Synthesis, Characterization and Luminescent Properties of a Novel Light Conversion Agent

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Abstract: The novel rare earth complex with multi-benzenoid, multi-carboxide and double carboxyl structure as core were synthesized. The IR, solid state ^{13}C NMR and fluorescent spectra of the complex were studied. IR absorption spectra indicate that the ligand is coordinated to the Eu^{3+} ion, and chemical bonds are formed between Eu^{3+} ion and nitrogen atoms of phen. The fluorescent spectra illustrate that the complex has an excellent luminescence, indicating the ligand favors energy transfer to the emitting energy level of Eu^{3+}.

Key words: rare earth; core-shell; light conversion; resource
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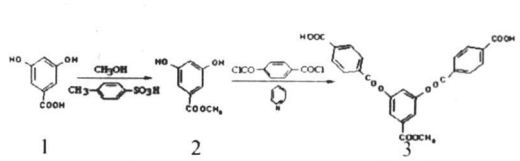
With the deficiency of the natural resources, the exploitation of the new resources has become more and more important. As a kind of important resource, the research and application of solar light have attracted the mankind's attention. The rare earth light conversion agent can transfer violet and green-yellow light in the solar rays into red-orange light and blue-violet light which are necessary to crop photo-synthesis due to some rare earth ions' special outer-shell electronic structure and multi-coordination. Thus not only can make the sunlight resource be rationally and effectively applied, but also let the crops early-cropping, increase production and finally improve the light-ecological environment of crop. So, the studies of the rare earth light conversion agent have attracted attention of many researchers[1-2].

In our work, we synthesized a novel core-shell polymeric rare earth light conversion agent. The core-shell polymeric light conversion agent has a better core-shell structure, outstanding luminescent character and excellent thermal stability. In this paper, Synthesis, Characterization and Luminescent Properties of the novel rare earth complex with multi-benzenoid, multi-carboxide and double carboxyl structure as the core are discussed.

1 Experimental

1.1 Synthesis of ligand L

The synthetic route for the ligand L is shown in Scheme 1. 3, 5-Dihydroxybenzoate (2) was prepared according to the literature[3]. The ligand L was synthesized as follow: p-Phthaloyl chloride (28 mmol) and 3, 5-dihydroxybenzoate (14 mmol) were added to the DMF solution (50 mL) containing pyridine (2.5 mL). The whole mixture was stirred at 95℃ under argon for 4 h. After being cooled down, the mixture was poured into water (100 cm^3). The resulted ligand L (3) (white powder) was filtered, washed with water and dried in vacuum oven at 105 ℃, yield 85%.



Scheme 1 The synthetic route for the ligand L

1.2 Synthesis of the complex

Eu_2O_3 was dissolved in 2 mol·L^{-1} HCl, evaporated to near dryness, finally dissolved in 99.7% ethanol

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to prepare 0.2 mol·L^{-1} $EuCl_3$ solution (Solution 1). 1.10-Phenanthroline (2 mmol) was dissolved in 99.7% ethanol (20 mL) (Solution 2). Ligand L (3 mmol) and DMF (40 mL) were mixed and stirred at 50℃ until the ligand L was dissolved (Solution 3). The pH of solution 3 was adjusted to the range 6 ~ 7 with aqua ammonia (25% ~ 28%, NH_3). Solution 1 (10 mL) and Solution 2 were stirred at 50℃ for 30 mins, and then Solution 3 was added. The mixtures solution was stirred at 50℃ for 2 h and at room temperature for 24 h. The synthesized complex was white solid powder, which was washed with ethanol and water, filtered and dried in vacuum oven at 160℃.

2 Results and discussion

2.1 The IR absorption spectrum of the complex

In the IR spectra of the complex and phen, the characteristic peak of ν_{COOH} for the ligand L (1699 cm^{-1}) disappears when the complex are formed. The asymmetric and symmetric stretching vibrations of carboxylic group are appearing at 1657 and 1520 cm^{-1} in the complex. These facts prove that the coordinate bonds are formed between oxygen atom in carboxylic group and the rare earth ion. In the other hand, the benzene ring ν_{C-H} bending vibration peaks of phen in high frequency region appearing at 854 and 739 cm^{-1} are shifted to 847 and 731 cm^{-1}, indicating that the chemical bonds are formed between rare earth ion and nitrogen atoms of phen[2]. Finally the absorption peak at about 451 cm^{-1} can be assigned to the Eu—O vibration absorption band. According to the analysis of the IR spectra of the complex and ligand L, the novel Eu^{3+} complex with ligand L and phen is formed.

2.2 The Solid State ^{13}C NMR spectra of the complex

In the solid state ^{13}C NMR spectra of ligand L and the complex, the peaks of ligand L at 53.16 and 131.12 are not obviously changed. The peak at 173.0 is disappeared, and the two peaks at 162.2 and 148.6 are enhanced. These results indicate that the ligand L has coordinated with Eu^{3+} ion. Furthermore, the new peaks lie in 163.9, 127.5 and 121.6 correspond to the δ_C of C=N and C—H for phen, respectively. These mean that the phen is coordinated with Eu^{3+} ion. So that, the analyzing results of solid State ^{13}C NMR spectra of the ligand L and complex further verify those of IR absorption spectra of the complex.

2.3 Fluorescence spectra of the complex

The fluorescent spectra of the complex show that the complex has excellent luminescent property. The excitation and emission spectra of complex (pH=8.5) are recorded in the Fig.1. The strong and smooth bands observed (200 ~ 400 nm) could be assigned to the efficient $\pi \rightarrow \pi^*$ transition based on the conjugated double bands of ligand L and phen. The fact indicates that Eu^{3+} ion can be well excited in 330 ~ 360 nm wavelength range, and the optimum excitation wavelength is 347 nm.

The fluorescence emission peaks of the complex are all from $^5D_0 \rightarrow {}^7F_{J(0-4)}$ transition. The $^5D_0 \rightarrow {}^7F_2$ transition is an electric dipole transition, it can be detected as a relatively strong peak when Eu^{3+} does not lie in centrosymmetric ligand field. The $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition, and its fluorescence intensity becomes the most intensive only when Eu^{3+} ion is center of inversion[5]. In the Fig.1, the corresponding emission peaks base on the $^5D_0 \rightarrow {}^7F_1$ (601.6 nm), $^5D_0 \rightarrow {}^7F_2$ (625.0 nm), $^5D_0 \rightarrow {}^7F_3$ (660.5 nm) and $^5D_0 \rightarrow {}^7F_4$ (706.3 nm) transitions are observed. The strongest emission peak is at 625 nm, which belongs to $^5D_0 \rightarrow {}^7F_2$ transition. The result presents that the Eu^{3+} lies in a non-centrosymmetric ligand field in the complex[6]. The luminescent intensity of rare earth complex has relationship with the excellent absorption coefficient of the ligand and the high efficient ligand-to-trivalent rare earth ion energy transfer. In the ligand L, the lone-pair electron of oxygen atom of the carbonyl group and benzene ring can form hyperconjugation effect (Scheme 2). This makes ligand L possesses rigid structure, good structure stability. Furthermore, the absorption energy of ligand L can be efficiently transferred to the Eu^{3+} ion. These facts will endue the complex with strong luminescent property. In the Fig.1 the strong emission peaks also prove that the luminescent property of the complex is excellent.

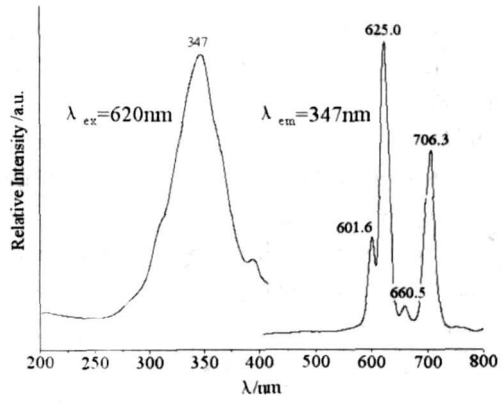
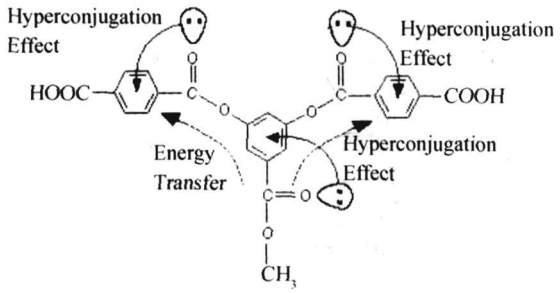


Fig.1 The excitation and emission spectra of the complex Scheme 2 The energy transfers diagram of the ligand L

3　Conclusion

The complexes of trivalent europium with ligand L and phen have also been studied. The complexes exhibit characteristic emission peaks of Eu^{3+} ion and strong luminescent intensity under the excitation spectrum. The excellent luminescent properties of the complexes indicate that there exists high efficient energy transfer between ligand L and trivalent europium ion.



Scheme 2　The energy transfers diagram of the ligand L

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一种新型的光能转换剂的合成、表征和荧光性能

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摘　要：合成了一种作为核的带有多苯环联结结构、多羰基、双羧基的新型稀土配合物，对配合物的红外光谱，固相核磁碳谱和荧光光谱进行了研究。红外光谱表明所制备的新型配体与稀土 Eu^{3+}进行了配位，而邻菲啰啉中的氮原子也与稀土离子进行了成键。所制备的配合物的荧光光谱表明配合物具有优异的荧光特性，同时配体与稀土离子间具有较好的能量转换性能。

关键词：稀土；核壳；光转换；能源

中图分类号：O43；O63