hydrogen-bonded zipper structures were prepared by introducing thiophene- and ethylenedioxythiophene-based phosphine oxide bridges. The zig-zag orientation of single polymer chains induced the formation of densely packed coordination structures with multiple CH/F and CH/ interactions, resulting in thermal stability above 300 degrees C in particular for the thiophene-bridged polymer. The dramatically high ligand-to-metal energy transfer efficiencies of up to 80 percent were observed in solid state, which would be correlated to the intra-ligand charge transfer (ILCT) states of antenna ligands.

In Chapter 3, the control of energy transfer efficiency between Ln(III) ions in coordination polymers is studied for wide-range temperature-sensitivity. The Tb(III)/Eu(III) mixed coordination polymers with 4,4'-substituted biphenylene bridges were prepared to investigate the energy transfer efficiency between these ions in solid state. The emission color change depending on temperature and energy donor/acceptor concentration ratios were successfully observed. In the case of Tb(III) coordination polymers with a small amount of Eu(III) ions, longer excited state lifetimes of Tb(III) ions were observed, compared to a pure-Tb(III) compound. The author consider this to be responsible for the suppression of concentration quenching of Tb(III)-centered luminescence.

In Chapter 4, the glass forming ability of assembled Ln(III) coordination compounds is exhibited to provide transparent and highly processable luminescent materials. Here, 1,2-, 1,3-, and 1,4-substituted benzene with ethynyl groups were utilized as bridging ligands. The Eu(III) coordination compounds with 1,2- and 1,4-substituted phenylene bridges formed dimer and polymer structures, respectively, which was confirmed by single crystal X-ray analyses. On the other hand, the complex with 1,3-substituted phenylene bridge formed amorphous solid, and pseudo-C<sub>3</sub> symmetrical trimer structure was assumed based on the mass spectrometry, elemental analysis, and DFT optimization. Their coordination structures and glass formability were found to depend on the regiochemistry of substitution in regard to the internal phenylene core.

In Chapter 5, systematic construction of Ln(III) coordination glasses and their temperature-sensitive luminescence in glassy state are described. The bridging ligands with thienyl, naphthyl, phenyl cores and ethynyl groups were synthesized and glass transition points for corresponding coordination compounds were clearly observed. The glass transition points were

considered to depend on the molecular weight and availability of  $\pi$ -aromatic surface of bridging ligands. Based on the molecular strategy in Chapter 3 and 4, the Tb(III)/Eu(III) mixed coordination glass (Tb/Eu = 50) was also prepared for the phenylene-bridged type. The obtained compound exhibited green, yellow, orange, and red photoluminescence (PL) depending on temperature. The energy transfer efficiency between Ln(III) ions was estimated to be as high as the previously reported Ln(III)-mixed coordination polymer.

In Chapter 6, the triboluminescence (TL) of Ln(III) coordination polymers is described to explore their potential as novel class of shock sensors and security materials. The relationships between TL activity and crystal packing structures were systematically investigated using Eu(III) coordination polymers with thiophene-, ethylenedioxythiophene-, and furan-based bridging ligands. The author confirmed the disordered alignment of CF<sub>3</sub> substituents between single polymer chains lead strong TL. Since the TL is generated while crystal destruction, the author considers the thermodynamically or mechanically unstable crystal structures with disordered polymer chains would induce strong TL. The PL efficiency was found to be independent of the TL activity. The different luminescence colors between TL and PL in Tb(III)/Eu(III) mixed coordination polymers were also observed, which directly indicated the existence of discrete excitation mechanisms of these two physical phenomena. Based on these observations, the excitation process was proposed that the TL occurred through both ligand-excitation and direct Ln(III)-excitation, unlike PL with specific excitation wavelength. In Chapter 7, summary and outlook of this study are described. The novel designs of bridging ligands for specific assembled structures would lead to development of functional luminescent materials.