



EVA film doped with β -diketones macromolecular lanthanide complexes: Preparation, characterization and application



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ARTICLE INFO

Article history:

Received 19 February 2014

Received in revised form 4 July 2014

Accepted 5 July 2014

Available online 16 July 2014

Keywords:

Organometallic compounds

Luminescence

Photoluminescence spectroscopy

Electron microscopy

Optical properties

Electrical properties

ABSTRACT

In this study, the β -diketones groups functionalized polymer D-HEA-C was first synthesized by chemically attaching D-HEA to the side chains of polycaprolactone and then coordinated with Eu(III) to form β -diketones macromolecular complexes. ¹H NMR, FT-IR, GPC, ICP-AES, ultraviolet absorption and fluorescence emission were used to characterize the polymeric rare earth complex materials composed of D-HEA-C and Eu³⁺ ion. The synthesized β -diketones macromolecular complexes were doped into EVA film to test the energy conversion efficiency. TGA, Transmittance, UV absorption spectra, fluorescence emission and SEM were used to study the properties of the doped EVA film. The macromolecular complexes could not only limit the coordination of small molecules to effectively avoid the fluorescence quenching, but also enhance the fluorescence intensity of the complex. Moreover, the β -diketones macromolecular complexes have good compatibility with the EVA matrix, and could increase the photovoltaic conversion efficiency and service life of EVA film. Therefore, the β -diketones macromolecular complexes could act as efficient light conversion molecular devices, and have a broad prospect in the solar packaging film.

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1. Introduction

Luminescent rare earth complexes have attracted considerable attentions in display devices, fluorescent probes, biological labels, polyvinyl chloride polymer (PVC) heat stabilizers and agricultural film light conversion fields due to their outstanding luminescent characteristics, such as high luminous intensity, long luminous lifetime and extremely sharp emission band during electronic transitions to 4f energy levels [1–7]. Europium itself has a very low molar absorptivity; however, it has been shown that certain ligand can absorb ultraviolet radiation and transfer this energy to bound lanthanide ion, from which available light is emitted [8,9]. Usually, organic small-molecule rare earth complexes

are used to dope into matrixes, while there are some limitations in practical applications, such as poor mechanical property, poor physicochemical stability and harsh processability as well as the incompatibility with the matrixes. Besides, organic small-molecule rare earth complexes contain inner-coordinated water molecules, resulting in low emission quantum efficiency due to the non-radiative dissipation of energy which is caused by the high energy vibration of –OH group [4,10]. In contrast, polymeric rare earth complex materials, in which lanthanide ions are directly linked to polymers via coordinating bond between the functional pendant groups of polymers and lanthanide ions, not only possess unique fluorescence properties of the rare earth ions and good mechanical toughness, chemical stability. Polymers can also shield the metal centers from water and solvent molecules and lend excellent processability to the luminescent materials [11,12]

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Recently, polymeric rare earth complexes have drawn many attentions for their potential applications. At present, there are two main methods to prepare polymer–rare earth complexes: (1) Small-molecule rare earth complexes containing polymerizable double bond as monomer are polymerized or copolymerized with other monomers resulting in polymeric rare earth complex materials; (2) Rare earth ions coordinate with the side groups of polymer chains to form polymeric rare earth complex materials [11,13]. In general, the latter method is more feasible because the small-molecule rare earth complexes containing polymerizable double bond are difficult to obtain. In this paper we used the latter method.

At present, most literatures have focused on the carboxylic acids based macromolecular lanthanide complexes, only a few reports studied on β -diketones macromolecular lanthanide complexes [2,10,11,13]. Due to the high UV absorption coefficient and well complex ability of dibenzoylmethane (DBM) and its derivatives, it could be used as lanthanide organic complexes. The plastic or film under illustrated, as we all know, is easy to be aged; however, it will be stable rather than exhausted if doped with the ultraviolet absorbing agent of dibenzoylmethane (DBM) or its derivatives. Therefore, the β -diketones macromolecular lanthanide complexes doped plastic or film has broad prospects.

Ethylene vinyl acetate (EVA) plays an important role in photovoltaic module manufacturing. It is used to encapsulate solar cells in a lamination process. Solar cell modules utilize EVA as a sealant due to its excellent light transmission ability, moisture resistance, and good adhesion to glass. The deterioration of EVA during its service life is impacted by heat, moisture absorption, and oxygen, especially ultraviolet radiation from sunlight [14–16]. Hence, β -diketones macromolecular lanthanide complexes were doped into EVA film in our research which could not only limit the coordination of small molecules to effectively avoid the fluorescence quenching [17–19], but also enhance the fluorescence intensity of the complex to a certain extent. Moreover, the β -diketones macromolecular complexes have good compatibility with the EVA matrix, and could increase the photovoltaic conversion efficiency and service life of EVA film.

In this study, the β -diketones group functionalized polymer D-HEA-C was first synthesized by chemically attaching D-HEA to the side chains of polycaprolactone and then coordinated with Eu(III) to form β -diketones macromolecular complexes. FT-IR, ^1H NMR, GPC, ICP-AES, ultraviolet absorption and fluorescence emission were used to characterize the polymeric rare earth complex materials composed of D-HEA-C and Eu^{3+} ion. Then the β -diketones macromolecular complexes were doped into EVA film. TGA, Transmittance, UV absorption spectra, fluorescence emission and SEM were used to study the properties of the doped EVA film.

2. Materials and methods

2.1. Materials

ϵ -Caprolactone (aladin, dried over CaH_2 and distilled prior to use), dibenzoylmethane (purified by recrystallization

from ethanol), 2-hydroxyethyl acrylate (aladin HPLC grade), Eu_2O_3 (Europium content 99.9%), (R)-(–)-1, 1-Binaphthyl-2, 2-diyl-Hydrogen Phosphate (R-BNPH). Eu (DBM-d)₃(D-HEA and the reaction of acryloyl chloride, then made with rare earth europium), PAA–Eu (acrylic acid homopolymer formed macromolecules and then with the rare earth europium) and other reagents were used as received without further purification.

2.2. Preparation and characterization of D-HEA

DBM (14.2 g, 0.063 mol) was added into a three-necked flask which equipped with a magnetic stirrer, dissolving 80 ml of CH_2Cl_2 . HEA (14.3 g, 0.123 mol) and the catalyst $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.6 g) were dissolved in 100 ml of CH_2Cl_2 , then dripped them into the DMB solution gradually. After reaction at 60 °C for 8 h, washed the mixture by distilled water for four times first, and then washed by ethanol. Subsequently, dried the mixture over anhydrous sodium sulfate and kept it overnight. After that, the CH_2Cl_2 solvent was made to product of D-HEA by Rotary evaporation. The FT-IR spectra were carried out with Nicolet 5700 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded on an AVANCE III instrument Bruker company in CDCl_3 . All signals of the various protons were observed.

2.3. Preparation and characterization of polymer D-HEA-C

A representative procedure was proposed. Added D-HEA (10.06 g) and caprolactone (16.9 g) to a dried flask (it needs to be pointed out that the molar ratio of D-HEA to caprolactone was 1:10). Filled nitrogen into the flask and added 25 ml solution of BNPH into it. Mixing all of them to be reactive under 80 °C for 24 h. Cooled down the reaction mixture, precipitated it with 300 ml cold MeOH as precipitators. The product was collected on a fine frit, and dissolved in 80 ml of CH_2Cl_2 . Washed the mixture with additional cold distilled ion, got the product of D-HEA-C as a red-brown viscous liquid by rotary evaporation.

2.4. Preparation and characterization of polymeric rare earth complexes D-HEA-C–Eu(III)

Eu_2O_3 (0.352 g) was dissolved in 100 ml of 20% HCl solution, and heated until transparent. Then, the solution was cooled down, and 25 ml of distilled water was added. After completely dissolving, the content was heated and concentrated until crystalline grains were produced and a lot of crystals were separated out. Then placed the crystals in a vacuum oven at 25 °C, obtained the crystals of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The modified D-HEA-C was dissolved in 80 ml of N, N-dimethyl formamide (DMF), and the pH value was adjusted to 6–7 by triethylamine. Subsequently, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was added, and the coordination reaction between β -diketones of D-HEA-C and the ligand Eu^{3+} ion was conducted for 24 h at 60 °C with stirring (it is to be noted here, the molar ratio of the β -diketone ligand D-HEA-C to Eu^{3+} ion was 3:1 in the above coordination system, so the coordination reaction could be carried out smoothly). After finishing the coordination reaction

between β -diketones contained D-HEA-C and Eu^{3+} ion, the crude product was dripped into cold methanol (200 ml) and stirred. The mixture was centrifuged. The supernatant was decanted, and the remained solid was washed with cold methanol (100 ml) and dried to get D-HEA-C-Eu(III) as white powders. The molecular weight of the copolymer was determined by RID-10 gel permeation chromatography, using THF as an eluent. UV-vis spectra were recorded on a 3010UV spectrophotometer (Hitachi Co., Japan). The PL measurements were conducted in a 5301 fluorescence spectrophotometer. ICP was used to test the content of europium. Lanthanide complexes were dissolved in hydrochloric acid after calcinations.

2.5. Preparation and characterization of EVA films

The EVA pellets (0.5 g) were dissolved in 80 ml of chloroform followed by adding 1% (w/w%) of D-HEA-C-Eu(III) complex (0.005 g) which was also dissolved in chloroform. After blending, equal amounts of the solution were kept in the covered Petri dishes of the same dimension to keep the thickness for all the complexes approximately the same. The resulting solution was kept in a vacuum oven at 60 °C overnight, and then the polymer film (denoted as 1% Eu/EVA film) was obtained after the evaporation of excess solvent at 60 °C. TGA was achieved with a TG 209 F3 thermobalance (Mettler-toledo). Transmittance was recorded on a 3010UV spectrophotometer (Hitachi Co., Japan). The PL measurements were conducted in a 5301 fluorescence spectrophotometer. Photoelectric conversion efficiency was recorded by Keithley 2400 through a silicon solar cell. SEM was observed in a microscope SUPRA55 by a means of sputtering technique using N_2 crisp paragraph.

3. Results and discussion

3.1. Preparation and characterization of D-HEA-C-Eu(III) complex

Michael addition reaction between DBM and HEA was used to produce diketones contained primary alcohol groups, which acted as initiator for the ring opening polymerization of caprolactone (in Scheme 1). Subsequently, the macroligands were produced by continued ring opening polymerization of caprolactone [20]. The coordination reaction between the macromolecular ligand D-HEA and Eu^{3+} ion was carried out in a solution with DMF as solvent, obtained the solution containing polymeric rare earth complex materials D-HEA-C-Eu(III), and finally the complex was precipitated from the solution by using cold methanol as precipitator. The chemical process of preparing the functional polymer D-HEA-C as well as the complex D-HEA-C-Eu(III) was expressed schematically in Scheme 1.

Although ϵ -caprolactone polymerizations with DBM initiators were not strictly living, it was still possible to prepare macroligands with low PDIs and monomodal GPC traces for use in coordination reaction with careful selection of reaction condition. The molecular weight and molecular weight distribution of resulting macroligands D-HEA-C were analyzed by GPC. The data ($M_n = 3465$,

$M_w = 3645$, $M_w/M_n = 1.052$) displayed a very low PDI of the obtained macroligands.

3.2. Characterization of D-HEA-C and D-HEA-C-Eu(III)

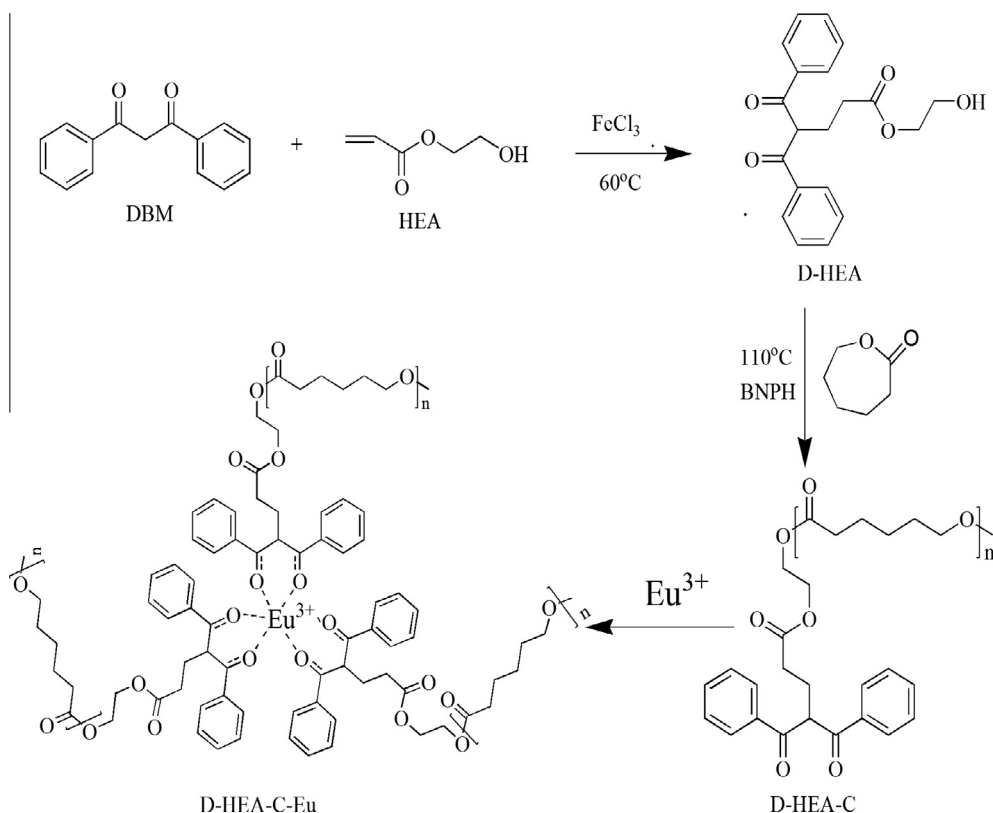
3.2.1. ^1H NMR spectrum

As shown in Fig. 1, diketones resonances from D-HEA-C were clearly evident in the ^1H NMR spectrum. The resonance absorption peak of various protons in the bonded phenyl ring was clearly displayed: $\delta 7.53$ – 8.02 ppm (8H, benzene). The $-\text{CH}_2-$ protons of the caprolactone absorption peaks also appeared [$\delta 4.08$ – 4.11 ppm (2H, h- CH_2), $\delta 2.29$ – 2.31 ppm (2H, i- CH_2), $\delta 1.59$ – 1.62 ppm (2H, j- CH_2), $\delta 1.39$ – 1.42 ppm (2H, k- CH_2)] and their apparent absorption intensity suggested the ring-opening reaction of caprolactone. At the same time, the resonance absorption peak of the protons in the double bond of HEA [$\delta 6.46$ ppm (1H, C=C), $\delta 6.24$ ppm (1H, C=C), $\delta 5.84$ ppm (1H, C=C)] disappeared, which further verified Michael addition reaction between HEA and DBM. The resonance absorption peaks of other protons were as follows: $\delta 6.82$ – 6.85 ppm (1H, c-CH), $\delta 2.59$ – 2.62 ppm (2H, d- CH_2), $\delta 2.42$ – 2.45 ppm (2H, e- CH_2), $\delta 4.32$ – 4.35 ppm (2H, f- CH_2), $\delta 3.65$ – 3.688 ppm (2H, g- CH_2).

3.2.2. Fourier transmission infrared spectra

The infrared spectra of HEA, D-HEA and D-HEA-C-Eu(III) are presented in Fig. 2. In the spectrum of HEA, all characteristic absorption bands of HEA were displayed. The band at 1630 cm^{-1} was attributed to the stretching vibration absorption of double bond ($-\text{C}=\text{C}-$), and the band at 811 cm^{-1} was ascribed to the bending vibration absorption of double bond. The stretching vibration absorption of $-\text{OH}$ group at 3440 cm^{-1} was also observed. In the spectrum of D-HEA, the band of double bond ($-\text{C}=\text{C}-$) at 1630 cm^{-1} and 811 cm^{-1} disappeared, while two new absorption bands at 1694 cm^{-1} and 1671 cm^{-1} were observed, which were assigned to the stretching vibration absorption of the carbonyl group $-\text{C}=\text{O}$ from DBM. At the same time, the bands at 1580 cm^{-1} , 1448 cm^{-1} and 1407 cm^{-1} were corresponding to the characteristic absorption of benzene ring, which confirmed the result of the Michael addition reaction between HEA and DBM, indicating HEA had been bonded onto DBM.

According to the spectrum of D-HEA-C-Eu(III), the stretching vibration absorption of methylene at 2940 cm^{-1} and 2840 cm^{-1} were strengthened greatly. However, the stretching vibration absorption of the carbonyl group $\text{C}=\text{O}$ from caprolactone at 1730 cm^{-1} and the stretching vibration absorption of $-\text{OH}$ group at 3440 cm^{-1} were not changed, indicated these groups did not participate in the coordination to Eu^{3+} ion. On the other hand, the bands at 1694 cm^{-1} and 1671 cm^{-1} had been weakened severely, implied that the carbonyl group $\text{C}=\text{O}$ from DBM converted diketo form into enol form, which further verified that the group had participated in the coordination to Eu^{3+} ion. Besides, the band at 460 cm^{-1} might be ascribed to the stretching vibration absorption of $\text{Eu}-\text{O}$ bond. The facts above showed that the ligand β -diketones in the chain end of D-HEA-C had coordinated to Eu^{3+} ion in a bidentate coordination form, formed the polymeric



Scheme 1. Schematic expression of chemical process of complex D-HEA-C-Eu(III).

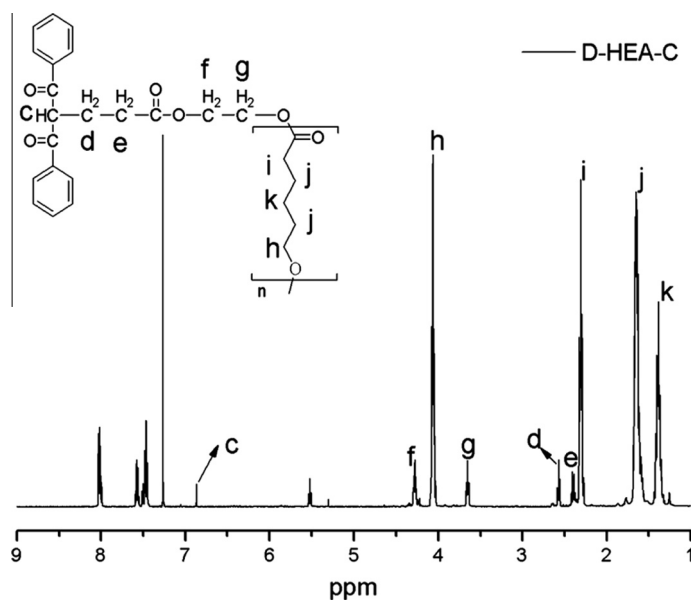


Fig. 1. ^1H NMR spectra of D-HEA-C.

rare earth complex materials D-HEA-C-Eu(III). Besides, the coordinated content of Eu^{3+} was determined by ICP, with a content of about 1.57%.

3.2.3. UV absorption spectra of D-HEA-C and complex

Fig. 3 shows the UV absorption spectra of D-HEA-C and D-HEA-C-Eu(III). In the spectrum of D-HEA-C, there were

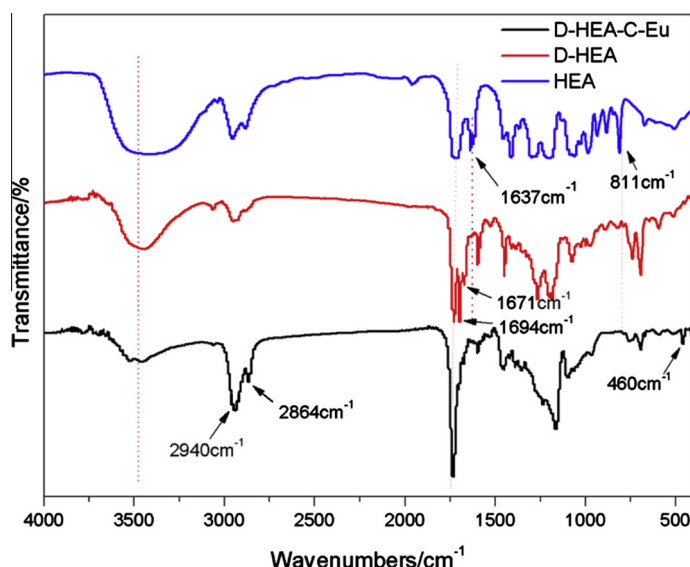


Fig. 2. FTIR spectra of HEA, D-HEA and D-HEA-C-Eu(III).

two strong absorption peaks at 246 nm and 340 nm. The former might be attributed to the absorption of DBM-keto isomer, and the latter could be attributed to DBM-enol isomer absorption [21]. The spectrum of D-HEA-C-Eu(III) had similar peaks to D-HEA-C, implied that the UV absorptions of the complexes came from the D-HEA-C. Besides, the band of long wavelength showed an obvious bathochromic shift (from 340 nm to 358 nm) relative to their free ligand and the absorption was strengthened significantly, while the absorption peak at 246 nm was observed as a shoulder with lower intensity. The absorption shift and intensity variation in the spectrum of the D-HEA-C and D-HEA-C-Eu(III) originated from the metalation which can readily covert diketo form into enol form, increased the conjugation and delocalization of the whole electronic system and led to the energy change of the $\pi \rightarrow \pi^*$ transition of the conjugated chromophore [22]. According

to the strong absorption of the compounds in near ultraviolet region, these bands cannot come from f–f or f–d electron transition of the rare earth ions, which were generally too weak and could be covered up easily, but probably raised from the energy change of the intense transitions of the conjugated chromophore due to the chelation between metal ions and D-HEA-C.

3.2.4. Fluorescence excitation and emission spectra of complex

The fluorescence emission spectrum of D-HEA-C-Eu(III) in DMF solution was obtained by monitoring the emission of Eu^{3+} ion at 616 nm, and 375 nm was found to be the optimal excitation wavelength. The fluorescence emission spectrum of EuCl_3 in DMF solution was also determined. It needs to be pointed out that the concentrations of Eu^{3+} ion in the two solutions were identical, and they were 3.01×10^{-4} mol/l. Results are presented in Fig. 4. The

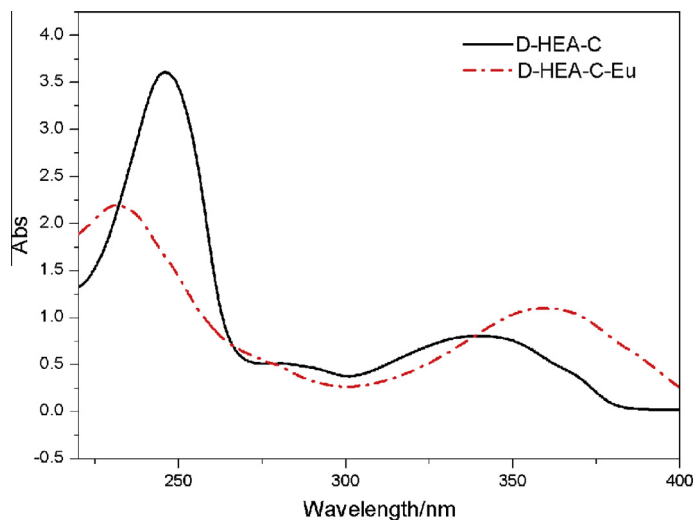


Fig. 3. UV absorption spectra of D-HEA-C and D-HEA-C-Eu(III), solvent: DMF.

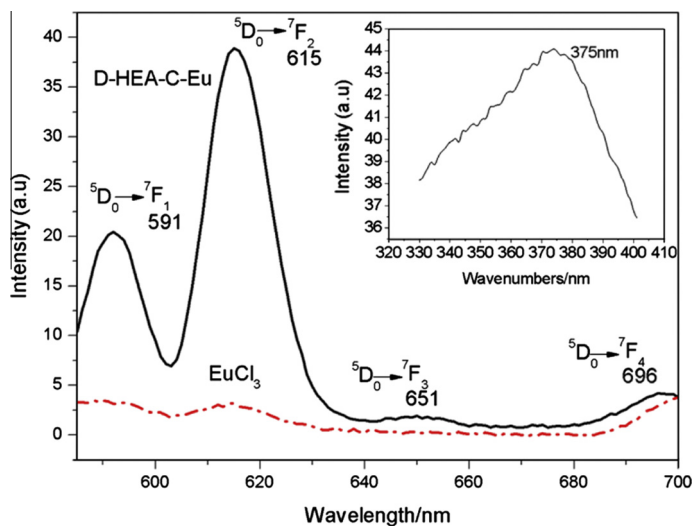


Fig. 4. Excitation (330–400 nm) and emission (570–700 nm) spectra of D-HEA-C-Eu(III) and EuCl_3 , solvent: DMF; the concentrations of Eu^{3+} ion were 3.01×10^{-4} mol/l.

emission spectrum of D-HEA-C-Eu(III) was similar to that of EuCl_3 in spectrum shape and band positions, implying that the complex D-HEA-C-Eu(III) emitted the characteristic fluorescence of Eu^{3+} ion. The spectrum of D-HEA-C-Eu(III) displayed two main emission peaks at 591 nm and 615 nm. The former was assigned to the transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_1$, and the latter was ascribed to the transitions of $^5\text{D}_0 \rightarrow ^7\text{F}_2$. Under the condition of this investigation, molar ratio of β -diketones ligand D-HEA-C to Eu^{3+} ion was 3:1, the fluorescence emission intensity of the complex D-HEA-C-Eu(III) was far more stronger, about 8 times higher than that of EuCl_3 .

It is well known that Eu(III) ion has a low extinction coefficient. The above results showed that the macromolecular ligand D-HEA-C obviously sensitized the fluorescence emission of Eu(III) ion, and the macromolecular ligand D-HEA-C coordinated to the Eu^{3+} ion, namely an apparent “Antenna Effect” has been produced, resulted in the strong characteristic fluorescence emission of Eu^{3+} in the D-HEA-C-Eu(III) complex [2].

3.3. Analysis of EVA film doped with rare earth complex

3.3.1. Thermal gravimetric analysis

Fig. 5 shows the thermogravimetric curves of D-HEA-C-Eu(III), $\text{Eu}(\text{DBM-d})_3$, PAA-Eu, undoped EVA polymer and EVA doped with the D-HEA-C-Eu(III) complex at a ratio of 1% under an inert N_2 atmosphere. As can be seen in inset of Fig. 5, in the range of 120–200 °C, the small molecular lanthanide complex $\text{Eu}(\text{DBM-d})_3$ and the linear homopolymeric lanthanide complex PAA-Eu exhibited had apparent weight loss which was caused by the vaporization of the coordinated solvent molecules (DMF) resulted from low coordination efficiency. While for the macromolecular complex D-HEA-C-Eu(III), no apparent weight loss occurred, indicated a higher coordination efficiency than $\text{Eu}(\text{DBM-d})_3$ and PAA-Eu.

Besides, the TGA curves of undoped and doped EVA films recorded in the temperature interval from 120 °C to 200 °C showed no mass loss. The fact revealed that the solvent molecules coordinated to the Eu^{3+} ion of the hydrate precursor complex were absent after the doping reaction. Therefore, the D-HEA-C-Eu(III) complex was embedded in the EVA polymer matrix by the chemical interaction between the Eu^{3+} complex and the oxygen atoms of the EVA polymer. These results agreed with other polymer systems previously analyzed [7,23]. It was also shown in Fig. 5 that the undoped EVA polymer film decomposed in a two-step event and its degradation occurred at about 354 °C and 467 °C. Similarly, the EVA films doped with Eu^{3+} complex also presented a curve of decomposition under an inert atmosphere with two decomposition events. The TGA curves of EVA films also indicated EVA doped with the Eu^{3+} complex at a doping ratio of 1% had no significant effect on the thermodynamic properties of EVA film.

3.3.2. Transmittance of EVA films

Fig. 6 gives transmittance of EVA films as a function of D-HEA-C-Eu(III) content. The results showed that the absorption of EVA film in the UV region was significantly increased with the addition of light conversion agent D-HEA-C-Eu(III). In particular, UV absorption around 350 nm was pronounced, which was due to the light conversion agent ligand D-HEA-C. The use of D-HEA-C-Eu(III) can improve the UV resistance of EVA film. Moreover, the solar battery can also be switched to use the red region of the ultraviolet light, thus improving energy conversion efficiency of the solar cell. The visible light transmittance of EVA films decreased slightly with the addition light conversion agent. When the light conversion agent was added in quantities of 1% or less, the film transmittance of visible light region did not change significantly, mainly because the following two aspects: First, the addition content of D-HEA-C-Eu(III) EVA film was relatively low, second, the compatibility of caprolactone modified ligand with EVA

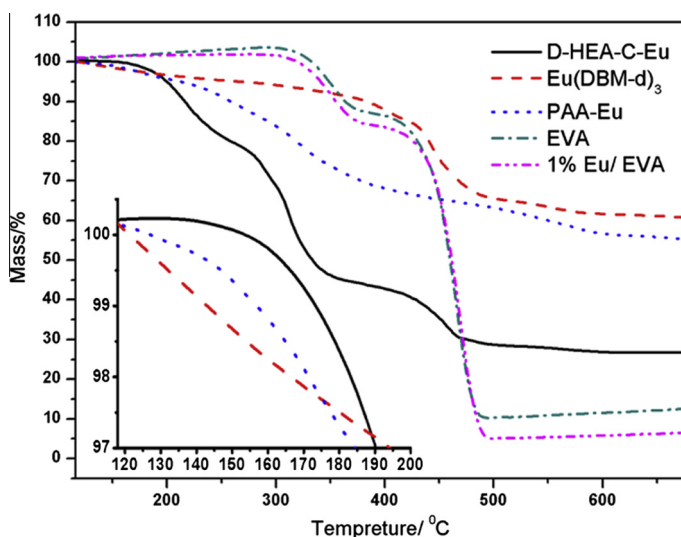


Fig. 5. TGA curves of D-HEA-C-Eu(III), Eu (DBM-d)₃, PAA-Eu, undoped EVA film and 1% Eu/EVA film. All these data were recorded under an inert atmosphere of dynamic N₂.

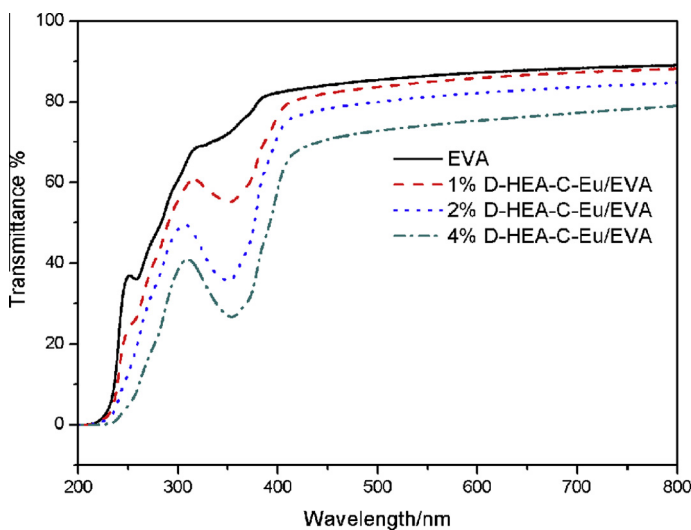


Fig. 6. Transmittance of EVA film as a function of D-HEA-C-Eu(III) content.

film was good (as can be seen in SEM images). However when the content of D-HEA-C-Eu(III) was greater than 1%, the visible light transmittance of EVA film decreased significantly, which would affect the absorption and utilization of visible solar panels. This was mainly because the agglomeration affect of light conversion agent as the added amount increased. Therefore, the appropriate amount of D-HEA-C-Eu(III) was about 1%.

3.3.3. Fluorescence excitation and emission spectra of EVA films

The inset of Fig. 7 presents the excitation spectra of the 1% Eu/EVA, 2% Eu/EVA, and 4% Eu/EVA blend films registered at room temperature by monitoring the luminescence intensity of the $^5D_0 \rightarrow ^7F_2$ transitions at 616 nm. It

is observed that in the spectral region from 320 to 550 nm, the blend films exhibit two intense broad excitation bands at about 370 nm and 465 nm, which can be attributed to transitions from the S_0 ground state to the S_1 excited state of the organic moiety. Furthermore, the typical intraconfigurational transitions of the trivalent europium ion exhibit very low intensity in these excitation spectra, corroborated with an efficient energy transfer from the organic moiety to the metal ion. These data suggested that the polymer matrices acted as luminescent co-sensitizers and the organic ligands were efficient sensitizers for the Eu^{3+} ions.

Fig. 7 also displays the emission spectra of the 1% Eu/EVA, 2% Eu/EVA, and 4% Eu/EVA blend films registered at room temperature under excitation at 394 nm in the

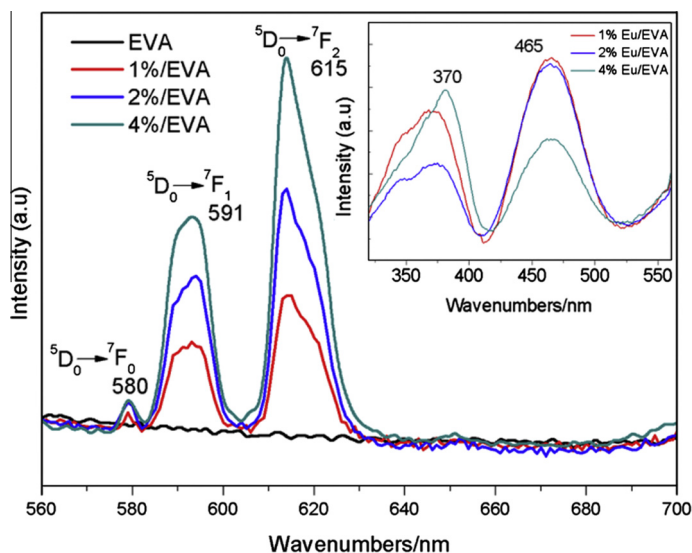


Fig. 7. Excitation (320–550 nm) and emission (560–700 nm) spectra of 1% Eu/EVA, 2% Eu/EVA, and 4% Eu/EVA blend films.

spectral range of 450–720 nm. These spectroscopic data exhibit the typical emission narrow bands assigned to the characteristic $^5D_0 \rightarrow ^7F_J$ transitions ($J = 0-4$) of the Eu^{3+} ion. The transitions displayed that the highest intensity was the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition at around 615 nm. In addition, the only sharp peak of the non-degenerate $^5D_0 \rightarrow ^7F_0$ transition at around 580 nm reveals a chemical environment around the Eu^{3+} ion of symmetry Cs, Cn or Cnv. The absence of the polymer broad emission band in the doped film in the range of 450–550 nm

presented the high efficiency of the intra molecular energy transfer process via the polymer matrix to the Eu^{3+} ion, corroborated the interpretation in which the polymer matrix acted as an efficient co-sensitizer of the Eu^{3+} photoluminescence [24,25]. Meanwhile, europium complexes with increasing amounts of dopant increased the film fluorescence intensity, indicated an increase of sensitizing effect. Further evidence of such lanthanide complexes also can be well applied in respect of EVA film as the light conversion agent.

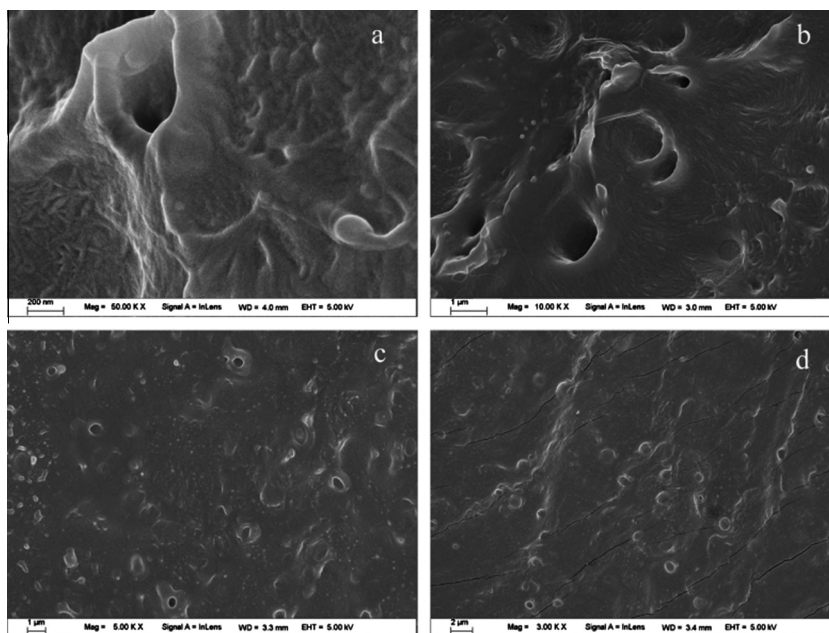


Fig. 8. SEM images of (a) $\text{Eu}(\text{DBM-d})_3$ small molecule lanthanide complexes doped into EVA film. (b, c and d) D-HEA-C-Eu macromolecular lanthanide complexes doped into EVA film with the amount of. (b) 1% D-HEA-C-Eu, (c) 2% D-HEA-C-Eu and (d) 4% D-HEA-C-Eu.

Table 1

Energy exchange efficiency of solar cell as a function of fluoresces content.

Sample	J_{sc} (mA)	V_{oc} (V)	FF ^a	Eff ^b (%)
EVA	29.96	0.5757	0.5037	8.688
1% Eu/EVA	29.71	0.5758	0.5267	9.010
2% Eu/EVA	28.96	0.5758	0.5095	8.494
4% Eu/EVA	28.35	0.5758	0.4925	8.040

^a $FF = P_{max}/J_{sc} * V_{oc}$.^b $Eff = P_{max}/P_{in}$.^c Illumination area: 4 cm² and illumination power: 100 mW/m².

3.3.4. Scanning Electronic Microscope (SEM) analysis of particles compatibility

The surface morphology of different EVA films was observed by Scanning Electronic Microscope (SEM) (Fig. 8a–d). When EVA film was co-doped with the rare earth complexes, the resulting films showed a uniform porous structure. As shown in Fig. 8a, the small molecules doped rare earth complexes of EVA film substrate interface significantly higher than macromolecular lanthanide complexes doped EVA film in Fig. 8b–d. No significant phase separation was observed within the obtained blend EVA films doped with the macromolecular Eu³⁺ complex, indicating that the framework on the surface was homogeneous. This is possibly due to the compatibility of caprolactone modified ligand with EVA film becomes better, through which all the compositions are mixed at a molecular level, indicating the occurrence of interaction between the Eu³⁺ complex and polymer matrix [26–28]. At the same time, Fig. 8b–d also showed that the compatibility of macromolecular lanthanide complexes became worse with the amount of complexes increased to 4%, which also suggesting a suitable adding amount of D-HEA-C-Eu(III) of 1%, in agreement with energy conversion efficiency test.

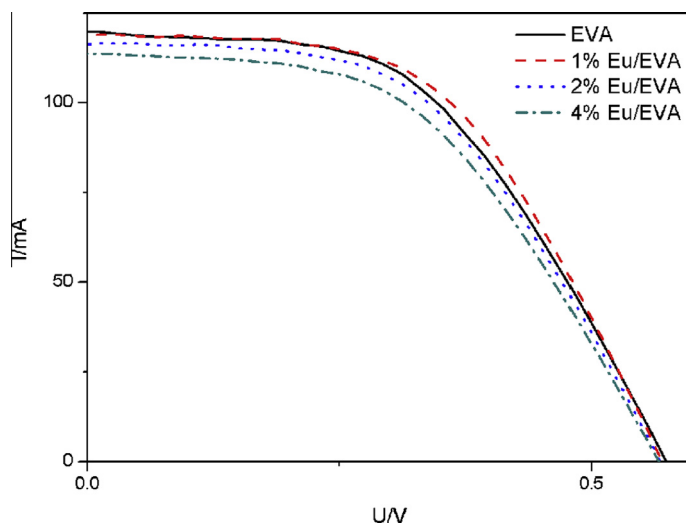
3.3.5. Energy conversion efficiency of solar cell

As shown in Table 1 and Fig. 9, the energy conversion efficiency of the solar cell is not regular with the increase

of light conversion agent content. When 1% complex was added in EVA film, the energy conversion efficiency increased from 8.688% to 9.010%, displaying an impressive improvement of nearly 0.31%. As can be inferred from the results, when the transfer agent was added the light transmittance of the film should be decreased, but actually it was increased, which might because the energy conversion efficiency played the dominating role. However, when the addition amount exceeded 1%, the energy conversion efficiency of solar cell decreased, which was due to the light transmittance of film decreased significantly with the increase of complex amount, thereby affecting film transmittance dominant factor, which was agree with the transmittance tests. Because the testing process was only covering the film on the surface of the solar cell, and did not follow the normal packaging process into solar cells, the test results were only doing relative comparisons. All the results suggest the most suitable amount of D-HEA-C-Eu(III) in EVA film is 1% or less.

4. Conclusions

In this study, the polymeric rare earth complexes D-HEA-C-Eu(III) were prepared, characterized and doped into EVA films to test the energy conversion efficiency. The fluorescence excitation spectrum of D-HEA-C-Eu(III) showed that the energy level of the triplet state in β -diketones of D-HEA-C might be better matched with the energy level of the lowest excitation state of Eu³⁺ ion based on the theory of antenna, which was an essential condition for an effective intra molecular energy transfer. So the complex not only played the role of a stabilizer and UV absorber, but also played the role of light conversion agent. The thermal behavior of EVA films doped with D-HEA-C-Eu(III) and undoped EVA film was similar. Transmittance (200–800 nm) proved the appropriate amount of D-HEA-C-Eu(III) in EVA film was less than 1%. The absence of the broad emission band of the polymer in the doped system indicated that intra molecular energy transfer via the

**Fig. 9.** Energy exchange efficiency of solar cell as a function of fluoresces content.

EVA polymer matrix to the Eu^{3+} ion was highly efficient, suggested that the EVA polymer matrix also acted as a photoluminescence co-sensitizer. In addition, the higher values of emission quantum efficiency of the emitting $^5\text{D}_0$ level for the doped polymer films corroborated with the substitution of water molecules by the polymer carbonyl groups. The photoelectric conversion efficiency spectra of EVA films further confirmed the suitable amount of D-HEA-C-Eu(III) added was less than 1%, with an improvement of EVA film photoelectric conversion efficiency of 0.32%. SEM also showed that rare earth complexes had good compatibility with the matrix macromolecules. Therefore, the β -diketones macromolecular lanthanide complexes could act as efficient light conversion molecular devices, and have a broad prospect in the solar packaging film.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (21304011), Science and Technology Support Plan of Changzhou (CE20130070) and a project funded by the priority academic program development of Jiang Su higher education institutions for their financial support.

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