Analysis of pH Dependent Luminescence of an Europium Complex

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Abstract. The pH dependence of the photoluminescence of an europium complex in aqueous solution was measured and investigated. The fluorescence emission spectra showed pH sensitivity. The analysis of the relative intensity ratio (R) of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transition and Judd-Ofelt experimental intensity parameters Ω_2 indicated that the local environment around the Eu^{3+} and the asymmetry of the Eu complex have been influenced by the pH value of the aqueous solution.

Introduction

The design of compounds that facilitate sensing is an active area of research [1]. Lanthanides possess intrinsic luminescence that originates from f-f electron transitions in the 4fn shell of the [Xe]5s25p6 configuration and offer unique properties for optical sensing. The unique luminescence properties of Eu(III) complexes, such as long luminescence lifetimes, sharp and intense emission bands, make them especially useful for the design of luminescent sensing materials[2~4].

In the fields of chemistry, biochemistry and environmental science, the detection and quantification of pH value is very important. In this work, the pH dependence of the photoluminescence of an europium complex in solution was measured and investigated by Judd-Ofelt theory. The result will provide useful information for designing lanthanide complex-based luminescent sensors.

Experimental

The molecular structure of the europium complex with cyclen derivative is shown in Fig.1 It was synthesized according to the procedure reported by Gunnlaugsson et al [5].Elemental analysis calculated for the europium complex ($EuC_{35}H_{51}N_{10}O_7F_3S$): C,43.57%; H,5.33%; N,14.52%; S,3.32%; found: C, 43.49%; H, 5.29%; N, 14.61%; S,3.30%.
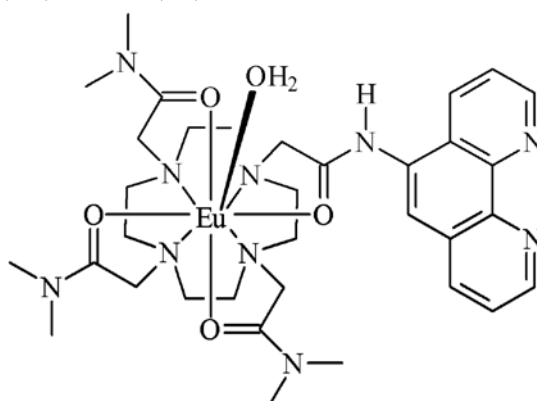

Fig. 1 Molecular structure of europium complex with cyclen derivative

Elemental analyses were performed using a Perkin-Elmer 2400CHN elemental analyzer. The fluorescence emission spectra of the europium complex were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The pH dependence of the Eu(III) emission was evaluated in H2O in the presence of 0.1 M tetramethylammonium perchlorate to maintain constant ionic strength.

Results and Discussion

PH Dependence of Fluorescence Emission Spectra of Eu Complex in Solution

The pH dependence of fluorescence emission spectra of Eu complex in solution are shown in Fig.2.
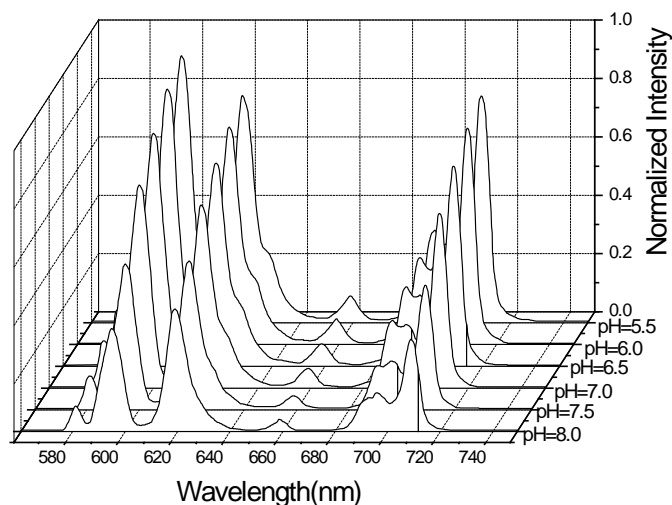

Fig.2 pH dependence of fluorescence emission spectra of Eu complex in solution

The emission spectrum was recorded form 550 nm to 750 nm under the excitation at 266nm. It can be found five emission peaks corresponding to $^5D_0 \rightarrow ^7F_{0,1,2,3,4}$ can be clearly distinguished for Eu complex in solution. The presence of only one $^5D_0 \rightarrow ^7F_0$ line indicates that the Eu^{3+} ion occupies only a single site and a single chemical environment exists around it [6].

It can be found in Fig.2 that the emission intensity decreased with the increase in pH. Through an intramolecular ligand to rare earth ion energy transfer process, the metastable state of the rare earth ion can be populated by pumping ligand absorption bands, which are much stronger than those of the rare earth. In this case, the population of the Eu(III) excited state (5D0) is achieved by the ligands antenna effect. Both the amide and the nitrogens of the phen ligand are sensitive to protonation, thus the emission intensity decreased significantly with the increase in pH.

Relative Intensity Ratio

The $^5D_0 \rightarrow ^7F_1$ transition is usually used as a reference because it is allowed by magnetic dipole and its intensity is independent of the environment. Because the variation of the relative intensity ratio (R) of 5D0→7F2 to 5D0→7F1 transition is very sensitive to the structural change in the vicinity of Eu3+ ions, it can be used to reflect the local structure and asymmetry in the vicinity of europium ions [7]. Fig.3 shows the R ratio values of Eu complex in solution with different pH.
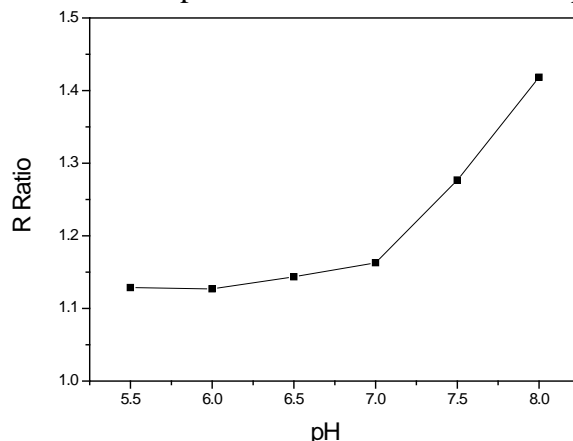

Fig.3 R ratio values of Eu complex in solution with different pH

In Fig.3, it can be found that the values of R ratio showed significant change with the increasing of pH. This indicates that there is also change in the local environment and asymmetry in the vicinity of europium ion when the pH is increased. According to the chemical structure of Eu complex showed in Fig.1, the ligands of the Eu complex are protonation sensitive. With the increasing of pH, the local environment around the Eu3+ has been changed, which leads to the significant variation of R ratio.

Judd-Ofelt Analysis

According to Judd-Ofelt theory, the calculated oscillator strength for an induced electric dipole transition from the ground state to an excited state is given by Eq.1 [8]:

$$f = \frac{8\pi^2 mcv}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda \left(\Psi J \left\| U^\lambda \right\| \Psi'J' \right)^2 \tag{1}$$

where n is refractive index of the medium, h is Planck's constant, J is the total angular momentum of the ground state, v is the wave number of the transition, Ω_λ ($\lambda=2$, 4, 6) are Judd-Ofelt intensity parameters and $\left\| U^\lambda \right\|^2$ ($\lambda=2$, 4, 6) are the doubly reduced matrix elements evaluated in the intermediate coupling approximation for a transition $\Psi J \rightarrow \Psi'J'$. The transition intensity f depends on the $\left\| U^\lambda \right\|^2$ values between ΨJ and $\Psi'J'$ manifold. Due to selection rules and the unique nature of transition intensities for Eu^{3+} ion, any one of the $\left\| U^\lambda \right\|^2$ parameters decide the intensities of the transitions since the remaining two are zero. Thus, Ω_λ ($\lambda=2$, 4, 6) parameters can be evaluated independently from the emission transitions of $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_6$, respectively [9]. The intensity of the $^5D_0 \rightarrow {}^7F_1$ fluorescent transition is found to be host independent whereas that of the $^5D_0 \rightarrow {}^7F_J$ transition depends on the Ω_λ parameters. This characteristic helps one to evaluate the Ω_λ parameters simply by the ratio of the intensities of the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions to the intensity of $^5D_0 \rightarrow {}^7F_1$ transition as Eq.2 [8].

$$\int I_J dv \bigg/ \int I_1 dv = A_J/A_1 = \frac{e^2}{S_{md1}} \frac{v_J^3}{v_1^3} \frac{n(n^2+2)^2}{9n^3} \sum \Omega_\lambda \left\| U^\lambda \right\|^2 \tag{2}$$

where S_{md1} refers to the strength of the magnetic dipole line strength of the $^5D_0 \rightarrow {}^7F_1$ transition in absorption.

The obtained values for parameter Ω_2 and Ω_4 of Eu complex in solution with different pH are listed in Table Ⅰ. The Ω_6 intensity parameter was not determined because the $^5D_0 \rightarrow {}^7F_6$ transition could not be experimentally detected.

Tab.1 Ω_2, Ω_4 parameters of of Eu complex in solution with different pH

pH	Ω_2	Ω_4
5.5	1.98×10^{-20} cm^2	7.89×10^{-20} cm^2
6.0	1.99×10^{-20} cm^2	7.97×10^{-20} cm^2
6.5	2.01×10^{-20} cm^2	7.84×10^{-20} cm^2
7.0	2.05×10^{-20} cm^2	7.84×10^{-20} cm^2
7.5	2.25×10^{-20} cm^2	7.67×10^{-20} cm^2
8.0	2.50×10^{-20} cm^2	7.97×10^{-20} cm^2

According to previous studies, Ω_2 is a useful parameter, because it is sensitive to the local symmetry of the ligand field and bond covalency [10]. The value of Ω_2 increases as the local symmetry of the ligand field decreases and as the bond covalency increases. It can be conclude that the decrease of the pH also increased the asymmetry of the Eu complex. The Ω_4 parameter has been related together to bulk properties of the lanthanide based hosts, but there is no theoretical prediction for this sensibility to macroscopic properties [11].

Summary

In conclusion, the pH dependence of the photoluminescence of an europium complex in aqueous solution was measured and investigated. The Judd-Ofelt phenomenological parameters, Ω_2 and Ω_4 were obtained from the fluorescence emission spectrum. The analysis of the relative intensity ratio (R) and Ω_2 indicated that the local environment around the Eu^{3+} and the asymmetry of the Eu complex have been influenced by the pH value of the aqueous solution.

Acknowledgement

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