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学 位 論 文 題 名

Study on the Energy Transfer Processes in Polynuclear Lanthanide Complexes
(多核希土類錯体におけるエネルギー移動過程に関する研究)

Luminescent materials are one of the most important materials used today in technology and science. In particular, lanthanides (Ln(III)) have been extensively used in spectral converters for fluorescent lamps and LEDs, optical fiber amplifiers, bioassay, and solid-state lasers. The emission intensity of Ln(III) ions is boosted in lanthanide complexes, where organic ligands absorb light efficiently and transfer its energy to the Ln(III) ion. As such, Ln(III) complexes have gained considerable attention for the potential increase in the efficiency of the current applications of Ln(III) ions.

In this study, the author focused on the factors that affect the emission quantum yield of polynuclear Ln(III) complexes, with emphasis on energy transfer processes, i.e., ligand-to-Ln(III) and Ln(III)-to-Ln(III). Such investigation is critical for obtaining insight into molecular designing strategies for the achievement of Ln(III) complexes with high quantum yield. Chapter 1 is the general introduction to this thesis. The chapter provides a brief background to the following chapters and includes, descriptions of light, luminescence, photophysics of lanthanides, Ln(III) complexes in general, and polynuclear Ln(III) complexes. The photophysical processes that affect the quantum yield of Ln(III) complexes are also explained. The objectives of the study are provided at the end of this chapter.

Chapter 2 describes the theory of radiative transition (the Judd-Ofelt theory) and energy transfer of Ln(III) ions, and the theory of kinetic analysis of excited state dynamics. The first half of the chapter provides equations that are essential to the calculation of radiative rate constants of Ln(III) ions and the energy transfer rate constant between Ln(III) ions in the formulation provided in the Judd-Ofelt theory. The latter half of the chapter provides matrix method of solving a system of linear differential equations for kinetic analysis of excited state dynamics, and the analytical solution for emission lifetimes and quantum yield for simple mononuclear Ln(III) complexes as an example. The theory shown in this chapter is particularly important in Chapters 3 and 6.

In Chapter 3, the concentration quenching induced by the energy transfer between Yb(III) ions in coordination polymers is described. Experimentally, Yb(III)/Gd(III) mixed coordination polymers with biphenylene bridging ligands were synthesized, where the Yb(III) ion concentration is controlled by Gd(III) ion. The effect of concentration quenching was elucidated mainly by emission lifetimes. Experimentally, the emission lifetimes of Yb(III) emission was monitored for each concentration. Theoretically, the theoretical lifetimes were calculated using the theory provided in Chapter 2 for three different models: no concentration quenching model, killer-site model, and phonon-assisted energy transfer relaxation model. The experimental lifetimes were qualitatively best consistent with the theoretical lifetimes when calculated for the phonon-assisted energy transfer relaxation model.

In Chapter 4, the effect of spin-orbit coupling on the ligand-to-Yb(III) sensitization efficiency in nonanuclear Yb(III)/Gd(III) or Yb(III)/Lu(III) clusters is described. Spin-orbit coupling mixes states of different multiplicity in the ligands (i.e., singlet and triplet states), and is induced by the intrinsic angular momentum and effective nuclear charge of Ln(III) ions. Since the energy transfer from the ligands to Ln(III) proceeds from the triplet excited state T_1 , singlet excited S_1 state to T_1 state intersystem crossing and T_1 state to singlet ground S_0 state relaxation affects the sensitization efficiency positively and negatively, respectively. The emission spectra of Yb(III)/Gd(III) or Yb(III)/Lu(III) mixed clusters showed that strong

spin-orbit coupling does not necessarily lead to high sensitization efficiency.

In Chapter 5, the factors that determine the Tb(III)-to-ligand back energy transfer rate constant is described. Tb(III)-to-ligand back energy transfer is known to be roughly dependent on the energy gap between the 5D_4 state of Tb(III) and T_1 state of ligands. The study involves the use of methyl salicylate and its derivatives with methyl substituent on the aromatic part of the methyl salicylate as ligands. The weakly electron-donating methyl substituent allowed slight modification of the excited state energies of the methyl salicylate ligands. The emission lifetimes of nonanuclear Tb(III) clusters using these ligands showed that the lifetimes were not consistent with the energy gap between 5D_4 and T_1 states. Arrhenius plot of the temperature dependence of emission lifetimes revealed that the Tb(III)-to-ligand back energy transfer rate constant is determined also by the activation energy and the frequency factor.

In Chapter 6, the influence of Tb(III)-to-Tb(III) energy transfer on the Tb(III)-to-ligand back energy transfer in nonanuclear Tb(III) cluster is described. First, the theoretical motivation of this study is explained using kinetic analysis modeling nonanuclear Tb(III) clusters. The analysis showed that there are two crucial factors for the suppression of Tb(III)-to-ligand back energy transfer: 1) the existence of the center Tb(III) ion the clusters that are unaffected by the ligand, and 2) fast Tb(III)-to-Tb(III) energy transfer. The combination of these two factors allows Tb(III)-to-Tb(III) energy transfer to the center Tb(III) ions, leading to the reduced contribution of Tb(III)-to-ligand back energy transfer. Experimentally, nonanuclear Tb(III)/Gd(III) mixed clusters were synthesized and the temperature dependence of emission lifetimes was qualitatively consistent with the lifetimes predicted by theoretical calculations. Therefore, Tb(III)-to-ligand back energy transfer was found to be suppressed in nonanuclear Tb(III) clusters.

Chapter 7 summarizes the studies described in this thesis, along with new insight into the strategies for designing highly efficient luminescent Ln(III) complexes by the use of Ln(III) clusters. Finally, the outlook of this study is provided to conclude this thesis.