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Effect of Electron-donating Substituent Groups on Aromatic Ring on Photoluminescence Property of Complexes of Benzoic Acid -Functionalized Polysulfone with Eu(Ⅲ) ion

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Abstract By molecular design and via polymer reactions, methoxybenzoic acid (MOBA) and hydroxybenzoic acid (HBA) were bonded onto the side chains of polysulfone (PSF), preparing two benzoic acid-functionalized PSFs, PSF-MOBA and PSF-HBA, respectively. On the basis of fully characterizing their structures, the two macromolecule ligands were made to coordinate to Eu^{3+} ion, and two binary polymer-rare earth complexes, PSF-$(MOBA)_3$-Eu(Ⅲ) and PSF-$(HBA)_3$-Eu(Ⅲ), were obtained. At the same time, using phenanthroline (Phen) as the second small-molecule ligand, the corresponding two ternary complexes, PSF-$(MOBA)_3$-Eu(Ⅲ)-$Phen_1$ and PSF-$(HBA)_3$-Eu(Ⅲ)- $Phen_1$, were also prepared. The photo physical behaviors of theses complexes were examined in depth, and the luminescent properties of these prepared polymer-rare earth complexes were mainly investigated. The experimental results show that the two electron-donating substituent groups on the aromatic ring of the bonded benzoic acid significantly affect the luminescence properties of these complexes of benzoic acid-functionalized PSF and Eu(Ⅲ) ion, and they can effectively strengthen the fluorescence emission intensities of the complexes. The possible reason is that through p-π conjugative effect, the two electron-donating substituent groups can remarkably decline the triplet state energy levels of the bonded ligand MOBA and HBA, and strengthen the matching degree of energy between the triplet state energy level of the ligand and the resonant energy level of Eu(III) ion to be strengthened, resulting in the enhancement of fluorescence emission intensities of the complexes. Besides, the fluorescence emissions of the binary complexes are stronger than that of the corresponding ternary complexes because of the synergistic coordination effect of Phen with the macromolecular ligand.

Keywords Polysulfone, Benzoic acid, Electron-donating substituent groups, Eu(Ⅲ) ion, Polymer-rare earth complex, Photoluminescence

1. Introduction

Photoluminescence rare earth metal complexes are a class of important luminescent materials, and they have attracted much attention due to their unique photo-physical features such as narrow emission bands, large stokes shift, and long luminescence decay time [1-4]. They are used in many technology fields, including organic electroluminescent devices, photoluminescence materials in display devices, chemical and biological sensors, laser, and so on [5-8]. Usually, organic small-molecule-rare earth complexes are used by simply doping them into matrixes, and there are some major limitations to their practical applications, such as their poor mechanical property, poor physicochemical stability, harsh processability and incompatibility with the matrixes [9,10]. In contrast, luminescent rare earth-polymers with bonding type, namely polymer-rare earth complexes, in whose structure, lanthanide ions are directly coordinated with the functional pendant groups of polymers, not only possess special fluorescence properties of the rare earth ions, but also have good mechanical toughness, chemical stability, and excellent processability of polymers [11-14], and furthermore, their interior exhibits a character of homogeneous phase. Therefore, polymer-rare earth complexes are a kind of luminescent materials with high performance. Especially in designing and fabricating electroluminescent devices, the polymer-rare earth complexes display some significant advantages [13,14]. Although at present there are still few reports on luminescent polymer-rare earth complexes, their development prospect is bright. Polysulfone (PSF) is an aromatic thermoplastic polymer with good mechanical property, excellent thermal stability, strong chemical stability and good processing property [15,16], especially excellent film-forming property [17,18], so it is suitable to use PSF as the framework material of polymer-rare earth complexes. In our previous study, two aryl carboxylic acids, benzoic acid and naphthoic acid, which have dual functions of coordination action and sensitization towards rare earth ions, were chemically attached to the side chain of PSF, and the macromolecular ligands that could strongly sensitize the fluorescence of rare earth ions were prepared. Finally some luminescent polymer-rare earth complexes with high performance were obtained [19,20].

For the small molecular aryl carboxylic acid-rare earth complexes, aromatic ring structure itself such as benzene ring or naphthalene ring can strongly affect the matching degree between the triplet state energies of organic ligands and the resonant energy levels of rare earth ions, influencing the luminescent property of the small molecule aryl carboxylic acid-rare earth complexes [21,22]. On the other hand, the substituent groups including their type and position on the aromatic ring of the aryl carboxylic acids also can produce a significant influence on the matching degree of the energy levels [23,24] so that they can obviously influence the luminescent property of the aryl carboxylic acid-rare earth complexes. In view of this, in the present work, we bonded two benzoic acid derivatives, on whose benzene rings an electron-donating substituent group, methoxy group or hydroxy group, is contained, to the side chains of PSF, respectively, and prepared some luminescent binary and ternary polymer-rare earth complexes. The effects of the two electron-donating substituent groups on the benzene ring of benzoic acid on the luminescent properties of theses polymer-rare earth complexes were investigated in depth. The matching degree of energy between the triplet state energy of benzoic acid itself and the resonant energy level of Eu^{3+} ion is poor, so the sensitization of small molecule benzoic acid towards the fluorescence emission of Eu^{3+} ion is weaker [25,26]. However, if there is an electron-donating substituent group on the benzene ring of benzoic acid, the triplet state energy of the bond benzoic acid may be changed and declined, and the energy matching degree may be obviously enhanced, resulting in a remarkable enhancement of the fluorescence emission intensity of the polymer-rare earth complexes. This is what we want to probe in this study. There is no report about the effect of the substituent group on the aryl ring on the luminescent property of aryl carboxylic acid-functionalized polymer-rare earth complexes. The result of this study has certain theoretical reference value for exploring the relationship between the structure and luminescent property of polymer-rare earth complexes, and it is also significant for designing and preparing photoluminescence polymer-rare earth complexes with high luminescent intensity.

2. Experimental

2.1. Materials and instrument

Polysulfone (PSF, $\bar{M}_r = 67000$) was of industrial grade and obtained from Shuguang Chemical Plant of Shanghai Plastic Industry Associated Company (China). Chloromethylated polysulfone (CMPSF) was self-synthesized with 1,4-bis (chloromethoxy) butane (BCMB) as chloromethylation reagent [27]. P-hydroxybenzoic acid (HBA), 4-Hydroxy-3-methoxybenzoic acid (HMOBA) and 3,4-Dihydroxybenzoic acid (DHBA) were all purchased from Shijiazhuang Henda Chemical Co., Ltd.(China). N,N-Dimethyl formamide (DMF) was supplied by Tientsin University Chemical Reagent Plant (China). Triethylamine (TEA) was obtained from Tientsin Tianli Chemical Reagent Beijing Co., Ltd. (China). Europium oxide (Eu_2O_3) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (China). 1, 10-Phenanthroline (Phen) was purchased from Shanghai Haoren Biotechnology Co., Ltd. (China). Other chemicals were all commercial reagents with analytical pure grade and were purchased from Chinese companies.

The instruments used in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, USA), Unic UV/Vis-2602 spectrophotometer (Unic Company, USA), DRX300 nuclear magnetic resonance spectrometer (Bruker Company, Switzerland) and HITACHI F-2500 fluophotometer (HITACHI Company, Japan).

2.2. Preparation and characterization of two functionalized PSF, PSF-MOBA and PSF-HBA

2.2.1 Preparation of chloromethylated PSF

According to the procedure described in Ref. [20], PSF was chloromethylated with BCMB as reagent, and the main process is briefly described as follows. PSF was dissolved in dichloromethane followed by adding Lewis acid catalyst, $SnCl_4$, and the chloromethylation reagent BCMB was added by dripping slowly from the dropping funnel. The chloromethylation reaction was carried out at room temperature for 8 h. Finally, the reaction solution was treated with diluted hydrochloric acid, and then the product polymer was precipitated with ethanol as precipitator. By washing and drying, the chloromethylated PSF, CMPSF, was obtained. The chloromethylation degree (mmol/g) of CMPSF, i.e. chlorine content, was determined by combustion-Volhard titration method, and CMPSF prepared in this study has a chlorine content of 1.75mmol/g.

2.2.2 Preparation of PSF-MOBA and PSF-HBA

Two benzoic acid derivatives, on whose benzene ring electron-donating substituent group, methoxy group or hydroxy group, is contained, were bound to the side chains of PSF, and two functionalized PSFs, PSF-MOBA and PSF-HBA, were obtained. The main procedure is described as follows by taking PSF-MOBA as example. DMF (50 mL) and CMPSF (0.5 g) were added into a four-necked flask equipped with a mechanical agitator, a reflux condenser and a thermometer, and CMPSF was allowed to be fully dissolved into the solvent, followed by adding 0.135 g of HMOBA and 0.45 mL of TEA as acid binding-agent. The nucleophilic substitution reaction between HMOBA and CMPSF was allowed to be conducted at 70 ℃ for 8 h with stirring. After finishing the reaction, 5 mL of HCl solution of 6M was added to acidify the solution, and the polymer was precipitated with ethanol as precipitator. The product polymer was separated out by filtering, and was washed alternately with ethanol and distilled water. By drying under vacuum, the obtained polymer was namely functionalized PSF, PSF-MOBA, in whose structure, methoxybenzoic acid as a derivative of benzoic acid was bond onto the side chain of PSF. The bonding amount (mmol/g) of MOBA group on PSF-MOBA was determined indirectly by ultraviolet spectrophotometry [20], and the PSF-MOBA prepared in this work has a MOBA bonding amount of 1.64mmol·g^{-1}. Another functionalized PSF, PSF-HBA, in whose structure, hydroxybenzoic acid as a derivative of benzoic acid was bond on to the side chain of PSF, was prepared using the same procedure, only the used reaction reagent was DHBA. The HBA bonding amount of PSF-HBA was equal to 1.68 mmol/g. For comparison, benzoic acid-functionalized PSF, PSF-BA, was also prepared with p-hydroxybenzoic acid as reagent.

2.2.3 Characterization of PSF-MOBA and PSF-HBA

The bonding amounts of MOBA and HBA groups on PSF-MOBA and PSF-HBA were determined as described above. The infrared spectra of PSF-MOBA and PSF-HBA were determined by KBr pellet method to characterize their structures. ^{1}H-NMR spectra of PSF-MOBA and PSF-HBA were recorded with deuterated chloroform ($CHCl_3$) as solvent to further confirm their structures, and the detailed data can be seen from the following nuclear magnetic resonance spectra.

2.3. Preparation and characterization of polymer-rare earth complexes

2.3.1. Preparation of binary polymer-rare earth complexes

Eu_2O_3 was dissolved in an aqueous solution of HCl (V/V=1:1). After evaporating the solution, the crystal of $EuCl_3 \cdot 6H_2O$ was separated out and obtained. The functionalized polymer PSF-MOBA (0.2 g) weighted accurately, in which 0.328 mmol of MOBA group was contained, was dissolved in 50 mL of DMF, and the pH value was adjusted to 6-7 with diluted NaOH solution. Subsequently, $EuCl_3 \cdot 6H_2O$ (0.04 g, 0.109 mmol) was added and gradually dissolved in the solution. Here in the solution, the molar ratio of the ligand of MOBA to Eu^{3+} ion was 3:1. The coordination reaction between PSF-MOBA and Eu^{3+} ion was conducted for 8 h at 50 ℃ with stirring. After finishing the reaction, the product was precipitated out with ethanol as precipitator, washed with ethanol and distilled water, and dried under vacuum. The resultant product was namely the first binary polymer-rare earth complex PSF-$(MOBA)_3$-Eu(Ⅲ).

With the same procedure, the second binary polymer-rare earth complex PSF-$(HBA)_3$-Eu(Ⅲ) was prepared, and merely the used functional macromolecular was PSF-HBA. Besides, for comparison, the third binary polymer-rare earth complex PSF-$(BA)_3$-Eu(Ⅲ) was also prepared with PSF-BA as functional polymer.

PSF has excellent film-forming property, and it leads to that the polymer-rare earth complexes prepared with PSF as polymer skeleton are also easy to form thin film. This advantage provides much convenience for the applications of these polymer-rare earth complexes. In this investigation, the solid films of the binary complexes as well as the following ternary complexes were prepared by using casting method, and the films are 60 μm thick.

2.3.2. Preparation of ternary polymer-rare earth complexes

By using Phen as small-molecule co-ligands and by controlling the molar ratio of various species including center ion, ligands bonded onto the side chains of the functionalized PSF and small-molecule ligand Phen, three ternary polymer-rare earth complexes, PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$, PSF-$(HBA)_3$-Eu(Ⅲ)-$(Phen)_1$and PSF-$(BA)_3$-Eu(Ⅲ) -$(Phen)_1$were prepared, respectively. Taking the ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$as an example, the preparation process are explained as follows. PSF-MOBA (0.5 g) weighted accurately, in which 0.81 mmol of MOBA ligand was contained, was dissolved in 100 mL of DMF, and the pH value was adjusted to 6-7 with diluted NaOH solution. And then accurately weighted 0.10 g (0.270 mmol) of $EuCl_3·6H_2O$ and 0.054 g (0.270mmol) of Phen were added. It is obvious that in the above coordination system, the molar ratio of the bonded MOBA to Eu(Ⅲ) ion and to Phen was 3:1:1. The above mixed solution was placed on a water bath of 50 ℃, and the coordination reaction was carried out for 8 h with stirring. After the reaction finished, the product was precipitated out by ethanol, then washed with ethanol and distilled water, and dried under vacuum. The resultant product was the ternary polymer-rare earth complex, PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$. In the same way, another two ternary polymer-rare earth complexes, PSF-$(HBA)_3$-Eu(Ⅲ)-$(Phen)_1$ and PSF-$(BA)_3$-Eu(Ⅲ) -$(Phen)_1$ were also prepared.

2.3.3. Characterization of complexes

The FTIR spectra of the prepared polymer-rare earth complexes including the binary and ternary complexes were determined with KBr pellet method to confirm their chemical structures, and detailed data can be seen from the following infrared spectra. Various binary complexes and ternary complexes were dissolved in DMF, and their UV absorption spectra were recorded.

2.4. Determination of florescence emission spectra of complexes

Various complexes as well as $EuCl_3$ were dissolved in DMF to form the solutions with a certain concentrations, respectively. Their excitation spectra were firstly monitored with the emission of the center Eu^{3+} ion, at 620 nm, so that their optimal excitation peaks were obtained. And then their fluorescence emission spectra were determined with the corresponding optimal excitation peaks.

As mentioned above, polysulfone has excellent film-forming property. In this work, the solid films of the binary complexes and ternary complexes were prepared with casting method. The complexes were first dissolved in chloroform, respectively, and then the cast films were formed on the several glass plates. The cast films were dried in oven at 40 ℃ to remove the solvent, obtaining various solid films of the complexes, respectively. The fluorescence emission spectra of the complexes films were also determined.

3. Results and discussion

3.1. Chemical structure of binary and ternary polymer-rare earth complexes

In this work, the nucleophilic substitution reaction between the chloromethyl group of CMPSF and the hydroxyl group of HMOBA and DHBA (the para-position hydroxyl group took part in the reaction, whereas the ortho-position hydroxyl group was reserved) were made to be conducted, and as a result, methoxybenzoic acid (MOBA) and hydroxybenzoic acid (HBA) as two groups were bonded onto the side chains of PSF, respectively, forming functionalized PSFs, PSF-MOBA and PSF-HBA, whose structure are shown in Scheme 1. It is obvious that in the structures of PSF-MOBA and PSF-HBA, each has an electron-donating substituent group on the benzene ring of the bonded benzoic acid, methoxy group for PSF-MOBA and hydroxyl group for PSF-HBA, respectively, and the two electron-donating substituent groups will play an important role in the luminescent properties of the following polymer-rare earth complexes, and the detailed discussion can be seen in the following sections.

Subsequently, in the solvent DMF, two functionalized PSFs as macromolecular ligands (actually, the bonded MOBA and HBA play the role of ligands) coordinate with Eu^{3+} ion in a predetermined ratio to form the binary polymer-rare earth complexes, PSF-$(MOBA)_3$-Eu(III) and PSF-$(HBA)_3$-Eu(III), and their structures are schematically presented in Scheme 2(A) .The two ternary complexes were also prepare in DMF solution with Phen as small ligand and in a predetermined ratio, and they are PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ and PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$. Their structures are schematically presented in Scheme 2 (B). However, an important concept, intramolecular or intrachain coordination complex, needs to be explained clearly for the polymer-rare earth complex formed in a solution. For all of the investigated solution systems of polymer-rare earth complexes, the corresponding polymer solutions are all dilute solutions, and the macromolecular coils are separated from each other. The coordination action between the ligands bonded on the macromolecules and rare earth ions should be classified into intramolecular or intrachain coordination action, namely it belongs to the coordination action of the ligands on the same macromolecular chain to rare earth ions, forming a kind of intrachain complexes. Otherwise, the closslinking phenomenon between macromolecules with rare earth ions as closslinking bridges would occur [28], and the solution would become turbid. The above concept of "intrachain coordination complex" has not been shown clearly in other literatures, and it was only clearly described in our previous study [29]. Therefore, the polymer-rare earth complexes prepared in the solution systems in this investigation should have the structure models as shown in Scheme 2.

Scheme 1

Scheme 2(A)

Scheme 2(B)

3.2. Characterization of functionalized PSFs and complexes

3.2.1. Characterization of functionalized PSFs

(1) Infrared spectra

The infrared spectra of PSF, PSF-MOBA and PSF-HBA are shown in Fig. 1.

Fig. 1

In the spectrum of PSF, all characteristic absorption bands of PSF are displayed. In comparison with the spectrum of PSF, in the spectra of the functionalized PSFs, PSF-MOBA and PSF-HBA, there are two obvious new bands. The first is the band at 1720 cm^{-1}, and it is ascribed to the stretching vibration absorption of C=O bond of carbonyl group in the bonded MOBA and HBA ligands. The second is the band at 3425 cm^{-1}, and it is assigned to the stretching vibration absorption of -OH group of carbonyl group. In the spectrum of PSF-HBA, the band at 3425 cm^{-1} seems to be wider because of the existing hydroxyl group on the benzene ring. The above spectrum changes fully show that via the nucleophilic substitution reaction between the chloromethyl group of CMPSF and the hydroxyl group of HMOBA or DHBA, MOBA and HBA ligands have been bonded to the side chains of PSF, respectively, and the functionalized PSFs, PSF-MOBA and PSF-HBA, have been formed.

(2) ^{1}H NMR spectra

Fig. 2 gives the ^{1}H NMR spectra of CMPSF, PSF-MOBA and PSF-HBA, and these spectra are designated as Fig. 2 (A), Fig. 2 (B) and Fig. 2 (C), respectively. At the same time, the correspondence between the various resonance peaks and all of hydrogen protons in the structures of the above three macromolecules are marked.

Fig. 2 (A)

Fig. 2 (B)

Fig. 2 (C)

In the spectrum of CMPSF, All signals of the various protons of CMPSF are displayed at a range of 6.923-7.910 ppm, and these various protons are denoted in the chemical structure formula of CMPSF. In particular, the resonance absorption peak of the protons in the methylene group -CH$_2$- in the chloromethyl group appears at 4.650 (i) ppm, and the resonance absorption peak of the protons of the isopropyl group of the bisphenol units appears at δ=1.649.

In the spectrum of PSF-MOBA, the resonance absorption peaks (j-l) of various protons in the structure of the bonded MOBA and the resonance absorption peaks (b-h) of PSF overlap each other, and a group of resonance absorption peaks in a range of 6.945-8.151 ppm are formed. The characteristic absorption peak of the hydroxyl group proton of the carboxyl group of the bonded MOBA appears at 9.500 (m) ppm, and the characteristic absorption peak of the methoxy group proton appears δ=3.884 (n). the resonance absorption peak of the protons in the methylene group -CH_2-, which comes from original chloromethyl group and now it has transformed into -CH_2-O- group as a bridge linking PSF skeleton and MOBA ligand, appears at 4.572（i）ppm. The above spectrum data once again confirm that via the nucleophilic substitution reactions between the chloromethyl group of CMPSF and the hydroxyl group of HMOBA, the functionalized polysulfone PSF-MOBA has been obtained.

In the spectrum of PSF-HBA, both the characteristic absorption peak of the hydroxyl group proton (m) of the carboxyl group of the bonded HBA as well as the characteristic absorption peak of the hydroxyl group proton (n) on benzene ring also appear at about 9.500 ppm, and the rest of the peaks are similar to that of PSF-MOBA. Similarly, the ^{1}H NMR spectrum data also confirm the formation of functionalized polysulfone PSF-HBA.

3.2.2. Characterization of complexes

(1) Infrared spectra

The infrared spectra of binary complex PSF-$(MOBA)_3$-Eu(III) and ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ are presented in Fig. 3(A), and the infrared spectra of binary complex PSF-$(HBA)_3$-Eu(III) and ternary complex PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$ are displayed in Fig. 3(B), respectively.

Fig. 3(A)

Fig. 3(B)

The following facts can be observed from Fig. 3(A). In the spectrum of PSF-MOBA, the band at 1720 cm^{-1} is attributed to the characteristic absorption of the carbonyl group of the carboxylic group. As compared with the spectrum of PSF-MOBA, in the spectrum of the binary complex PSF-(MOBA)$_3$-Eu(III), two new bands have appeared at 1540 and 1425 cm^{-1}, respectively. The first is the asymmetric vibration absorption (v_{as}, COO$^-$) band of the carboxylic group and the second is the symmetric vibration absorption (v_s, COO$^-$) band of the carboxylic group, clearly showing that the carboxylic groups acting as a bidentate ligand have coordinated to Eu^{3+} ion [30, 31], forming the chelating complex. Besides, in the spectrum of PSF-(MOBA)$_3$-Eu(III), the stretching vibration absorption of Eu-O bond can be observed at 414 cm^{-1}. The above spectrum data clearly confirmed that the binary polymer-rare earth complex PSF-(NA)$_3$-Eu(III) has been formed.

In the spectrum of the ternary complex PSF-(MOBA)$_3$-Eu(III)-(Phen)$_1$, similarly, the stretching vibration peak of C=O bond of the free carboxyl group at 1720 cm^{-1} has also disappeared, whereas the asymmetric and symmetric vibration absorption bands of the carboxylic group also appear at 1540 and 1425 cm^{-1} respectively, indicating the bidentate chelating coordination of the carboxylic group towards Eu^{3+} ion. Similarly, the stretching vibration absorption of Eu-O bond also appears at 414 cm^{-1}. Besides, the characteristic absorption band of C=N bond of Phen band appears at 1580 cm^{-1}. The above spectrum data fully demonstrate the ligand MOBA bonded on the side chains of PSF and small-molecule ligand Phen have synergistically coordinated to Eu^{3+} ion, and the ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ has been formed.

The following facts can be observed from Fig. 3(B). As compared with the spectrum of PSF-HBA, in the spectrum of the binary complex PSF-$(HBA)_3$-Eu(III), the asymmetric vibration absorption (v_{as}, COO^-) band and symmetric vibration absorption (v_s, COO^-) band of the carboxylic groups appear at 1540 and 1410 cm^{-1}, respectively, also clearly indicating that the carboxylic groups acting as a bidentate ligand have coordinated to Eu^{3+} ion, forming the chelating complex. Similarly, the stretching vibration absorption of Eu-O bond can be observed at 414 cm^{-1}. The above spectrum data also confirmed that the binary polymer-rare earth complex PSF-$(HBA)_3$-Eu(III) has been formed.

In the spectrum of the ternary complex PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$, similarly, the stretching vibration peak of C=O bond of the free carboxyl group at 1720 cm^{-1} has also disappeared, whereas the asymmetric and symmetric vibration absorption bands of the carboxylic group also appear at 1540 and 1410 cm^{-1} respectively, indicating the bidentate chelating coordination of the carboxylic group towards Eu^{3+} ion. Similarly, the stretching vibration absorption of Eu-O bond also appears at 414 cm^{-1}. Besides, the characteristic absorption band of C=N bond of Phen band also appears at 1580 cm^{-1}. Similarly, the above spectrum data fully demonstrate the ligand HBA bonded on the side chains of PSF and small-molecule ligand Phen have synergistically coordinated to Eu^{3+} ion, and the ternary complex PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$ has been formed.

(2) UV absorption spectra

Fig. 4(A) and Fig. 4(B) give the UV absorption spectra of MOBA series and HBA series including ligands and complexes, respectively.

Fig. 4(A)

Fig. 4(B)

In Fig. 4(A), the UV absorption spectra of PSF-MOBA as macromolecule ligand, Phen as small molecule ligand, the binary complex PSF-$(MOBA)_3$-Eu(III) and ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ are presented. It can be seen that PSF-MOBA has strong UV absorption in a range of 280-340 nm. There is one strong absorption peaks at 300 nm, and it is ascribed to the π-π^* electron transition of the benzene ring and carbonyl group of MOBA ligand of PSF-MOBA. In the spectrum of the free ligand Phen, there are two absorption peaks at 293 and 321 nm, and they are assigned to the π-π^* electron transition and n-π^* electron transitions, respectively.

The binary complex PSF-$(MOBA)_3$-Eu(III) also have strong UV absorption. However, its spectral profile is very similar to that of PSF-MOBA, and only the characteristic absorption slightly red-shifts from 300 nm to 303 nm. The red shift of the absorption peak of the binary complex implies that the bonded ligand MOBA of PSF-MOBA has coordinated to Eu^{3+} ion. The spectrum similarity of PSF-$(MOBA)_3$-Eu(III) with PSF-MOBA suggests that the strong UV absorption of the binary complex PSF-$(MOBA)_3$-Eu(III) comes from the macromolecular ligand PSF-MOBA and it is unrelated to the central Eu^{3+} ion because the UV absorption of Eu^{3+} ion is very weak. Therefore, a strong sensitization effect, namely the energy transfer from PSF-MOBA to Eu^{3+} ion, should be responsible for the strong fluorescence emission of the binary complex PSF-$(MOBA)_3$-Eu(III) as discussed below.

In the spectrum of the ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$, there are two strong absorption peaks at 307 nm and 323 nm. The former peak results from the overlapping of the absorption peak of PSF-MOBA and a part of Phen peak with 293 nm as centre, while the latter is attributed to the second absorption band of Phen. As compared with the spectrum of the macromolecular ligand PSF-MOBA, the red shift of the adsorption spectrum of the ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ is more obvious, and it is caused by the co-coordination of the bonded ligand MOBA and the small-molecule ligand Phen to Eu^{3+} ion. After coordinating of two O atoms of the carboxyl group of the bonded MOBA and N atom of Phen to Eu^{3+} ion, multiple chelating rings around the center ion are formed, and it makes the conjugation system to be enlarged and makes the density of π electron cloud around the central ion to be increased. As a consequence, the electron delocalization degree increases and the electron transition energy decreases, resulting in the greater red shift of the absorption bands. The above spectrum data fully demonstrate that the coordination bonds between Eu^{3+} ion and two ligands, macromolecular ligand PSF-MOBA and small-molecule ligand Phen, have formed, forming the ternary complex. At the same time, the above spectrum data also indicate that the UV absorption of the ternary complex comes from the macromolecular ligand PSF-MOBA and small-molecule co-ligand Phen, and the strong fluorescence emission of the ternary complex PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ that will be discussed below is caused by the energy transfer from two ligands to Eu^{3+} ion.

Fig. 4(B) gives the UV absorption spectra of PSF-HBA as macromolecule ligand, Phen as small molecule ligand, the binary complex PSF-$(HBA)_3$-Eu(III) and ternary complex PSF-($HBA)_3$-Eu(III)-$(Phen)_1$. The shown regularity in Fig. 4(B) is similar to that in Fig. 4(A).

In a word, for the above two series of polymer-rare earth complexes, whether it is the binary complex or the ternary complex, all of their UV absorptions come from the ligands, macromolecular ligand or the cooperation of macromolecular ligand and small-molecule ligand Phen, and their fluorescence emission is caused by the energy transfer from the ligands to Eu^{3+} ion as discussed below.

3.3. Fluorescence emission spectra of complexes and strengthening effect of electron-donating substituent on aromatic ring

3.3.1. Fluorescence emission spectra of binary complexes

The two binary complexes, PSF-(MOBA)$_3$-Eu(III) and PSF-(HBA)$_3$-Eu(III), as well as PSF-(BA)$_3$-Eu(Ⅲ), on whose aromatic ring there is no electro-donating substituent, were all dissolved in DMF, and three complex solutions were prepared with an identical concentration of 4.0×10^{-4} mol/L based on the concentration of central Eu(Ⅲ) ion. The excitation spectra of the three binary complexes were first obtained by monitoring the emission spectrum of Eu(Ⅲ) ion at the emission of 620 nm in the range of 250–400 nm, and the corresponding optimal excitation peaks were obtained. And then by exciting of their optimal excitation peaks as shown in Fig. 5, their fluorescence emission spectra in DMF solutions were recorded. At the same time, the fluorescence emission spectrum of EuCl$_3$ in DMF solution (also with a concentration of 4.0×10^{-4} mol/L) was also recorded in order to make comparisons. These recorded fluorescence emission spectra are presented in Fig. 5.

Fig. 5

In Fig. 5, the following facts can be found: (1) The emission spectra of the three binary complexes are similar to that of EuCl$_3$ in shape and band positions, suggesting that these binary complexes emit the characteristic emission of Eu^{3+} ion, namely all of the three macromolecular ligands can sensitize the fluorescence emission of Eu^{3+} ion. In these spectra, three main emission peaks at 580, 593 and 620 nm are displayed, and they are assigned to the transitions of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, respectively. Among these bands, the $^5D_0 \rightarrow {}^7F_2$ at 620 nm is the strongest emission as shown in Fig. 5. (2) The fluorescence emissions of the three binary complexes are far stronger than that of $EuCl_3$ under the same conditions, especially that of PSF-$(MOBA)_3$-Eu(III) and PSF-$(HBA)_3$-Eu(III), and it fully display that both the two functionalized PSFs, PSF-MOBA and PSF-HBA, strongly sensitize the fluorescence emission of Eu^{3+} ion, and a strong “Antenna Effect” has produced, resulting in the strong characteristic fluorescence emissions of Eu^{3+} ion. That is, MOBA of PSF-MOBA or HBA of PSF-HBA is first excited to the excited singlet state (S_1) by UV absorption, and then relaxes to the triplet state (T_1) via intersystem crossing. Subsequently, the energy is nonradiatively transferred from the triplet state of MOBA of PSF-MOBA or that of HBA of PSF-HBA to the resonance state of the coordinated Eu^{3+} ion. Finally, the Eu^{3+} ion emits its characteristic fluorescence in the visible region by a multiphoton relaxation from the exited state to the ground state. (3) It is obviously that the emissions of PSF-$(MOBA)_3$-Eu(III) and PSF-$(HBA)_3$-Eu(III) are far stronger than that of PSF-$(BA)_3$-Eu(Ⅲ), and the intensity of the former is 21 times stronger than that of PSF-$(BA)_3$-Eu(Ⅲ) and the intensity of the latter is 17 times stronger than that of PSF-$(BA)_3$-Eu(Ⅲ). This fact clearly indicates that the bonded ligands MOBA and HBA can produce much stronger sensitization action towards Eu^{3+} ion than the bonded ligand BA and suggests that the two electron-donating substituent groups on the benzene ring of the bonded benzoic acid, methoxy group and hydroxyl group, can apparently strengthen the florescence emission of the polymer-rare earth complexes. The reason is explained as follows.

According to the Antenna effect theory, for the fluorescent intensity of rare earth complexes, the energy matching degree between the triplet state energies of organic ligands and the resonant level energies of rare earth ions is one of the most important factors affecting the intramolecular energy transfer efficiency, and the better the energy matching degree is, the higher energy transfer efficiency is, and the stronger the emission intensity of the complex is [32,33]. For the sensitization effect of organic ligands towards Eu(III) ion, as the energy gap between the triplet level of the ligand and the resonant level of Eu(III) ion is about 3000 cm^{-1}, the energy transfer efficiency is the highest [32]. The triplet level of benzoic acid (BA) ligand is 25,641 cm^{-1}, whereas the resonant level ($^5D_0$) of Eu(III) ion is 17,200 cm^{-1}[23]. It is obvious that the energy difference between the two is 8440 cm^{-1}($>>$3000cm^{-1}), and so the energy gap is too big and the energy levels are unmatched. Therefore, the fluorescence emission intensity of the complex of benzoic acid and Eu(Ⅲ) ion as well as that of the binary complex PSF-$(BA)_3$-Eu(Ⅲ) is low. However, once there exists one electron-donating substituent group on the benzene ring of benzoic acid, the triplet state energy of benzoic acid will be obviously declined, and the energy matching degree may be obviously enhanced[23,32]. For example, the triplet state levels of *para*-ethoxybenzoic acid and *ortho*-hydroxybenzoic acid, whose structures are similar to that of the bonded MOBA and HBA ligands, are 24625 and 24155 cm^{-1}[32], respectively, and they have been declined greatly compared to that of benzoic acid (25,641 cm^{-1}), leading to that the energy gaps apparently decrease from 8440 cm^{-1} to 7425 and 6955 cm^{-1}. Similarly, for the bonded MOBA and HBA ligands on PSF-MOBA and PSF-HBA, their triplet state levels will be also obviously declined. The basic cause lies in the electron-donating effect of the substituent caused by p-π conjugative effect. For the O atom of the methoxy group in the structures of the bonded MOBA of PSF-MOBA and for the O atom of the hydroxy group in the structures of the bonded HBA of PSF-HBA, there are lone pair electrons, and so the p-π conjugative effect between the methoxy group and benzene ring for the bonded MOBA or between the hydroxy group and benzene ring for the bonded HBA will arise. This p-π conjugative effect will increase the electron cloud density of benzene ring, and will decrease the energy of π-π* electron transition. As a result, the energy of the excited singlet state of the bonded ligand MOBA or HBA will decline, and it will result in the decline of the triplet state energies of the two bonded ligands. Consequently, the energy gap between the triplet level of the ligand and the resonant level of Eu(III) ion will dramatically decrease, and the energy matching degree will be strengthened, leading to that the two binary complexes, PSF-$(MOBA)_3$-Eu(III) and PSF-$(HBA)_3$-Eu(III), emit much stronger fluorescence than the binary complex PSF-$(BA)_3$-Eu(Ⅲ).

Fig. 5 also displays that the fluorescence emission intensity of the binary complex PSF-$(MOBA)_3$-Eu(III) is stronger than that of PSF-$(HBA)_3$-Eu(III), namely the ligand MOBA has stronger sensitization action than the ligand HBA. Perhaps, this result is caused by that the energies of the excited singlet state and the triplet state of the bond ligand MOBA is lower than that of the bonded ligand HBA because the ability of giving electrons of methoxy group is stronger than that of hydroxy group, and the p-π conjugative effect may be stronger.

The actual images of PSF-$(MOBA)_3$-Eu(III), PSF-$(HBA)_3$-Eu(Ⅲ), PSF-$(BA)_3$-Eu(Ⅲ) and $EuCl_3$ solutions under UV radiation are presented in Fig. 6, and they are denoted as A, B, C and D, respectively. By comparison, the PSF-$(MOBA)_3$-Eu(III) solution displays strong red luminescence, and exhibits good photoluminescence property; the PSF-$(HBA)_3$-Eu(Ⅲ) solution also exhibit red luminescence, displaying better photoluminescence property, but its color is slightly weaker than that of PSF-$(MOBA)_3$-Eu(III) solution because of the stronger electron-donating property and stronger p-π conjugative effect of the methoxy group of the bonded ligand MOBA than that of the hydroxyl group of he bonded ligand HBA; the PSF-$(BA)_3$-Eu(Ⅲ) solution is slightly red, indicating very weak photoluminescence property; $EuCl_3$ solution is colorless.

Fig. 6

Fig. 7

The fluorescence emission spectra of the solid films of the three binary complexes are displayed in Fig. 7. The fluorescence emission spectra of the solid films of the three binary complexes, PSF-(MOBA)$_3$-Eu(III), PSF-(HBA)$_3$-Eu(III) and PSF-(BA)$_3$-Eu(III), also show the photo physical behaviors similar to that in Fig. 5. Besides, it can be observed that the fluorescence intensity of the complexes in solid film is higher than that in solution. The reason for this is that in the solid film, the motion freedoms of the molecules as well as that of the fluorophores of the complexes are much smaller than in solution, and the fluorescence quenching caused by collision can be effectively avoided, resulting in higher intensity of the fluorescence emission of the complexes in solid film.

In a word, both the two electron-donating substituent groups on the benzene ring of the bonded benzoic acid, methoxy group and hydroxy group, greatly intensify the sensitization action of benzoic acid ligand towards the fluorescence of rare earth Eu(Ⅲ) ion because of p-π conjugative effect.

3.3.2. Fluorescence emission spectra of ternary complexes

By using Phen as small-molecule co-ligand, the two ternary complexes, PSF-(MOBA)$_3$-Eu(III)-(Phen)$_1$ and PSF-(HBA)$_3$-Eu(III)-(Phen)$_1$ were prepared, and their DMF solutions with a concentration of 4.0×10^{-4} mol/L based on the concentration of the central Eu(III) ion also prepared. The fluorescence emission spectra of the two complex solutions were determined, and the determination result is shown in Fig. 8. For comparison, the solution of the ternary complex PSF-(BA)$_3$-Eu(III)-(Phen)$_1$ also prepared, and its fluorescence emission spectrum is also shown in Fig. 8. The fluorescence emission spectra of the solid films of the above three ternary complexes are presented in Fig. 9.

Fig. 8

Fig. 9

Similarly, from Fig.8 it also can be seen that the fluorescence emission intensities of the two ternary complexes, PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ and PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$, are much higher than that of the ternary complex PS-$(BA)_3$-Eu(Ⅲ)-$(Phen)_1$, and it still reflects the strengthening effect of the two electron-donation substituent groups (methoxy graoup and hydroxy group) for the fluorescence emission of the complexes of benzoic acid-functionalized polysulfone and Eu(Ⅲ) ion. Of course, Fig.8 also displays the same rule, namely the fluorescence emission intensities of the solid films of the ternary complexes, PSF-$(MOBA)_3$-Eu(III)-$(Phen)_1$ and PSF-$(HBA)_3$-Eu(III)-$(Phen)_1$, are much higher than that of the solid film of the ternary complex PS-$(BA)_3$-Eu(Ⅲ)-$(Phen)_1$.

Besides, by comparing Fig. 8 and Fig. 5, it can be found that the fluorescence emission intensities of the ternary complexes are higher than that of the corresponding binary complexes, and it fully reflects the role of the second small-molecule ligand Phen. In the ternary complex, the addition of the second ligand makes the number of coordinated ligands around rare earth ions to be increased and the conjugated system around the central ions to be enlarged. The synergistic coordination effect of the two ligands, macromolecular ligand and small-molecule ligand Phen, will enhance the UV absorption ability of the complexes and strengthen the intramolecular energy transfer [9,34], resulting in the enhancement of the fluorescence intensity [14,34]. Of course, in the synergistic coordination action, the energy matching degree between the triplet state energies of co-ligand Phen and Eu(III) ion is also very important. The triplet state energy of Phen is 22,100 cm^{-1}[35], and the energy difference between the two is 4800cm^{-1}. It is obvious that this energy gap is closed to 3000cm^{-1}, and so the energy levels are matched. Therefore, there is a good synergistic coordination effect of the co-ligand Phen with the macromolecular ligands, PSF-MOBA and PSF-HBA.

Another reason is that the second ligand can effectively substitute the coordinated water molecules around the central ion as shown in Scheme 1, and avoid the fluorescence quenching caused by the vibration of the hydroxyl groups of water molecules [26,34]. It is the above two factors that make the ternary complexes to have stronger fluorescence emission than the binary complex. As compared with Fig.6, Fig.8 also displays the same rule, namely the fluorescence emission intensities of the solid films of the ternary complexes are higher than that of the solid films of the corresponding binary complexes.

4. Conclusions

In this work, via polymer reactions, methoxybenzoic acid (MOBA) and hydroxybenzoic acid (HBA), were bonded onto the side chains of PSF, respectively, and two functionalized PSFs, PSF-MOBA and PSF-HBA, in whose structures there is an electron-donating substituent group, methoxy group and hydroxyl group, on the benzene ring of bonded benzoic acid, respectively, were prepared. By using the two functional PSFs as macromolecular ligands and Phen as the second ligands and with Eu(Ⅲ) ion as central ion , some luminescent binary and ternary polymer-rare earth complexes were prepared. We put emphasis on investigating the effect of the two electron-donating substituent groups on the luminescent properties of those complexes, and the experimental results were explained with the corresponding optical physics theory and the Antenna effect theory. A p-π conjugative effect will arise between the two electron-donating substituent groups and the benzene ring. This conjugative effect will effectively decline the energy of the excited singlet state and the triplet state energies of the two bonded ligands, MOBA and HBA, and as a result, the energy matching degree between the triplet state energies of the bonded ligands and the resonant level energy of Eu(III) ion will become better, leading to remarkably strengthening of the fluorescence emissions of these polymer-rare earth complexes. Besides, the fluorescence emission intensities of the ternary complexes are higher than that of the binary complexes because of the synergistic coordination effect of Phen and the macromolecular ligands. The fluorescence emission spectra of the solid films of these complexes also reflect the similar status.

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Figure Captions

Scheme 1 Schematic expressions of structures of PSF-MOBA and PSF-HBA

Scheme 2(A) Schematic expressions of structures of two binary complexes

Scheme 2(B) Schematic expressions of structures of two ternary complexes

Fig. 1 FTIR spectra of functionalized PSFs

Fig. 2(A) ^{1}H-NMR spectrum of CMPSF

Fig. 2(B) ^{1}H-NMR spectrum of PSF-MOBA

Fig. 2(C) ^{1}H-NMR spectrum of PSF-HBA

Fig. 3(A) FTIR spectra of complexes of MOBA series

Fig. 3(B) FTIR spectra of complexes of HBA series

Fig. 4(A) UV absorption spectra of ligands and complexes of MOBA series

Solvent: DMF

Fig. 4 (B) UV absorption spectra of ligands and complexes of HBA series

Solvent: DMF

Fig. 5 Fluorescence spectra of binary complexes and $EuCl_3$

Solvent: DMF; Concentration of Eu^{3+} ion: 4.0×10^{-4} mol/L

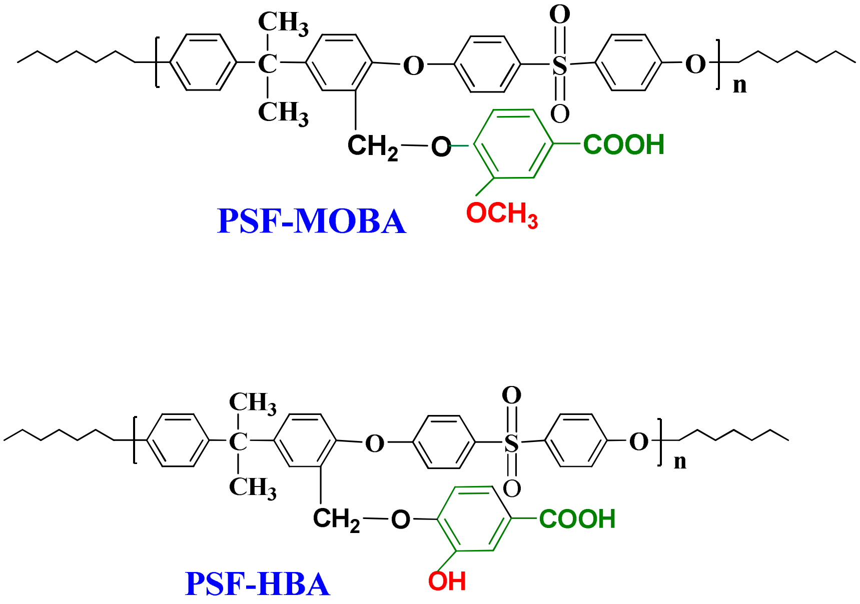
Fig. 6 Images of binary complex solutions under UV radiation

Fig. 7 Film fluorescence spectra of binary complexes

Fig. 8 Fluorescence emission spectra of ternary complexes

Solvent: DMF; Concentration of Eu^{3+} ion: 4.0×10^{-4} mol/L

Fig. 9 Film fluorescence spectra of ternary complexes


CH3
C
CH3
O
O
S
O
O
n
CH2
O
COOH
OCH3
PSF-MOBA
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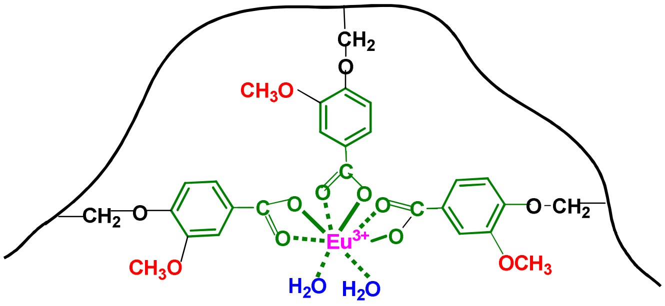
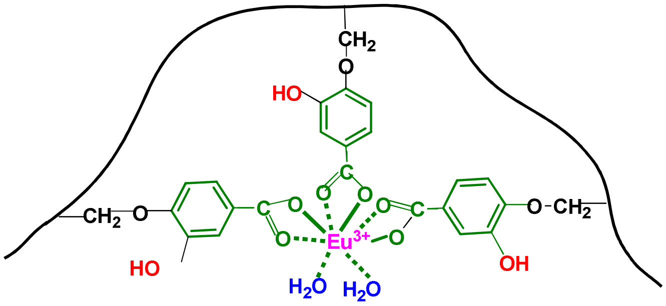
C
CH3
O
O
S
O
O
n
CH2
O
COOH
OH
PSF-HBA

Scheme 1

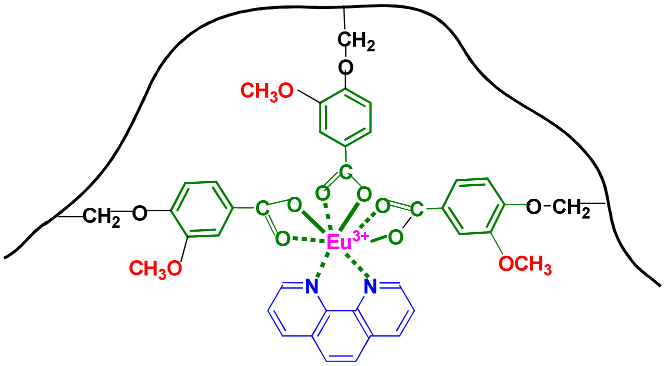


PS-(MOBA)$_3$-Eu(III)

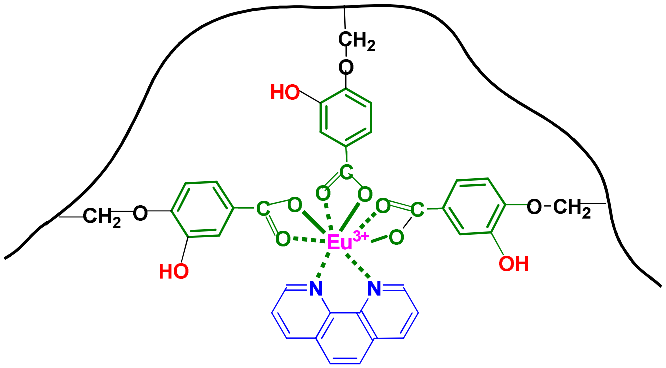


PS-(HBA)$_3$-Eu(III)

Scheme 2(A)



PS-(MOBA)$_3$-Eu(III)-(Phen)$_1$



PS-(HBA)$_3$-Eu(III)-(Phen)$_1$

Scheme 2(B)

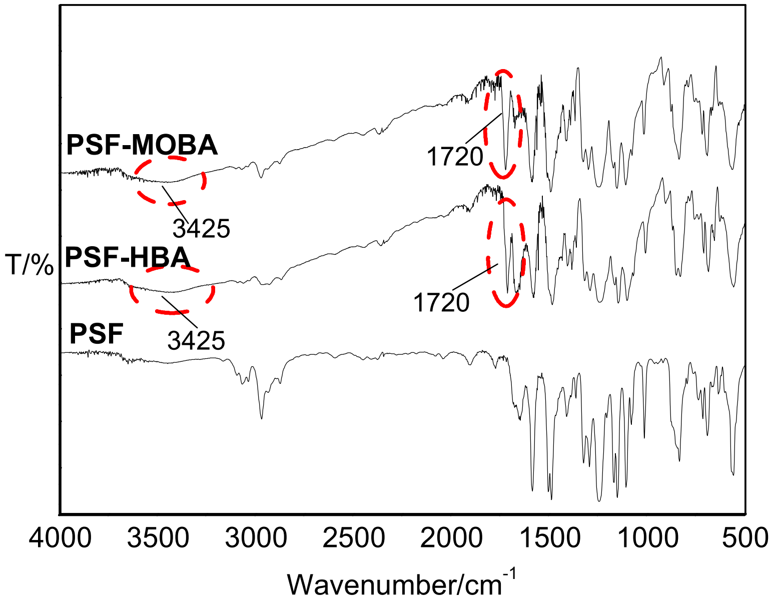
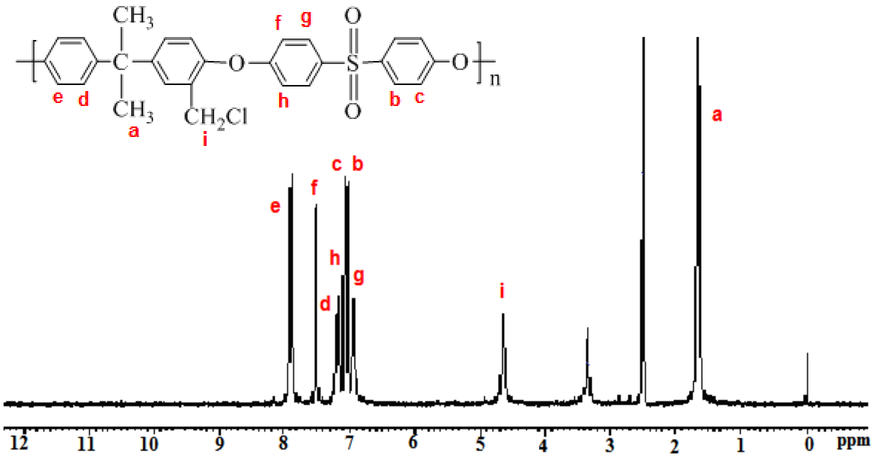

PSF-MOBA
PSF-HBA
PSF
3425
3425
1720
1720
T/%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber/cm^{-1}

Fig. 1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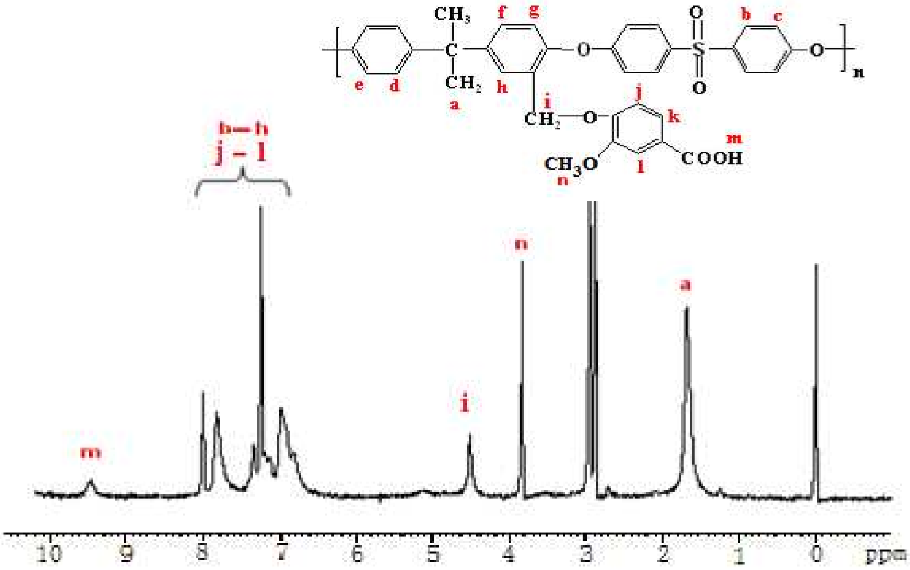
CH$_3$
CH$_2$Cl
O
S
O
O
O
n
e d a i f g h b c
e f c b h d g i a
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm

Fig. 2(A)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CH$_2$
CH$_2$
O
COOH
CH$_3$O
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O
O
n
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b—h
j – l
m i n a
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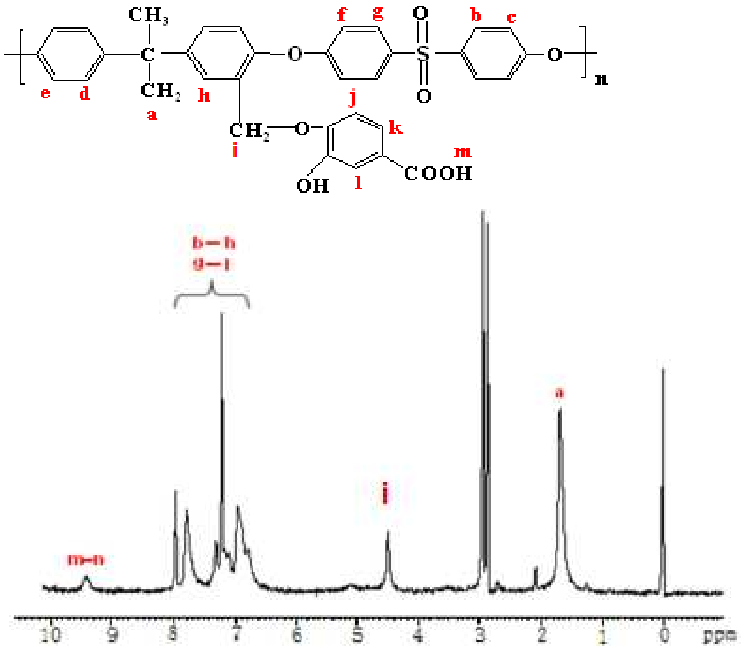
Fig. 2(B)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C
CH2
e
d
a
h
O
f
g
S
O
O
b
c
O
n
j
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i
O
k
m
COOH
OH
l
b—h
g—i
m-n
i
a
10
9
8
7
6
5
4
3
2
1
0
ppm

Fig. 2(C)

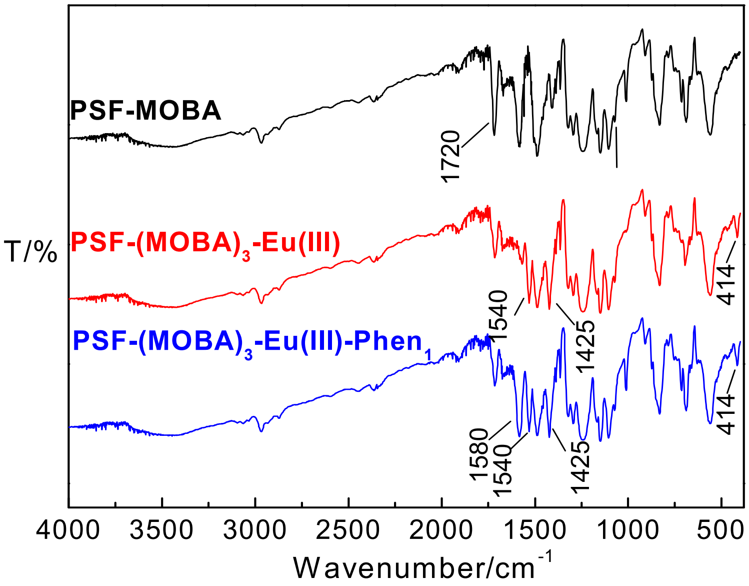
PSF-MOBA
1720
T/%
PSF-(MOBA)$_3$-Eu(III)
1540
1425
414
PSF-(MOBA)$_3$-Eu(III)-Phen$_1$
1580
1540
1425
414
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber/cm^{-1}

Fig. 3(A)

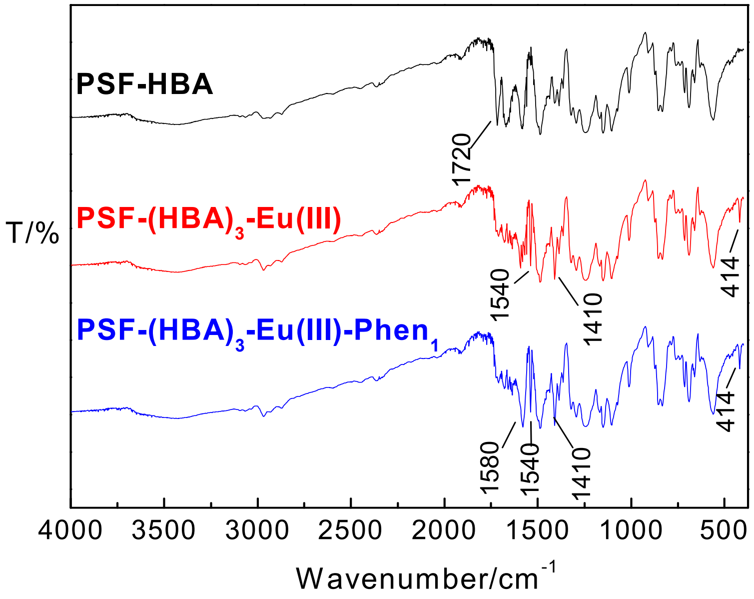
PSF-HBA
PSF-(HBA)$_3$-Eu(III)
PSF-(HBA)$_3$-Eu(III)-Phen$_1$
T/%
1720
1540
1410
414
1580
1540
1410
414
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber/cm^{-1}

Fig. 3(B)

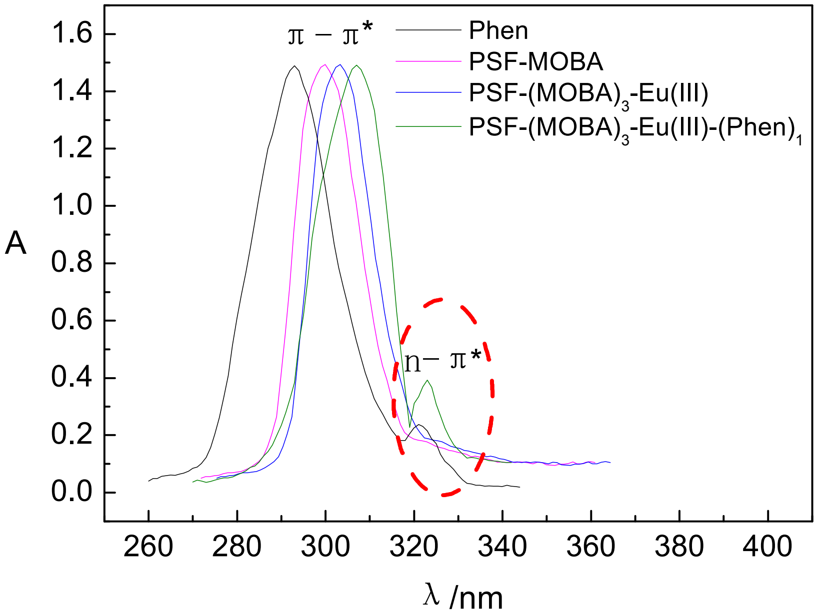
π − π*
Phen
PSF-MOBA
PSF-(MOBA)$_3$-Eu(III)
PSF-(MOBA)$_3$-Eu(III)-(Phen)$_1$
n− π*
A
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
260
280
300
320
340
360
380
400
λ /nm

Fig. 4(A)

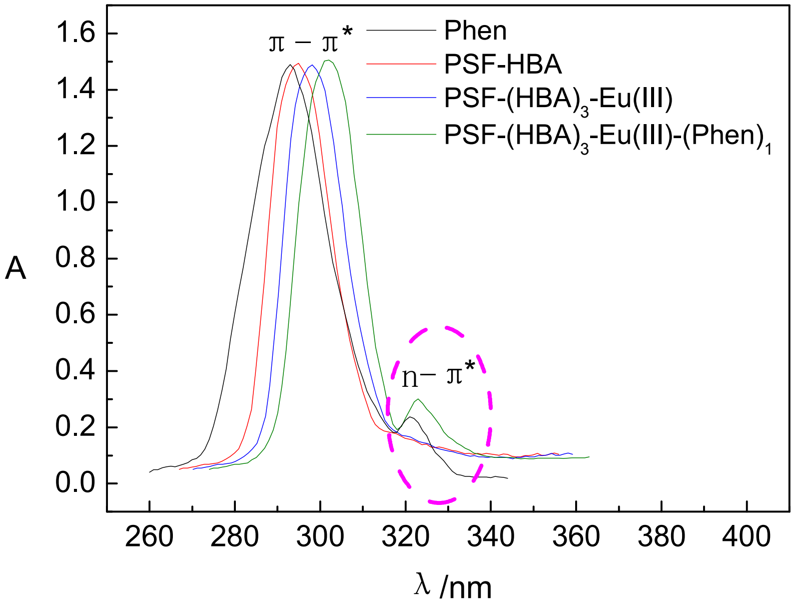
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A
260
280
300
320
340
360
380
400
λ /nm
π − π*
n− π*
Phen
PSF-HBA
PSF-(HBA)₃-Eu(III)
PSF-(HBA)₃-Eu(III)-(Phen)₁

Fig. 4(B)

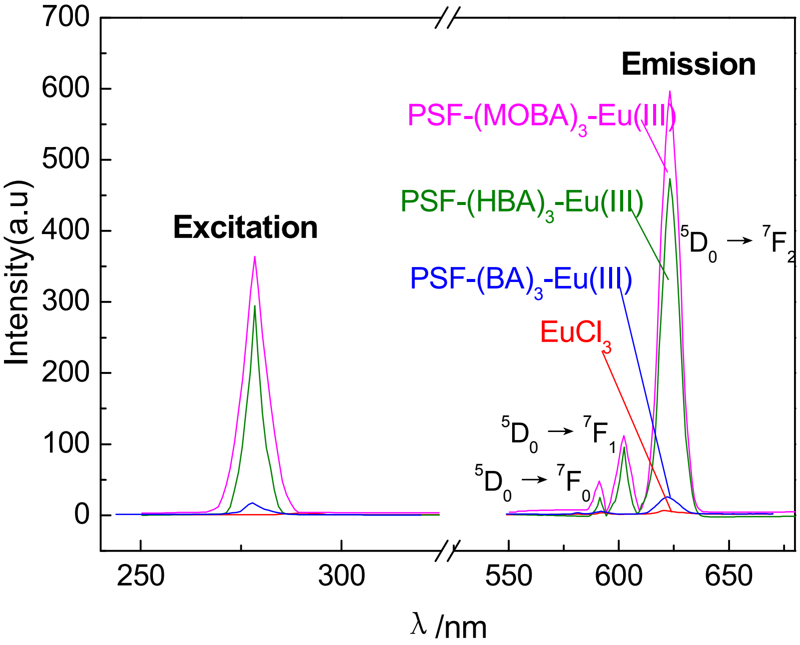
700
600
500
400
300
200
100
0
Intensity(a.u)
250
300
550
600
650
λ /nm
Excitation
Emission
PSF-(MOBA)$_3$-Eu(III)
PSF-(HBA)$_3$-Eu(III)
PSF-(BA)$_3$-Eu(III)
EuCl$_3$
$^5D_0 \rightarrow {}^7F_2$
$^5D_0 \rightarrow {}^7F_1$
$^5D_0 \rightarrow {}^7F_0$

Fig. 5

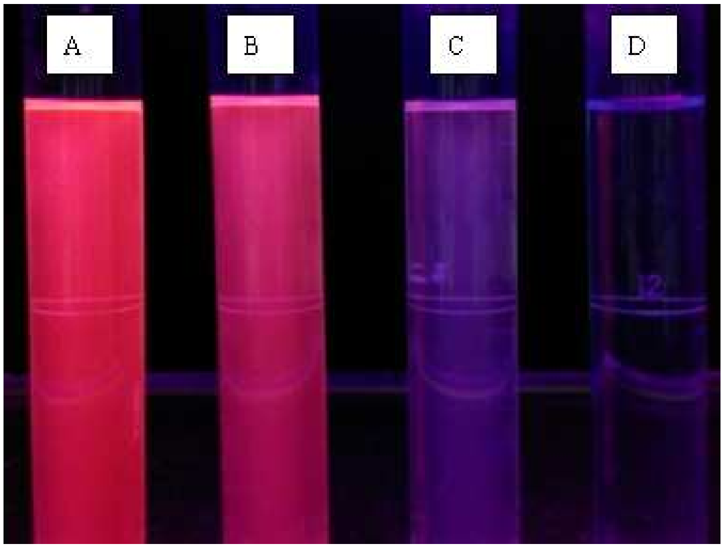

Fig. 6

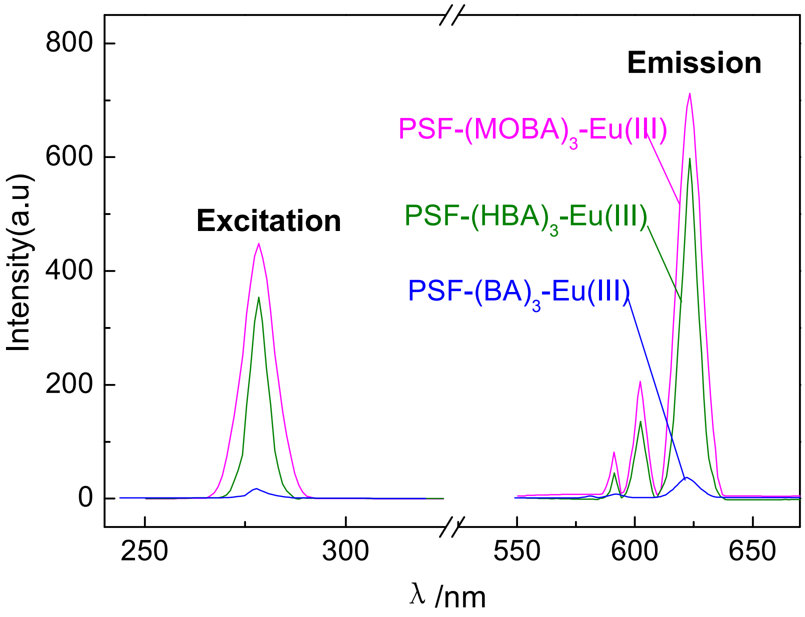
800
600
400
200
0
Intensity(a.u)
Excitation
Emission
PSF-(MOBA)$_3$-Eu(III)
PSF-(HBA)$_3$-Eu(III)
PSF-(BA)$_3$-Eu(III)
250
300
550
600
650
λ /nm

Fig. 7

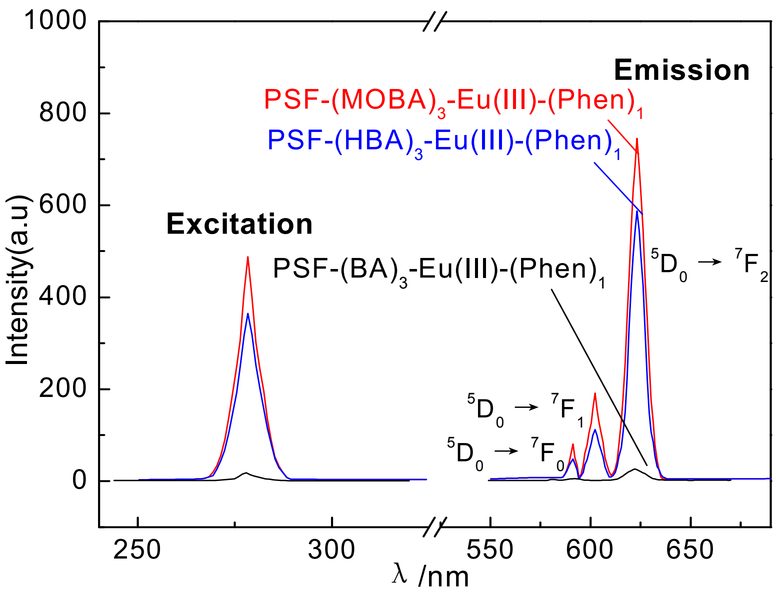
1000
800
600
400
200
0
Intensity(a.u)
250
300
550
600
650
λ /nm
Excitation
Emission
PSF-(MOBA)$_3$-Eu(III)-(Phen)$_1$
PSF-(HBA)$_3$-Eu(III)-(Phen)$_1$
PSF-(BA)$_3$-Eu(III)-(Phen)$_1$
$^5D_0 \rightarrow {}^7F_2$
$^5D_0 \rightarrow {}^7F_1$
$^5D_0 \rightarrow {}^7F_0$

Fig. 8

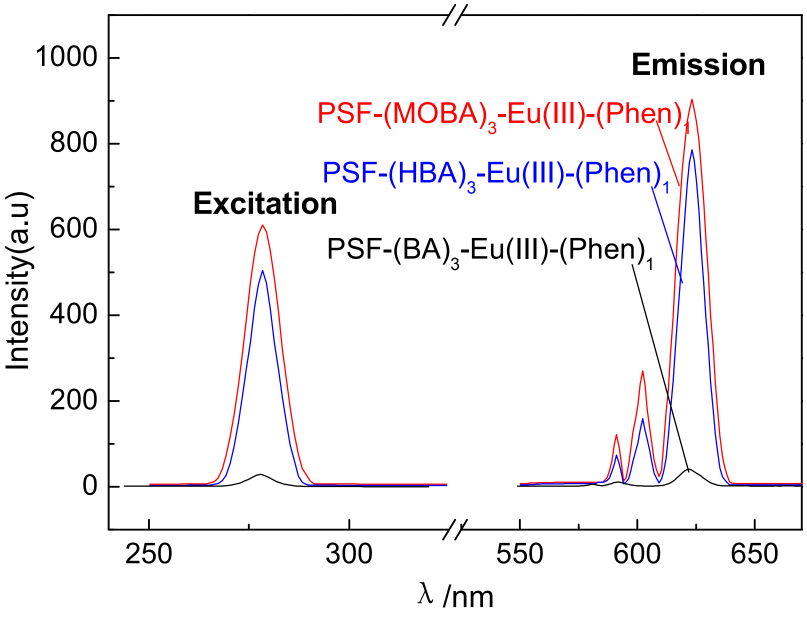
Emission
Excitation
PSF-(MOBA)$_3$-Eu(III)-(Phen)$_1$
PSF-(HBA)$_3$-Eu(III)-(Phen)$_1$
PSF-(BA)$_3$-Eu(III)-(Phen)$_1$
Intensity(a.u)
1000
800
600
400
200
0
250
300
550
600
650
λ /nm

Fig. 9