

Preparation and luminescent properties of the novel polymer-rare earth complexes composed of Poly(ethylene-co-acrylic acid) and Europium ions

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ABSTRACT

A series of novel polymer-rare earth complexes with Eu^{3+} ions have been synthesized and investigated successfully, including the binary complexes containing the single ligand poly(ethylene-co-acrylic acid) (EAA) and the ternary complexes using 1,10-phenanthroline (phen), dibenzoylmethane (DBM) or thenoyltrifluoroacetone (TTA) as the second ligand. Their structures have been characterized by Fourier transform infrared spectroscopy (FT-IR), elemental analysis and X-ray diffraction (XRD), which confirm that both EAA and small molecules participate in the coordination reaction with rare earth ions, and they can disperse homogeneously in the polymer matrixes. Both ultraviolet–visible (UV–vis) absorption and photoluminescence tests for the complexes have been recorded. The relationship between fluorescence intensity of polymer-rare earth complexes and the quantity of ligand EAA has been studied and discussed. The films casted from the complexes solution can emit strong characteristic red light under UV light excitation. All these results suggest that the complexes possess potential application as luminescent materials.

1. Introduction

Poly(ethylene-co-acrylic acid) (EAA), polymerized by ethylene and acrylic acid, is one of important industrial materials with various acrylic acid contents. As the acrylic acid units strengthening interchain interaction through hydrogen bond, EAA has outstanding toughness, prominent resistance to many organic solvents and excellent film-forming ability, which has been used in a wide range of applications such as interfacial agent [1], packaging [2], biomedical science [3,4] and compatibilization [5,6]. EAA bears free carboxyl groups onto the polymer backbone, turning it into an excellent candidate for coordination reactions with rare earth ions. We have synthesized two fluorescent films by amidation reaction on the surface of EAA films [7]. However, limited by current knowledge in this field, the fluorescence performance of EAA coordinated with rare earth ions has not been reported yet.

Lanthanide ions have aroused widespread attention due to the monochromatic emission colors, intense emission bands and long lifetime resulting from the shielding of the 4f electronic states of rare earth ions by the outer 5s and 5p electrons and effective transitions of 4f–4f and 4f–5d [8–10]. Lanthanide materials have been widely used in lighting, display techniques, chemosensors, light emitting diodes and some other fields [11,12]. To solve the problem of weak luminescence intensity of bare lanthanide ions caused by the limitations in f-f

transitions, a large number of lanthanide complexes containing organic chromophores have been synthesized and studied [13]. Generally, organic low-molecular rare earth complexes are simply doped into matrixes [14,15]. However, there are some serious limitations in practical applications due to the poor mechanical property, bad physicochemical stability and harsh processability as well as the incompatibility with the matrixes [16]. In addition, another disadvantage of organic low-molecular rare earth complexes is water molecules coordination, which bring about low emission quantum efficiency because of the non-radiative dissipation caused by the energy vibration of hydroxyl groups [17]. As a comparison, through the coordination bonds between the rare earth ions and the function pendant groups of polymers, the polymer-rare earth complex materials not only possess intrinsic fluorescence properties of the rare earth ions, but also exhibit good toughness, high chemical stability and excellent process ability [18–20]. Furthermore, the polymer-rare earth complexes can be easily formulated into films from their solution at relatively low temperature.

Two methods can be employed to prepare polymer-rare earth complexes [21]. The first one is that low-molecular rare earth complexes containing polymerizable double bond as monomer are polymerized or copolymerized to manufacture polymer-rare earth complexes, but it is difficult to prepare such low-molecular rare earth complexes. The other is a direct method, in which the reaction takes place between rare earth ions and groups on the polymer chains to

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obtain polymer-rare earth complexes. As a result, so the latter is a better and more feasible way compared with the former one.

In this work, using EAA as macromolecular ligand and Eu^{3+} ions as central atoms, various luminescent binary polymer-rare earth complexes were prepared. At the same time, with 1,10-phenanthroline (phen), dibenzoylmethane (DBM) or thenoyltrifluoroacetone (TTA) as small-molecule co-ligands, various ternary polymer-rare earth complexes were also produced. In the present work, we focused on investigating the relationship between fluorescence intensity of polymer-rare earth complexes and the quantity of ligand EAA. To the best of our knowledge, the similar investigations have been rarely reported. The new complexes not only can emit strong red light, but also have excellent film-forming performance, which would be meaningful for further application of EAA.

2. Experimental

2.1. Raw materials

All chemicals were obtained from commercial sources and used without further purification. Europium(III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99 wt%) was purchased from Adams Reagent Co., Ltd. 1,10-Phenanthroline (phen), dibenzoylmethane (DBM), thenoyltrifluoroacetone (TTA), methylbenzene, ethyl acetate and dimethylformamide (DMF) were all analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Poly(ethylene-co-acrylic acid) (EAA, PRIMACOR 1410, 9.5 mol% acrylic acid) was purchased from Dow Chemical Co. The amount of carboxyl groups in EAA is 3 mmol/g.

2.2. Preparation of binary complexes $\text{Eu}(\text{EAA})_n$

The binary complexes were carried out according to the following procedure. First, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) was dissolved in 5 mL DMF. Second, the EAA (0.5 g), in which 1.5 mmol carboxyl groups is contained, was dissolved in 10 mL methylbenzene, and the solution was stirred and refluxed at 80 °C for 15 min to make it completely dissolved. Third, the DMF solution of EuCl_3 was added dropwise into EAA methylbenzene solution with the molar ratio of 3:1. Then the mixture was performed at 80 °C for 5 h with stir and reflux. Finally, the mixture was dried in a vacuum oven at 60 °C for 24 h. The complex was denoted as $\text{Eu}(\text{EAA})_3$. By changing the molar ratio of EAA to Eu^{3+} ions, the binary complexes with other compositions were prepared.

2.3. Preparation of ternary complexes

The ternary complexes were synthesized following a similar procedure. EAA (0.5 g), in which 1.5 mmol carboxyl groups is contained, was dissolved in 10 mL methylbenzene, and then a solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) in 5 mL of dry DMF was added with the molar ratio of 1:3. Also, the DMF solution of phen with the molar ratio of 1:1 was slowly added to the mixture. The reaction solution was stirred and refluxed for 5 h at 80 °C. Finally, the mixture was dried in a vacuum oven at 60 °C for 24 h. The complex was denoted as $\text{Eu}(\text{EAA})_3\text{-phen}$. By changing the second ligand and the molar ratio of EAA to Eu^{3+} ions, the ternary complexes with other compositions such as $\text{Eu}(\text{EAA})_n\text{-DBM}$ and $\text{Eu}(\text{EAA})_n\text{-TTA}$ were prepared.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were obtained by using a Bruker Vertex 70 FT-IR spectrometer in the range of 4000–600 cm^{-1} . Ultraviolet–visible (UV–vis) absorption spectra were recorded on a UV-3600 spectrophotometer. Elemental analyses were performed using an Elementar Vario EL III elemental analyzer. X-Ray Diffraction (XRD) measurements were recorded by a X'Pert-Pro MPD diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) over a 2θ range of 10–90°. The

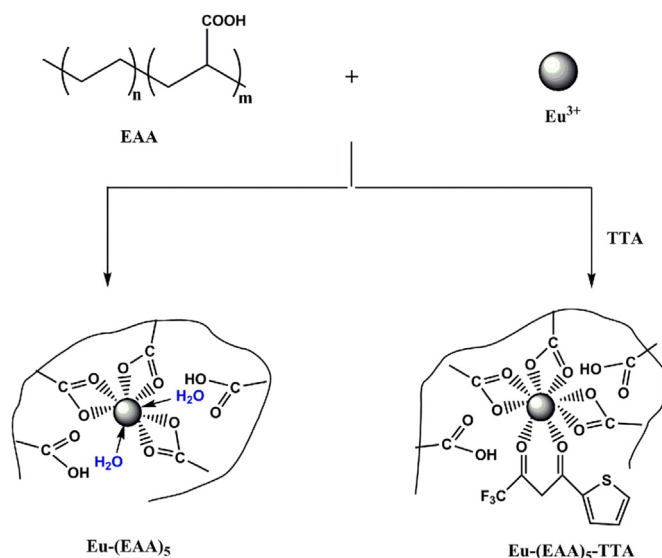


Fig. 1. The preparation and chemical structures of $\text{Eu}(\text{EAA})_5$ and $\text{Eu}(\text{EAA})_5\text{-TTA}$.

luminescence emission and excitation spectra were measured on the FLS920 fluorescence spectrometer at room temperature. LabRAM HR800 PL/Raman system was used to obtain the decay lifetime.

3. Results and discussion

3.1. Characterization of polymer-rare earth complexes

The preparation and chemical structures of $\text{Eu}(\text{EAA})_5$ and $\text{Eu}(\text{EAA})_5\text{-TTA}$ are illustrated in Fig. 1.

Elemental analytical data for the complexes are listed in Table 1. The experimental data are in a good accord with the theoretical values.

The FT-IR spectra of EAA, $\text{Eu}(\text{EAA})_4$ and $\text{Eu}(\text{EAA})_3\text{-TTA}$ are shown in Fig. 2. The neat EAA shows a peak at 1737 cm^{-1} , which is characteristic of the carbonyl stretching of the carboxylic acid [22]. After the coordination reaction, the 1737 cm^{-1} peak disappears, and the 1542 and 1436 cm^{-1} peaks can be observed as shown in $\text{Eu}(\text{EAA})_4$, which are assigned to the typical asymmetric and symmetric stretching vibration of the carbonyl groups [23]. Also, any acid peak can't be observed in the spectrum of $\text{Eu}(\text{EAA})_4$, indicating that coordination bonds are formed between Eu^{3+} ions and the oxygen atoms of carboxyl groups.

From the FT-IR spectra of EAA and $\text{Eu}(\text{EAA})_3\text{-TTA}$, after coordination to Eu^{3+} ions, it is found that the strong peak at 1737 cm^{-1} corresponding to carboxyl groups is essentially absent. Alternatively, the typical symmetric and asymmetric stretching vibration of the carbonyl groups at about 1436 and 1543 cm^{-1} are detected. The FT-IR spectrum of $\text{Eu}(\text{EAA})_3\text{-TTA}$ shows the -C=O stretching vibration of TTA in the complex is moved to lower frequencies, from 1661 cm^{-1} of free TTA to 1619 cm^{-1} of coordinated TTA. The bands at 1140 and 1375 cm^{-1} are assigned to -C=C stretching vibration and -C-H in-plane bending vibration of thiophene ring. In addition, the peak at

Table 1

Elemental analysis of $\text{Eu}(\text{EAA})_4$, $\text{Eu}(\text{EAA})_3\text{-phen}$, $\text{Eu}(\text{EAA})_3\text{-DBM}$ and $\text{Eu}(\text{EAA})_3\text{-TTA}$.

Complexes	C (Cal) (%)	H (Cal) (%)	N (Cal) (%)
$\text{Eu}(\text{EAA})_4$	69.55 (69.61)	11.01 (11.04)	0 (0)
$\text{Eu}(\text{EAA})_3\text{-phen}$	69.07 (69.02)	9.83 (9.82)	2.3 (2.1)
$\text{Eu}(\text{EAA})_3\text{-DBM}$	69.41 (69.44)	9.71 (9.79)	0 (0)
$\text{Eu}(\text{EAA})_3\text{-TTA}$	63.18 (63.29)	9.23 (9.29)	0 (0)

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