

Preparation of Luminescent Lanthanide Complexes and Characterization for Luminescence Property

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Abstract

Lanthanide complex have excellent luminescence properties: narrow emission peak width and long fluorescence lifetime. Although the photoluminescence of lanthanide ions is an effective process, all lanthanide ions have weak light absorption. The molar absorption coefficient of most trivalent lanthanide ions is lower than the normal level, and only very limited emission can directly absorb energy in the 4f orbit, so ligands are needed to absorb energy to provide the central lanthanide ions. If the lanthanide ion is excited to a non-emitting level, either directly through the 4f level or indirectly through the energy transfer, the excited energy will be dissipated through the non-radiating process until the resonant level is reached. At this time, the excited transition becomes competitive with the non-excited process, and the emission of lanthanide center ions can be observed. The linear emission of lanthanide central ions is possible only if the non-excitation process is disabled and the molecular fluorescence and phosphorescence energies are minimized. In order to fill the resonant level of lanthanide ions, the lowest triplet state of the complex must be located near or above the resonant level of lanthanide central ions, rather than below it. When the energy level of organic ligand is lower than the resonance level of lanthanide central ion, only fluorescence or phosphorescence of organic ligand molecules can be observed, or no light emission can be observed at all. Therefore, the observed luminescence of the lanthanide complex is the level of the lowest triple energy level of the complex relative to the resonant energy level of the lanthanide ion. Since the position of the triplet energy level depends on the type of ligand, we can control the luminescence intensity of a given lanthanide central ion by the change of ligand.

Keywords

Preparation of Luminescent, Lanthanide Complexes.

1. Introduction

The energy level of organic ligand has the highest degree of binding with Eu^{3+} ions, the β -diketone antenna ligand can perfectly match the 5D0 orbital of Eu^{3+} ions due to its unique diketone structure.[1,2,3] The absorption energy provides the transition energy for the 5D0 orbital and effectively activates the lanthanide central ions. At present, these β -diketones are the most widely and deeply studied luminescent lanthanide complexes. Part of the reason for its popularity is that it is extremely easy to get and relatively cheap to buy, and it is relatively easy to synthesize the corresponding lanthanide complex without going through a lot of organic synthesis, but the main reason is its excellent luminous performance. However, the bad side is that β -diketone ligands are poorly light stable and need to be stored at low temperature away from light. β -diketone ligands show excellent luminescence performance when they bind Eu^{3+} ions, which is one of the most suitable ligands for Eu^{3+} ions, while terbium ligands exhibit poor luminescence performance. The main reason is that the trivalent resonance levels of many β -diketones ligands with aromatic substituents are lower than those of aromatic ligands.

Although europium (III) β -diketones often exhibit excellent luminescence properties, their luminescence intensity is closely related to the type of β -diketones ligands and the type of complexes. [4,5] In addition, it is difficult to compare the luminescence output efficiency of different complexes. The luminescence intensity is related not only to the quantum yield of luminescence, but also to the

energy absorbed by radiation. Thus, the luminescence of a solid sample will also depend on the position of the sample in the beam used for excitation. The luminescence intensity of the ligand-excited lanthanide complexes is more temperature-dependent than that observed in the direct excitation of the f-f energy level. However, only the luminescence of lanthanide complexes in solution was studied in this study, so the influence of temperature was ignored. Some rules can be found in the luminescence of europium (III) β -diketone complexes. The triisopropyl ethyl sulfonyl complexes have the weakest luminescence properties. The luminescence intensity of lewis base complex was higher than that of tetra - ketonic diester complex. Aliphatic β -diketone ligands (acetylacetone, trifluoroacetone, or hexafluoroacetone) have weak luminescence intensity, because the energy gap between the larger Eu^{3+} ion resonance level and the ligand triplet reduces the energy transfer efficiency to europium (III) ions. The combination of aromatic -diketone ligands and aliphatic substituents (benzoyl acetone, benzoyl trifluoroacetone, 2-benzyl-trifluoroacetone) enables better luminescence of europium (III) ion complexes, where energy transfer from complex ligands to lanthanide central ions is more efficient. The increase in luminescence intensity in this system is also attributed to the increase in the anisotropy around Eu^{3+} ions.

In optical application technology, lanthanides are a hot spot in recent years, and one of the notable features is the high emission purity of lanthanides. [6] The synthesis of organic and inorganic materials for the synthesis of lanthanide elements is also a great concern. In these systems (such as sol-gel derivatives), or inorganic lanthanide compounds (such as polyoxide metallic acid salts or lanthanides) embedded in the organic polymer matrix, the study of lanthanides in the hybrid materials is not only of important theoretical significance, but also has broad application vision (optical amplifiers, drug testing, optical wave conductance, etc.). In general, these hybrid luminescent materials have better mechanical properties and processing energy than the simple lanthanides. [7] In addition, the embedded lanthanides in the mixed matrix are also beneficial to its thermal stability and luminescent output. Protein crystals are the crystalline material materials that are interesting and widely applied in the context of their porous, biocompatibility, high density functional group share in space, and they are often modified by molecular biology or chemical biology.

The preparation process of luminescent lanthanide complexes is simple, and different types of lanthanides emit different visible light due to their different outermost electrons. When discussing the light emission of lanthanides, we often use the term "luminescence" instead of "fluorescence" or "phosphorescence". This is because the terms fluorescence and phosphorescence are used to describe the light emission of organic molecules, and these terms contain information about the emission mechanism: fluorescence is single-point to single-point emission (i.e. Although the 4f electrons of lanthanide are difficult to absorb the external excitation spectrum due to the stability of their structure, it is this structure that gives the antenna ligand to bind lanthanide and provide the energy of photon transition. Antenna ligand refers to the extremely low absorbance of lanthanide due to its own 4f layer electron confinement transition, which provides energy for the complex. The screening of organic ligand molecules usually need to have a rigid structure and large conjugated system, [8,9,10] they have good electron mobility and in a particular band has strong absorbency, according to the energy level matching theory put forward by the Sato and Wada (that is, the complexes of fluorescence quantum efficiency and Δv (T_1 (L) - RE^{3+})), the triplet energy level slightly higher than the center lanthanide ions lowest excited level $2500 + 400 \text{ cm}^{-1}$ to maximize antenna ligands with center lanthanide ions between the energy transfer efficiency. The complex used in this study is $\text{Eu}(\text{TTA})_3\text{phen}$. In this complex, 2-thiophenotrifluoroacetone (TTA) and phen (phen) are antenna ligands, and the addition of phen removes the weak luminescence caused by water-bound lanthanide and can replace the position of water.

In the lewis base adduct, β -diketone ligands and phenanthroline are easily soluble in anhydrous ethanol, which meets our experimental requirements, and the complexes have excellent luminous properties. Therefore, β -diketones -thiophenotrifluoroacetone (TTA) was selected as the first ligand, and phen was selected as the second ligand to be complexated with Eu^{3+} to prepare $\text{Eu}(\text{TTA})_3\text{phen}$. In this chapter, we first synthesized $\text{Eu}(\text{TTA})_3\text{phen}$, a rare earth hybrid material, and performed a series

of characterization and analysis on the shape and luminescence performance of the rare earth complex with instruments such as high resolution transmission electron microscope.

2. Experiment process

100 mL 0.1 M EuCl_3 ethanol solution: precision electronic balance, weighing 1.7596 g Eu_2O_3 powder in 150 mL beaker, add 1.5 cm rotor magnetic stirring will according to deionized water volume ratio V: V strong dilute hydrochloric acid = 1:3 12 mol/L strong hydrochloric acid into 6 mol/L slowly stir in magneton after dilute hydrochloric acid in the beaker, sets the reaction temperature to 55 °C water bath heating, adjust speed to 150 r/min. Continue adding diluted hydrochloric acid to the white emulsion in the beaker to become clear, stop adding hydrochloric acid, continue stirring and heating in the fume hood, and get transparent and moist $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ crystal after HCl volatilization in the beaker. At this time to stop heating, clean liquid in the beaker to 40 °C in the vacuum drying oven baked to become completely transparent crystal. An appropriate amount of anhydrous ethanol was added to dissolve and rinse the dried $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ crystals into a 100 mL volumetric flask for constant volume, and 0.1m EuCl_3 ethanol solution was made. An appropriate amount of 0.1 M EuCl_3 ethanol solution was diluted into three concentrations of 0.01 M, 0.001 M and 0.0001 M respectively for use.

Preparation of 100 mL 0.3m anhydrous ethanol solution: accurately weigh 6.66g - thiophenoformyltrifluoroacetone (TTA) in a beaker, slowly add an appropriate amount of anhydrous ethanol solution to its complete dissolution, and then transfer to 100 mL volumetric flask for constant volume, get 0.3 M of ethanol solution transferred into 100 mL conical flask. An appropriate amount of 0.3m TTA anhydrous ethanol solution was diluted into three concentrations of 0.03 M, 0.003 M and 0.0003 M respectively for use.

Preparation of 100mL 0.1m phen anhydrous ethanol solution: 1.8g phen crystal powder was accurately weighed and placed in a 100mL beaker. The phen was completely dissolved by slowly adding an appropriate amount of anhydrous ethanol solution, which was then transferred to a 100mL volumetric flask for constant volume. The 0.1m phen anhydrous ethanol solution was transferred to a 100mL conical flask. An appropriate amount of 0.1m phen anhydrous ethanol solution was diluted into three concentrations of 0.01 M, 0.001 M and 0.0001 M respectively for use.

Four concentration gradient $\text{Eu}(\text{TTA})_3\text{phen}$ complexes, 0.001m, 0.001m, 0.01 M and 0.1m, were prepared respectively. The following example was 0.1m $\text{Eu}(\text{TTA})_3\text{phen}$ in the same volume. The 0.3m TTA and 0.1m phen anhydrous ethanol solution were placed in a beaker. At the same time of magnetic stirring, 0.1m EuCl_3 anhydrous ethanol solution of the same volume was slowly added and stirred for 10min to obtain 0.1m $\text{Eu}(\text{TTA})_3\text{phen}$ anhydrous ethanol solution.

3. Results and discussion

It is well known that europium trivalent ions have a very low intrinsic molar absorption rate in the 200-400 nm ultraviolet region, which is the result of the forbidden transition between the 4f electron layers within the ions. In order to improve this inherent defect, organic ligands with excellent molar absorbance in the 200-400 nm ultraviolet region such as TTA were introduced into the complex system as "antennas". Due to the strong coupling between the excited triplet state of the ligand and the excited state energy level of europium trivalent ions, europium trivalent ions can effectively obtain energy from the antenna ligand and emit dazzling red light. The fluorescence intensity of the complexes prepared in the mixed solvent of ethanol was significantly higher than that obtained by using ethanol as a single solvent. In addition, the color of the complex is more uniform and bright. Since the pH of the complex in this paper is controlled at about 7.5, and fluorescence quenching occurs after the agglomeration of the rare earth complex, this is mainly related to the agglomeration degree of the complex in the solvent. The complexes were agglomerated to a large extent in the ethanol solvent, especially when the complex concentration was not less than 0.01 M.

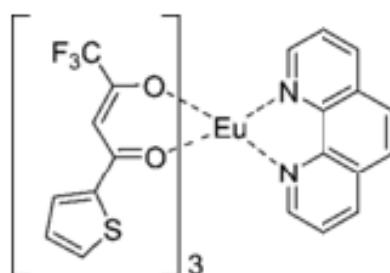


Figure 1 The schematic diagram of $\text{Eu}(\text{TTA})_3\text{phen}$

The photoluminescence performance of 0.01 m $\text{Eu}(\text{TTA})_3\text{phen}$ without water ethanol solution was characterized. The emission wavelength of the rare earth complex is 579 nm, 612 nm, 651 nm, 651 nm, the five characteristics of the five characteristics of the launch peak respectively correspond . TTA, as an arylalkyl substituted diketone, after complexation with Eu^{3+} , creates an asymmetric field around europium trivalent ions. This asymmetry significantly improves the efficiency of energy transfer to ions, which makes the excited state energy of Eu^{3+} more inclined to radiative transition between 7F energy levels rather than dissipating energy as heat through molecular thermal vibration. 1, 10-phenanthroline (phen) is used as the second ligand here, because one of the roles of phen is to eliminate the possibility of water molecules participating in complexation and thus reduce the possibility of heat dissipation of the triple energy. The single peak emission peak at 579nm is derived from the transition from $5D_0$ to $7F_0$. Due to the particularity of the transition from $5D_0$ to $7F_0$, only one emission peak is sufficient, indicating that only one type of europium complex (i.e. $\text{Eu}(\text{TTA})_3\text{phen}$) is formed in both test samples. If more than one peak appears, we may infer the existence of isomers or multiple LC species . The transition from $5D_0$ to $7F_0$ can be used as an index for Eu^{3+} ions to have the symmetry transitions are all susceptible to local coordination electric field. In contrast, the $5D_0 \rightarrow 7F_1$ transition can be used as a reference to indicate the ligand difference of the complex system since it can specifically respond to the characteristics of magnetic moment. TTA disturbs the idealized Oh symmetry of Eu^{3+} at the center, and further induces the symmetry of Eu^{3+} crystal field into or lower symmetry. This distortion of the symmetry of the crystal field results in the splitting of Eu^{3+} $5D_0$ $7F_1$ transition. Although generally for complex crystal fields with C_{2v} point group symmetry, the emission peak splitting type of $5D_0$ $7F_1$ transition should be triple peak splitting [84], the specific information of peak splitting cannot be observed due to the low spectral separation rates.

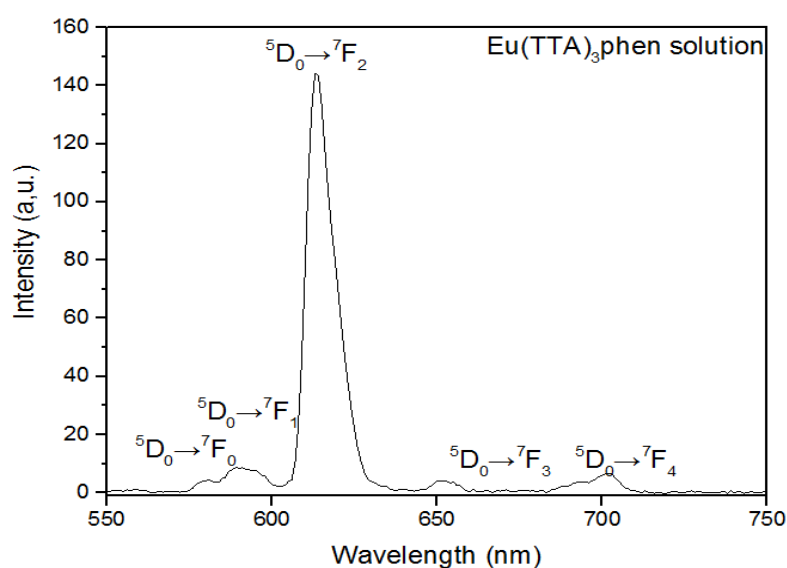


Figure 2 The emission spectra for 0.01 m $\text{Eu}(\text{TTA})_3\text{phen}$.

It is well known that the three-valence europium ion has the inherent extremely low natural absorption rate in the 400 nm ultraviolet region, which is the result of the non-resistance transition of the 4f electron layer inside the ion. In order to improve the inherent property defects of the complex, the organic complex ligand of the excellent molar absorption rate in the 400 nm ultraviolet region of the area. As "antenna ligand" is introduced into the complex system. The antenna ligand is matched with the center ion level, which is strongly coupled by the combination of the ligand, which stimulates the triple state and the three-valence europium, so the three-valence europium ions can effectively obtain energy from the antenna ligand, and the red light of the light is brilliant.

In this case, the highest fluorescence intensity of the launch peak corresponds to the $eu^{3+} 5d_0-7f_2$ molecule transition, because the molecule transition is far more sensitive to the electric field of the surrounding ligand ligands than the other four molecules, which is also a dipole moment transition.

In this study, we used high resolution transmission electron microscopy (HRTEM) to characterize the morphology of lanthanide luminescence complexes. The projected sample is prepared before the high resolution transmission microscope characterization. Firstly, a 0.01 mol/L $Eu(TTA)_3phen$ anhydrous ethanol solution was prepared according to the above process, and adjusted to a suitable pH value for preservation. We use thin carbon film to the preparation of the projection electron microscope samples, ultrathin carbon membrane is a kind of micro grid, but on the surface of the micro grid overlay a very thin layer of carbon membrane, the purpose is to put the micro grid pore blocking, this layer of carbon film thickness for 3 to 5 nm, the aim is for dispersion of good material, can prevent the drop, on the other hand, if all gathered at the edge of a micro grid is likely to affect the result of the experiment. If the copper mesh is used directly, the lanthanide rare earth complex may fall from the pores of the copper mesh, affecting the electron microscopic observation.

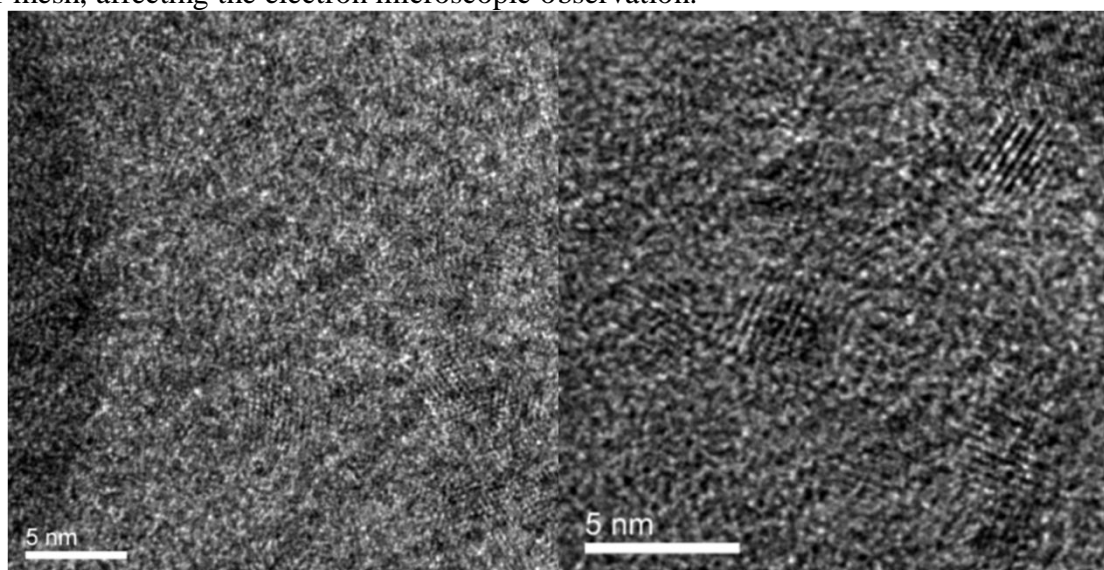


Figure 3 HRTEM images of $Eu(TTA)_3phen$

Sample preparation for high resolution transmission microscope: firstly, take the filter paper and place it on the experimental table. Carefully remove the ultrathin carbon film with tweezers and put it on the filter paper for later use. The 0.01 mol/L $Eu(TTA)_3phen$ anhydrous ethanol solution was removed and placed in the centrifuge tube for about 1.5 mL. After the solution was sealed, ultrasound was performed for 30 min. The main purpose of this step was to prevent the rare earth complexes from agglomerating together and to better disperse the rare earth complexes. After the ultrasonic treatment, the rare earth complex was removed, and the centrifugal tube was wiped clean. The $Eu(TTA)_3phen$ anhydrous ethanol solution was removed with a plastic dropper. The solution was added to the ultrathin carbon film for 2-3 times.

High resolution transmission electron microscope shows that when the resolution is small, the rare earth complexes are distributed in small spheres on the ultrathin carbon film, and the darkest color is the place with the most rare earth complexes. This is because we repeatedly drop the anhydrous

ethanol solution of rare earth complexes on the ultrathin carbon film, resulting in the overlap of rare earth complexes. In the further amplification process, it can be seen that at the nanometer level, $\text{Eu}(\text{TTA})_3\text{phen}$ exists in the form of nanocrystals, and we can see different lattice stripes in the figure.

4. Conclusion

In this chapter, 0.001M rare earth complex was synthesized in anhydrous ethanol with Eu^{3+} as the central ion and alpha-thiophenotrifluoroacetone (TTA) and phen as the first antenna ligand and the second ligand. The properties of the products were tested by fluorescence spectrophotometer and high resolution transmission electron microscope. The specific synthesis process of rare earth complexes is provided, and how to prepare high resolution transmission microscope samples of rare earth complexes is described in detail. Through the analysis and discussion of the experimental results, the following conclusions are drawn: $\text{Eu}(\text{TTA})_3\text{phen}$ with 0.01mol/L has excellent luminous performance and obvious emission characteristic peak. Macroscopically, rare earth complexes are in the form of pellets, in the nanometer scale, in the form of crystals, with obvious lattice structure.

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