Synthesis and luminescent properties of novel red-emitting Eu(III) complexes based on alanine aliphatic derivatives with different optical rotation

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Abstract
A series of novel luminescent amino acid-rare earth complexes (denoted as Eu(L/D-SA)₃-Phen) have been successfully synthesized. Using stearoyl alanine (denoted as SA) with different optical rotations as the first ligand and 1,10-phenanthroline (Phen) as the second ligand, the products were prepared by solution chemical reaction. Fourier transform infrared spectrometer (FT-IR), nuclear magnetic resonance spectroscopy (¹H NMR), x-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet and visible spectrum (UV) and photoluminescence spectroscopy were used to characterize the properties of Eu(L/D-SA)₃-Phen. FT-IR, ¹H NMR and XRD indicate that ligand SA and Phen were prepared and successfully combined with Eu³⁺ ions. SEM analysis shows relatively uniform morphological structure. Eu(L/D-SA)₃-Phen exhibit a typical luminescence emission peak at 614 nm. In addition, the lifetimes of Eu(L/D-SA)₃-Phen are in scale of millisecond. The relationship between fluorescence intensity of Eu(L/D-SA)₃-Phen and the optical rotation of ligand SA has been studied and discussed. Based on the results, Eu(L/D-SA)₃-Phen have excellent luminescent performance and possess potential application as luminescent materials.

1. Introduction

Rare earth elements are a group of elements that are of great concern to material experts at home and abroad. Most rare earth elements have unfilled 4f electron layer structures, which make the rare earth ions rich in multi-state energy levels [1, 2]. The absorption and emission of rare earth ions mainly come from the electronic transition among the unfilled 4f layers. The photon energy emitted by the rare earth ions’ electrons among these energy levels is mostly distributed in the visible region (400~800 nm) and the near infrared region (800~1700 nm) [3]. Due to the special 4f electronic energy level structure and the effective transition of 4f-4f and 5d-4f, the rare earth ions have many particular advantages, such as large Stokes shift, long lifetime, high conversion efficiency and so on [4, 5]. However, since the F-f electric dipole transition is prohibited [6], the luminescence intensity of the naked lanthanide ions is weak [7, 8]. Therefore, it is necessary to obtain the organic lanthanide complexes with higher luminescence intensity by using the organic chromophores [9–11]. The organic chromophores ligands are effective in absorbing and transferring energy to the lanthanide ions, which also known as the ‘antenna effect’ [6, 12–15]. The application field of rare earth elements has been broadened by the antenna effect, for example, LED lights, x-ray enhancement screens, emergency signs, fiber lasers and so on [16–19].

The binary rare earth complexes formed by 20 kinds of amino acids required by the human body has attracted a lot of attention. As a result of the unique physicochemical properties, the amino acid-rare earth complexes have excellent stability and luminescent properties, such as high fluorescence emission intensity and long fluorescence lifetime [20, 21]. However, the research of amino acid-rare earth complex are still worthy of further study [22]. For example, the preparation and application of amino acid-rare earth complexes with
high-performance and low-toxic. These problems have not been substantially resolved, limiting the application of existing amino acid-rare earth complex.

Amino acid surface-active ligands are strong metal ion-binding ligands [22, 23]. However, rare earth complexes with novel amino acids as ligands still have lots of spaces to explore. Therefore, a series of novel stearoyl alanine-rare earth complexes have been synthesized and investigated. Eu$^{3+}$ ions have a strong characteristic red-light emission after sensitization, so Eu$^{3+}$ ion is selected as the central ion to synthesize a variety of amino acid-rare earth complexes. In order to improve the luminescent property of the complex [24], stearyl alanine (denoted as SA) was used as the first ligand. As an electron donating group, the long carbon chain can increase the electron cloud density and the molar absorptivity of the ligand [25, 26]. It also promotes the formation of the coordination bonds between the ligands and the rare earth ions. Consequently, the long carbon chain structure of the first ligand can significantly improve the intermolecular energy transfer and the luminescent property of the complex. Moreover, rare earth ions tend to be highly coordinated. The electric charge usually does not satisfy the coordination number when forming a complex. Therefore, solvent molecules are often involved in coordination. Due to the high-frequency vibration of O-H in the solvent molecule, part of the energy absorbed by the ligand is transferred to the solvent molecule [27–29]. Finally, the energy was lost in the form of thermal vibration, resulting in a decrease of the fluorescence of the complex. Thence, 1,10-phenanthroline (Phen) with stronger coordination ability has been chosen as the second ligand to exclude the coordination of solvent molecules [30]. This method reduces the energy loss and improves the fluorescence intensity of the rare earth complexes [31].

In this work, a series of novel amino acid–rare earth complexes have been successfully synthesized by using long chain aliphatic amino acid (SA) as the first ligand and 1,10–phenanthroline (Phen) as the second ligand. The physical and chemical properties of the complexes were characterized. From the characterization results, Eu(L/D-SA)$_3$-Phen have excellent luminescence performance and possess potential application as luminescent materials.

2. Experimental

2.1. Raw materials

Stearic acid (C$_{17}$H$_{35}$O$_2$), thionyl chloride (SOCl$_2$), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetone (C$_6$H$_{12}$O), toluene (C$_7$H$_{16}$), chloroform(CHCl$_3$) and ethanol (C$_2$H$_5$OH) were all purchased from Sinopharm Chemical Reagent Co., Ltd. L-alanine and D-alanine were obtained from Shanghai Haohong Technology Co., Ltd. Europium(III) chloride hexahydrate (EuCl$_3$ · 6H$_2$O, 99.99 wt%) and 1,10-Phenanthroline (Phen) were purchased from Bomeida Chemical company. All regents are analytical grade and used directly.

2.2. Preparation of stearoyl chloride

Stearic acid (150.0 g, 0.53 mol) and thionyl chloride (73 ml, 1.0 mol) were mixed into a 500 ml eggplant type bottle, stirred and refluxed at 80 °C for 0.5 h. Then the mixture was heated to 100 °C and refluxed for 2 h to obtain a yellow liquid product. After the reaction, atmospheric distillation was carried out to remove unreacted thionyl chloride. Finally, the mixture was distilled under reduced pressure (external temperature 180~195 °C, internal temperature 160~180 °C) to obtain stearoyl chloride. Stearoyl chloride was a colorless liquid and became white solid after cooling (depending on temperature).

2.3. Preparation of stearoyl alanine (L/D-SA)

L-alanine (13.98 g, 0.157 mol), NaOH (6.25 g, 0.157 mol), deionized water (100 ml) and acetone (200 ml) were mixed into a 500 ml three-necked flask (1:2 ratio of water to acetone) and stirred at 0 °C. At the same time, stearyl chloride (50.0 g, 0.157 mol) and NaOH (6.25 g, 0.157 mol) aqueous solution were added dropwise to the mixture to adjust the solution to strong acidity (pH = 1~3). Then the mixture was extracted with chloroform and water, and the product in organic layer was collected. Finally, the product was dried and steamed to obtain a solid product, which was then recrystallized from toluene to obtain pure white powder (L-SA). D-SA was prepared by the same method as above.

2.4. Preparation of Eu(L/D-SA)$_3$-Phen

First, L-SA (1.065 g, 0.003 mol), EuCl$_3$ · 6H$_2$O (0.366 g, 0.001 mol), Phen (0.180 g, 0.001 mol) and NaOH were separately dissolved in ethanol (5 ml). Second, EuCl$_3$ · 6H$_2$O solution was added dropwise to the L-SA solution to obtain the mixture. Then, Phen solution was added dropwise to the mixture. Third, NaOH solution was added into the mixture to adjust the solution to weakly acidity (pH = 5~6) and stirred at 80 °C for 5 h. The
molar ratio of EuCl$_3$·6H$_2$O to L-SA was 1:3, and the molar ratio of EuCl$_3$·6H$_2$O to Phen was 1:1. Then the mixture was centrifuged to obtain a solid. Finally, the solid was dried in a vacuum oven for 10 h to obtain the fluorescent powder, denoted as Eu(L-SA)$_3$-Phen. Eu(D-SA)$_3$-Phen was prepared by the same method as above.

2.5. Characterization

The preparation method and chemical structures of L-SA and Eu(L-SA)$_3$-Phen are illustrated in figure 1. Fourier transform infrared (FT-IR) spectra were obtained by using a Bruker Vertex70 FT-IR spectrophotometer in the range of 400–4000 cm$^{-1}$. $^1$H NMR spectra of the samples were recorded using FTNMR-JOELAL300 system at 400 Hz. X-Ray Diffraction (XRD) measurements were recorded by a X’Pert-Pro MPD diffractometer with Cu K$_\alpha$ radiation ($\lambda$ = 1.54 Å) over a $2\theta$ range of 10–90°. The morphology of the amino acid-rare earth complexes was researched by S-4700 scanning electron microscope (SEM). Ultraviolet-visible (UV–vis) absorption spectra were recorded on a UV-3600 spectrophotometer. The luminescence emission and excitation spectra were measured on the FLS920 fluorescence spectrometer at room temperature. Lifetime of the radiative levels was estimated by fitting the decay curve in an exponential function.

3. Results and discussion

3.1. Structural characterization

3.1.1. Fourier transform infrared (FT-IR) analysis

The FT-IR spectra of Phen, Eu(L-SA)$_3$-Phen, Eu(D-SA)$_3$Phen, L-SA and D-SA are shown in figure 2. The spectrum of the complex substantially reflects the characteristic vibration of ligands. It also reflects the changes of the groups in the ligands before and after coordination.

The spectrum of Eu(L-SA)$_3$-Phen can be observed to be significantly different from that of L-SA. The spectrum of L-SA shows a band at 1703 cm$^{-1}$, which is characteristic of the carbonyl stretching of the carbonyl group. In the spectrum of L-SA, the bands at 930 and 1416 cm$^{-1}$ are assigned to the out-of-plane and in-plane bending vibration of the di-associated –O–H in carboxyl. Also, the stretching vibration of –C=O occurred at 1250 cm$^{-1}$. From the spectrum of Eu(L-SA)$_3$-Phen, it is found that the strong peak at 1703 cm$^{-1}$ corresponding to carboxyl groups is essentially absent after the coordination reaction with Eu$^{3+}$ ions. Alternatively, the typical symmetric and asymmetric stretching vibration of the carbonyl groups at about 1419 and 1558 cm$^{-1}$ are detected. The peaks at 930, 1250 and 1416 cm$^{-1}$ corresponding to carboxyl groups are absent. It indicates that carboxyl oxygen atoms have coordinated with Eu$^{3+}$ ions [32–34].

Simultaneously, the –CONH– absorption bands can be seen both in the spectrum of L-SA and Eu(L-SA)$_3$-Phen, located at 3311, 1644 and 1536 cm$^{-1}$. It indicates that the –CONH– groups in L-SA are not involved in the coordination. The bands at 1471, 2848 and 2916 cm$^{-1}$ presented in the spectrum of L-SA are assigned to the long chain structure of (C$_{17}$H$_{35}$), which still exist in the spectrum of Eu(L-SA)$_3$-Phen.

The –C=H out-of-plane bending vibration bands of phenanthroline were detected at 733 and 841 cm$^{-1}$. The stretching vibration bands of –C=N and –C=C were detected at 1419 and 1500 cm$^{-1}$. After the formation of the
complex, the $\text{-C-H}$ out-of-plane bending vibration band moved to around 721 cm$^{-1}$. The $\text{-C=N}$ and $\text{-C=C}$ stretching vibration bands on the skeleton also changed which shows that the N atoms in Phen form a coordination bond with Eu$^{3+}$ ions [35].

The infrared spectrum of Eu(D-SA)$_3$-Phen is similar to Eu(L-SA)$_3$-Phen, indicating that ligands are successfully coordinated with the Eu$^{3+}$ ions.

### 3.1.2. Nuclear magnetic resonance (NMR) spectroscopy

$^1$H spectra were recorded for the samples (L-SA, D-SA and Phen) in standard DMSO-$d_6$ solution, and Eu(L/D-SA)$_3$-Phen in standard BENZENE-$d_6$ solution for detailed structural investigation. The $^1$H NMR data of L-SA, Phen and Eu(L-SA)$_3$-Phen are listed in Table 1. The chemical shift values of the complex protons deviate to different degrees from the ligands, indicating that the coordination of free ligands with Eu$^{3+}$ ions occurs.

Comparing the complex with the free ligand Phen, the hydrogen nuclear chemical shift values of $H_{2,9}$, $H_{3,8}$, $H_{4,7}$, and $H_{5,6}$ increased slightly after the formation of the complex. This is due to the electrons given by the nitrogen atom on the Phen ring after coordination, which reduces the density of the electron cloud on the phenanthrene ring, moves the hydrogen nuclei on each carbon to a low field, and increases the chemical shift [36]. The decrease in the chemical shift value of $H_{2,9}$ protons is due to the formation of hydrogen bonds between hydrogen atoms and oxygen atoms in the solvent or L-SA. As a result, the electron cloud density increases and the protons move toward the high field [37, 38].

Comparing the complex with L-SA, the peak at 12.5 ppm due to $\text{-COOH}$ proton disappeared, which shows the coordination of Eu$^{3+}$ ions with the carbonyl of L-SA. The changes of other chemical shift values are all attributed to electron-spin relaxation time and magnetic anisotropy of Eu$^{3+}$ ions [39, 40].

The $^1$H data of D-SA ligand and its complex are similar to L-SA and its complex.

### Table 1. $^1$H NMR data of ligands and complex.

| Compound | L-SA | Phen | Eu(L-SA)$_3$-Phen | $\Delta$ |
|----------|------|------|-------------------|---------|
| L/D-SA   | CH$_2$(CH$_2$)$_2$CH$_2$ | 1.20 (s, 3H) | 1.54 (s, 3H) | +0.34 |
|          | CHCOOH | 12.37 (s, 1H) | 7.15 (d, 1H) | −0.88 |
| Phen     | CONHCH | 8.03 (d, 1H) | 9.11 (s, 2H) | −0.02 |
|          | $H_{2,9}$ | 9.11 (s, 2H) | 9.09 (d, 2H) | −0.02 |
|          | $H_{3,8}$ | 7.78 (dd, 2H) | 7.96 (dd, 2H) | +0.18 |
|          | $H_{4,7}$ | 8.5 (dd, 2H) | 8.62 (dd, 2H) | +0.12 |
|          | $H_{5,6}$ | 8.0 (s, 2H) | 8.39 (s, 2H) | +0.39 |
3.1.3. X-ray diffraction analysis

Figure 3 shows the XRD patterns of L-SA, D-SA, Eu\(\text{L-SA}\)\_3-Phen, Eu\(\text{D-SA}\)\_3-Phen and small molecule EuCl\(_3\) \cdot 6\text{H}_2\text{O}. The XRD pattern of EuCl\(_3\) \cdot 6\text{H}_2\text{O} exhibits many extremely strong diffraction peaks, which suggests a perfect crystal lattice structure. The pattern of L-SA shows a broad hump and three weak peaks at \(2\theta\sim25^\circ\), indicating that L-SA has a higher amorphous nature than Eu\(\text{L-SA}\)\_3-Phen. Nevertheless, the pattern of Eu\(\text{L-SA}\)\_3-Phen retains an amorphous hump which similar to the first ligand, and most of the sharp peaks corresponding to EuCl\(_3\) disappear. The facts indicate that the Eu\(^{3+}\) ions are not simply doped in L-SA, but coordinated with the carboxyl groups on the ligands.

The XRD pattern of Eu\(\text{D-SA}\)\_3-Phen is similar with the pattern of Eu\(\text{L-SA}\)\_3-Phen, indicating that ligands are successfully coordinated with the Eu\(^{3+}\) ions.

3.1.4. SEM analysis

SEM images of Eu\(\text{D/L-SA}\)\_3-Phen) are given in figure 4. As shown in figure 4, the organic ligands have different morphology and are much larger than rare earth particles. The rare earth particles generally have a diameter of 0.1\sim0.5 \text{\mu m}, and exhibit a bright grainy appearance in a scanning electron microscope image. Moreover, the image shows that the rare earth particles are evenly distributed and firmly embedded in the organic ligands [41].

3.2. Optical characterization

3.2.1. UV–vis absorption spectra

The UV–vis absorption spectra of Phen, Eu\(\text{L-SA}\)\_3-Phen, Eu\(\text{D-SA}\)\_3-Phen, L-SA and D-SA are presented in figure 5. The spectra of L-SA and D-SA show the characteristic absorption band at around 203 nm, corresponding to the \(\pi \rightarrow \pi^*\) electronic transition of carboxyl groups. In the spectrum of Eu\(\text{L-SA}\)\_3-Phen, there are several absorption bands around 333, 261 and 204 nm, which are caused by overlapping of the absorption bands of L-SA and the second ligand. In the spectrum of Phen, the strongest absorption bands of free ligand Phen are 330 and 256 nm. It is obvious that the absorption band of Eu\(\text{L-SA}\)\_3-Phen has been red-shifted. The reason for the above facts can be explained as follows. The carboxyl groups in L-SA form the conjugation effect after the loss of hydrogen ions when L-SA coordinates with Eu\(^{3+}\) ions. When the carboxyl oxygen atoms coordinated with Eu\(^{3+}\) ions to form a larger conjugated system, the carboxyl \(-\text{C=O}\) bond strength becomes weak and the absorption band is red-shifted. Moreover, the formation of multiple chelating rings results in the greatly enhancement of the \(\pi\) electron cloud density around Eu\(^{3+}\) ions. Therefore, the conjugation effect is strengthened and the degree of electron delocalization reduces. These reasons bring about the red-shift of the absorption bands. The spectra prove that the coordination bonds between Eu\(^{3+}\) ions and L-SA or Phen have been formed.
By comparing the intensity of the absorption bands in the spectra of L-SA and D-SA, it can be seen the ultraviolet absorption capacity of L-SA is significantly stronger than that of D-SA. The spectral curves of the ternary complexes with different optical rotations are very similar, with the difference that the absorption
intensity of Eu(L-SA)$_3$-Phen is significantly higher than that of Eu(D-SA)$_3$-Phen. The ability to excite rare earth ions all comes from the ligand, and the larger the absorption coefficient of the ligand, the greater the energy it brings to the entire system [42, 43].

3.2.2. Fluorescence spectra
The excitation and emission spectra of Eu(L-SA)$_3$-Phen are shown in figure 6(a). The excitation spectrum was acquired by monitoring the fixed emission of Eu$^{3+}$ ions at 614 nm. The excitation spectra were recorded to confirm the possibility of energy transfer from SA ligands to Eu$^{3+}$ ions. Due to the $n \rightarrow \pi^*$ transition of the L-SA ligand, the spectrum exhibits a broad excitation band around 330 nm. In addition, a strong peak at 394 nm originate from $\pi \rightarrow \pi^*$ transitions of Phen. From the above, 330 nm was selected as the optimal excitation wavelength for Eu(L-SA)$_3$-Phen. When Eu(L-SA)$_3$-Phen are excited by 330 nm photon, the emission spectrum shows five emission peaks at 578, 591, 613, 649, 699 nm. These peaks belong to transitions from emitting level $^5D_0$ to $^7F_J$ ($J = 0 \sim 4$) of Eu$^{3+}$ [44]. Among the five emission peaks, the $^5D_0 \rightarrow ^7F_2$ transition (electric dipole transition) has the strongest intensity, and the $^5D_0 \rightarrow ^7F_1$ transition (magnetic dipole transition) has the second highest emission intensity. The strongest peak at 614 nm is a red-light emission, illustrating an effective energy transfer between L-SA and Eu$^{3+}$ ions.

Aliphatic alanine derivative (L-SA) with high-performance and low-toxic is selected as the first ligand for the amino acid-rare earth complex. As an electron donating group, the long carbon chain has a positive effect on the luminescence performance of Eu(L-SA)$_3$-Phen. It can increase the electron cloud density and the molar absorptivity of the ligand. Consequently, the attachment of the long carbon chain to the amino acid can significantly improve the intramolecular energy transfer and the luminescent property of the complex. In order to reduce the vibration energy loss of O–H in H$_2$O molecules, Phen with stronger coordination ability has been chosen as the second ligand to substitute the coordinated H$_2$O. Thus, energy loss is reduced and the fluorescence
intensity of Eu(L-SA)$_3$-Phen is improved. The strong and characteristic fluorescence emission shows that both L-SA and Phen can effectively transfer energy to Eu$^{3+}$ ions.

When Eu(D-SA)$_3$-Phen complex was excited with 330 nm photon, the emission spectrum shows characteristic peaks at 578, 591, 614, 649, 699 nm, similar to the optical rotation of the L type. Figure 6(b) shows that the fluorescence intensity of Eu(D-SA)$_3$-Phen is almost half of the fluorescence intensity of Eu(L-SA)$_3$-Phen. It indicates that the energy transfer efficiency between L-SA ligand and Eu$^{3+}$ ions is much higher than that between D-SA and Eu$^{3+}$ ions. The sensitization effect of L-SA is better than that of D-SA.

### 3.2.3. The fluorescence lifetime

The emission decay curves of Eu(L-SA)$_3$-Phen and Eu(D-SA)$_3$-Phen are shown in figure 7, which were monitored at room temperature under excitation at 330 nm and emission at 614 nm. The decay curves are well fitted into single-exponential function:

$$I(t) = I_0 \exp\left(-t/\tau\right)$$

where $I(t)$ and $I_0$ represent the luminescence intensity at time $t$ and 0, and $\tau$ is the decay time. The decay time of Eu(L-SA)$_3$-Phen and Eu(D-SA)$_3$-Phen are calculated as 0.65 and 0.52 ms, respectively.

### 4. Conclusion

High-performance and low-toxic amino acid-rare earth complexes should be used as a highly valuable fluorescent material and that’s why such research is conducted. The difference in rotation of amino acid also results in different fluorescence intensities. In summary, the novel luminescent amino acid-rare earth complexes (Eu(L, D-SA)$_3$-Phen) have been successfully prepared and investigated. Results from analysis further illustrate that the new complexes exhibit outstanding luminescence performance. The relationship between fluorescence intensity of amino acid-rare earth complexes and the optical rotation of ligand SA has been studied and discussed. Compared with Eu(D-SA)$_3$-Phen, Eu(L-SA)$_3$-Phen exhibits the stronger fluorescence intensity due to the higher sensitization and energy transfer efficiency of L-SA. The lifetimes of the amino acid-rare earth complexes are in scale of millisecond. All the research results suggest that Eu(L-SA)$_3$-Phen and Eu(D-SA)$_3$-Phen display potential applications as light emitting functional materials in the optical display field.

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