Research Article

Influence of Different Carboxylic Acid Ligands on Luminescent Properties of Eu(Lc)\textsubscript{3}phen (Lc = MAA, AA, BA, SA) Complexes

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A series of rare earth europium complexes with different carboxylic acid ligands Eu(Lc)\textsubscript{3}phen (Lc = MAA, AA, BA, SA) were synthesized. The complexes were characterized by FTIR, TG-DSC, XRD, UV absorption spectra, and photoluminescence spectra (PL) to study the structure, thermal stability, the energy absorption, and luminescent properties of the complexes. The results showed that the series complexes are all with good crystallization and relatively high thermal stability. The differences of the luminescent properties of complexes are caused by the different ligand structures. The absorption intensity of the carboxylic acid ligands, BA, was the strongest, followed by the MAA and AA and SA was the weakest. Therefore, the fluorescence intensity of the Eu(BA)\textsubscript{3}phen was the strongest, followed by the Eu(MAA)\textsubscript{3}phen and Eu(AA)\textsubscript{3}phen and the Eu\textsubscript{2}(SA)\textsubscript{3}phen\textsubscript{2} was the weakest. All complexes showed good luminescence properties.

1. Introduction

Rare earth organic complexes have become a family of luminescent materials. They are widely applied in laser, electroluminescent, photoluminescence, and so forth, especially as the emission layer for organic light emitting diode (OLED) [1–3]. As early as 1942, Weissman [4] reported that europium \( \beta \)-diketone complexes exhibited luminescence when the rare earth organic complex was irradiated by ultraviolet light. After that, the rare earth complexes containing \( \beta \)-diketonates have been deeply studied about applications for luminescence. Recently, there has been a great interest in the study of rare earth and carboxylic acid complexes due to their low cost, good thermal stability, long luminescence time, color purity, and intense luminescence [5–9]. Moreover, it was found that luminescent properties could be improved by changing the molecular structure and the electrically neutral ligand [10–14]. This is because the electrically neutral ligand can substitute H\textsubscript{2}O to enhance the luminescence intensity [15, 16]. From the previous experimental results, it can be concluded that 1,10-Phenanthroline monohydrate is better than 2,2'-dipyridyl as the electrically neutral ligand [17].

From the coordination chemistry point of view, the complexes contained europium ions tend to multiple coordination structure. The organic anions as the carboxylic acid ligands (first ligands) to satisfy charge balance. Electrically neutral ligands (second ligands) meet Ln ion coordination number. Liu et al. [18] described that the luminescence intensity of Eu(TTA)\textsubscript{3}phen and Eu(TTA)\textsubscript{3}Dipy is stronger than that of Eu(DMB)\textsubscript{3}phen and Eu(DMB)\textsubscript{3}Dipy. Yan et al. [11] studied the luminescent properties of the rare earth organic complexes containing terbium ions with different carboxylic acid ligands. The results show that different carboxylic acid ligands have a certain influence on the fluorescence intensity. Therefore, the efficiency of luminescence of organic rare earth complexes can be improved by adjusting the carboxylic acid ligands.

This paper focuses on the influence of different carboxylic acid ligands on luminescent properties of series rare earth organic complexes. In order to compare the luminescent properties with different complexes, some carboxylic acids containing specific radical group were selected. Methacrylic acid (MAA) contains methyl, and benzoic acid (BA) contains benzene ring. In addition, succinate was selected as
the carboxylic acid ligand. We compared the monocarboxylic acid and dicarboxylic acid as the carboxylic acid ligands on the luminescence properties. In this paper, four rare earth europium binary complexes Eu(MAA)$_3$phen, Eu(AA)$_3$phen, Eu(BA)$_3$phen, and Eu$_2$(SA)$_3$phen$_2$ were synthesized to study the influence of carboxylic acid ligand on the luminescent properties of binary complexes.

2. Experimental

2.1. Reagent and Synthesis of Binary Europium Complexes. Solution of rare earth chloride (0.25 mol/L) was prepared from high purity Eu$_2$O$_3$ (>99.99%, the others are analytical grade) by dissolving in concentrated hydrochloric acid (6 mol/L). MAA (methacrylic acid, 1.5 mol/L), AA (acrylic acid, 1.5 mol/L), BA (benzoic acid, 0.5 mol/L), and SA (succinic acid, 0.375 mol/L) were added in anhydrous ethanol and the pH adjusted to 7.0 with ammonium hydroxide.

All samples were synthesized by the coprecipitation method. With the synthesis method of Eu(MAA)$_3$phen, for example. MAA in anhydrous ethanol (15 mL) was dropwise added into the stirred solution of europium chloride in anhydrous ethanol (30 mL), and then the pH value of the mixture was adjusted to 6-7 using ammonium hydroxide. The mixture was stirred for 30 minutes, and then the solution of 1,10-Phenanthroline monohydrate (phen) in anhydrous ethanol (0.1 mol/L, 15 mL) was added dropwise. The resulting solution was stirred at room temperature for 3 hours and standing overnight. The precipitate was filtered and washed with anhydrous ethanol by 3 times, and finally dried at 80°C, to obtain Eu(MAA)$_3$phen. The preparation method of different carboxylic acid ligand complexes is basically same.

2.2. Measurement. The FT-IR spectra were recorded in the 4000–400 cm$^{-1}$ region by the NICOLET 5700 with KBr plates. The thermal gravimetric analyses (TG) and differential scanning calorimetry (DSC) of the complexes measured by the STA449C Thermo Gravimetric Analyzer (Netzsch, Germany) were made in N$_2$ with a heating rate 10°C/min in the range of 50 ~ 800°C. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (model D/MAX2500, Rigaku, Japan) with Cu Kα radiation (λ = 1.5406 Å) in the range of 5° ~ 80° with a step size of 0.02°. The absorption spectra were recorded using UV-Vis spectrophotometer (Shimadzu UV-3101). They were measured in 1 × 10$^{-5}$ mol/L DMSO solution at room temperature. The photoluminescence spectra of the rare earth organic complexes were measured using a Horiba Jobin Yvon fluorescence spectrophotometer (FL3-221, France) at room temperature.

### Table 1: The europium content in the Eu(Lc)$_3$phen complexes.

<table>
<thead>
<tr>
<th></th>
<th>Eu(MAA)$_3$phen</th>
<th>Eu(AA)$_3$phen</th>
<th>Eu(BA)$_3$phen</th>
<th>Eu$_2$(SA)$_3$phen$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical value</td>
<td>25.09%</td>
<td>26.83%</td>
<td>21.21%</td>
<td>28.82%</td>
</tr>
<tr>
<td>Experimental value</td>
<td>24.65%</td>
<td>26.69%</td>
<td>21.20%</td>
<td>28.10%</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Structure of Eu(Lc)$_3$phen Powders. The europium content was determined by the EDTA titration, and the results were shown in Table 1. We have synthesized Eu(Lc)$_3$phen (Lc = MAA, AA, BA, SA) complexes successfully, as the theoretical values and experimental values are similar.

Figure 1 reports the XRD patterns of four complexes: (1) Eu$_2$(SA)$_3$phen$_2$, (2) Eu(MAA)$_3$phen, (3) Eu(BA)$_3$phen, and (4) Eu(AA)$_3$phen. The main peaks of the complexes appear from 5° to 25° (2θ). Several intense diffraction peaks can be seen from the X-ray diffraction diagrams of the four complexes, indicating that the complexes are crystal.

Moreover, all diffraction peaks of the four complexes appear before 45°, the higher d-values were determined by large values of the interplanar spacing. Therefore, it has decrease effect between the europium ions itself.

Figure 2 reports the FT-IR spectra of the ligands and the four complexes. FTIR spectra of Eu(MAA)$_3$phen, Eu(AA)$_3$phen, Eu(BA)$_3$phen, and Eu$_2$(SA)$_3$phen$_2$ complexes have been recorded in the 400–4000 cm$^{-1}$ region. The IR spectra data is shown in Table 2.

It can be found that the characteristic peaks of ν$_{C\cdots O}$ in the MAA, AA, BA, and SA disappeared at about 1737 cm$^{-1}$, 1724 cm$^{-1}$, 1687 cm$^{-1}$, and 1694 cm$^{-1}$, respectively. The presence of carboxylate groups in the series complexes was definitely confirmed by both the symmetric stretching bands (ν$_{\nu\text{COO}^-}$) at about 1427 cm$^{-1}$ and the asymmetric stretching bands (ν$_{\alpha\text{COO}^-}$) at about 1562 cm$^{-1}$. These results showed that the carboxylate groups were coordinated with the europium ions [19]. In addition, the stretching vibration peak (ν$_{C\cdots N}$) at about 1643 cm$^{-1}$ in phen shifted from 1643
Figure 2: Continued.
Transmittance (%)

![Graph](image)

**Figure 2:** FT-IR spectra of ligands and Eu(Lc)phen complexes.

### Table 2: Character FT-IR bands (cm⁻¹) of the ligands and their complexes.

<table>
<thead>
<tr>
<th>Ligands and complexes</th>
<th>ν_O-H</th>
<th>ν_C=O</th>
<th>ν_as(COO⁻)</th>
<th>ν_s(COO⁻)</th>
<th>ν_C-N</th>
<th>ν_C=C</th>
<th>ν_C-H</th>
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<tr>
<td>MAA</td>
<td>2969</td>
<td>1737</td>
<td>1640</td>
<td>1353</td>
<td>1600</td>
<td>1639</td>
<td>850</td>
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<tr>
<td>AA</td>
<td>3447</td>
<td>1724</td>
<td>1636</td>
<td>1531</td>
<td>1601</td>
<td>1694</td>
<td></td>
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<tr>
<td>BA</td>
<td>3418</td>
<td>1687</td>
<td>1601</td>
<td>1531</td>
<td>1601</td>
<td>1636</td>
<td></td>
</tr>
<tr>
<td>SA</td>
<td>3386</td>
<td>1694</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu(MAA)₂phen</td>
<td>3445</td>
<td>1562</td>
<td>1427</td>
<td>1645</td>
<td>1529</td>
<td>1645</td>
<td>848</td>
</tr>
<tr>
<td>Eu(AA)₂phen</td>
<td>3409</td>
<td>1597</td>
<td>1453</td>
<td>1643</td>
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<td>1643</td>
<td>848</td>
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<tr>
<td>Eu(BA)₂phen</td>
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<td>1567</td>
<td>1422</td>
<td>1611</td>
<td>1531</td>
<td>1643</td>
<td>848</td>
</tr>
<tr>
<td>Eu₂(SA)₃phen₂</td>
<td>3415</td>
<td>1569</td>
<td>1427</td>
<td>1533</td>
<td>1533</td>
<td>1643</td>
<td>851</td>
</tr>
</tbody>
</table>

**3.2. Thermal Properties of Eu(Lc)phen Powders.** The thermal stability of rare earth organic complexes was studied by the TG-DSC analyses. Figure 3 shows the TG-DSC curves of Eu(AA)₂phen. Eu(AA)₂phen began to decompose from about 190°C and decomposed completely at about 800°C. The TG curve exhibited a little mass loss from 50 to 190°C, indicating that the series complexes have little water. A loss step with weight loss rate of 28.06% arose in the range of 285~326°C, which was caused by the skeleton fracture of the complex. It indicates that the complex has been partially decomposed which may be from the decomposition of free ligand AA and part decomposition of phen. It arose an exothermic peak at 340°C accompanied by a slow weight loss process. This may be generated by further heat of the intermediate products produced in the decomposition process of complexes [11]. The complexes began to turn into violent decomposition at 426.9°C taking off the AA and phen with weight loss to 25.07%. The DSC curves tend to be flat when closed to 800°C. Complexes decomposed completely with residue of rare earth oxides. Residual quantity bigger than the theoretical value may because of it was tested in the nitrogen atmosphere. In the environment which is lack of oxygen, the carbonatomin thecomplexescannot completely transform into CO₂ or CO which carbonization phenomenon occurs [21].

The similar thermal analysis curves show the series complexes have similar thermal decomposition process. The thermal decomposition temperature of Eu(MAA)₂phen, Eu(AA)₂phen, Eu(BA)₂phen, and Eu₂(SA)₃phen₂ is about 210°C, 190°C, 200°C, and 180°C. The results show that these series complexes have good thermal stability.

**3.3. Energy Absorption of Eu(Lc)phen Powders.** Figure 4 shows the UV-Vis absorption spectra of five different ligands. The UV absorption of the phen is significantly stronger than
the various carboxylic acid ligands. A large absorption peak occurred at 286 nm and a weak absorption peak at 324 nm. It can be seen that the maximal peaks were located at 282 nm for carboxylic acid ligands, which was attributed to the $\pi \to \pi^*$ transition [22]. The ligand BA absorption in the ultraviolet region is relatively the strongest, followed by the MAA and AA, and SA was the weakest. It implies that most of the energy absorption comes from phen, which suggests that the antenna effect of phen is more efficient than that of carboxylic acid ligands.

From the UV-Vis absorption of the complexes, phen in the complexes is not only a coligand to transfer energy, but also the main components of the absorption energy, providing additional energy for the complex fluorescence emission.

The UV-Vis absorption spectra of Eu(Lc)$_3$phen complexes are shown in Figure 5. As the absorption of rare earth ions is weak in the ultraviolet region, it is overlapped by the absorption of the ligand. The complex absorption peak relative to the ligand is slightly red shifted and the intensity increases. The absorption intensity order in the ultraviolet region is BA $>$ MAA $>$ AA $>$ SA, the corresponding complexes of UV-Vis absorption intensity of Eu(AA)$_3$phen $>$ Eu(MAA)$_3$phen $>$ Eu(BA)$_3$phen $>$ Eu$_2$(SA)$_3$phen$_2$ in the complexes. This phenomenon attributes to the mutual effect of the carboxylic acid ligands and the electrically neutral ligand.

3.4. Luminescence of Eu(Lc)$_3$phen Powders. Figure 6 shows the emission spectra of Eu(MAA)$_3$phen, Eu(AA)$_3$phen, Eu(BA)$_3$phen, and Eu$_2$(SA)$_3$phen$_2$ complexes under the excitation of optimal excitation wavelength. The strongest excitation wavelengths of Eu(MAA)$_3$phen, Eu(AA)$_3$phen, Eu(BA)$_3$phen, and Eu$_2$(SA)$_3$phen$_2$ were 342 nm, 344 nm, 349 nm, and 368 nm, respectively. In the emission spectra, the positions of emission peaks of all complexes were almost the same. They all emitted the typical sharp emission bands at 590 and 614 nm, corresponding to the transitions of the $^5D_0 \to ^7F_1$, $^5D_0 \to ^7F_2$ of Eu$^{3+}$ ion [23]. The local symmetry of the crystal field around the Eu$^{3+}$ will cause
peak splitting. Therefore, in Figure 6, emission peak appears at 620 nm from the 614 nm due to the formation of split peak. Adding different carboxylic acid ligands changes the luminescence intensity of complexes without changing their positions of emission peaks.

Different carboxylic acid ligands caused that the coordination environment has changed, luminescence intensity of these four complexes subjected to the impacted. In addition, the luminescence intensity of Eu(BA)$_3$phen and Eu(AA)$_3$phen is stronger than that of Eu(MAA)$_3$phen and Eu$_2$(SA)$_3$phen$_2$.

From the front UV-Vis absorption spectrum, it is indicated that different carboxylic acid ligands and phen provided additional energy for the series complexes. Phen is the main source of energy for the complexes. The lowest triplet state energy level of the MAA and AA is at about 24800 cm$^{-1}$. And the lowest triplet state energy level of the phen is at about 22132 cm$^{-1}$. They are close to the excited state energy level of europium ion (17300 cm$^{-1}$ for the $^5D_0$ level) [24]. So the energy can be transferred to the excited states of europium ions effectively. The structure of the ligand plays an important role in the luminescence properties of complexes. Generally, the higher rigidity of the ligand is conducive to enhance fluorescence efficiency of the complexes [25, 26]. Benzoic acid has high conjugated rigid. Consequently, the fluorescence intensity of Eu(BA)$_3$phen is the highest.

Although succinic acid and its complex exhibited weak absorption in the ultraviolet region but the dicarboxylic acid has better transfer efficiency relative to a monobasic acid. It compensated for the lack of fluorescence properties to some extent caused by the weak ligand absorption [27]. Succinic acid is capable of delivering more efficient energy to complexes. It is also conducive to enhance the fluorescence intensity of the complexes.

4. Conclusion

In this paper, series of rare earth Europium complexes with different carboxylic acid ligands Eu(L)$_3$phen (L = MAA, AA, BA, SA) were synthesized. The complexes with good crystallization showed relatively high thermal stability and their decomposition temperatures were above 180°C. The energy of the series rare earth organic complexes mainly depends on the absorption of the carboxylic acid ligands and 1,10-Phenanthroline monohydrate. The ability to absorb energy of carboxylic acid ligands is BA > MAA > AA > SA. The ability to absorb energy of the formatted complexes was Eu(AA)$_3$phen > Eu(MAA)$_3$phen > Eu(BA)$_3$phen > Eu$_2$(SA)$_3$phen$_2$. The steric hindrance effect and level matches between the carboxylic acid ligands and heterocyclic ligand have a significant impact on the energy absorption efficiency of complexes. The fluorescence intensity of the series rare earth complexes was Eu(BA)$_3$phen > Eu(AA)$_3$phen > Eu(MAA)$_3$phen > Eu$_2$(SA)$_3$phen$_2$. All complexes show excellent luminescence characteristics. These results indicated that the series europium (III) complexes have great potential as the emission layer for organic molecular-based light-emitting diodes.

Acknowledgments

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