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Preparation of Molecularly Imprinted Polymer Fluorescence Probe Modified by Lanthanide Eu^{3+} Complex and Hemoglobin Sensing Detection

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Abstract: Molecularly imprinted polymer probes (Eu-MIPs) modified by lanthanide complexes were prepared by chemical bonding of molecularly imprinted polymers (MIPs) and lanthanide Eu^{3+} complex-functionalized ionic liquid ($[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$) by sol-gel method. The structure and properties of the probe molecules were analyzed by characterization methods such as FT-IR, XPS, UV-Vis, and PL. The results show that the Eu-MIPs fluorescent polymer has excellent fluorescence properties. In addition, by further studying the fluorescence sensing performance of Eu-MIPs for hemoglobin (Hb), it was found that Hb can produce a significant quenching effect on the fluorescence of Eu-MIPs, which may be due to the competitive absorption of UV light by Hb and ionic liquid ligands, and then the energy transfer process between ligands and rare earths is affected, resulting in the fluorescence quenching of Eu-MIPs. At the same time, Eu-MIPs have strong selectivity and anti-interference ability to Hb, and are expected to be used as fluorescent probes for the specific detection of Hb.

Key words: molecularly imprinted polymers; lanthanide complexes; fluorescence probe; sensing detection

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镧系 Eu^{3+} 配合物修饰的分子印迹 聚合物荧光探针制备及其对血红蛋白的传感检测

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摘要: 采用溶胶凝胶法将分子印迹聚合物(MIPs)与镧系 Eu^{3+} 配合物功能化的离子液体($[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$)进行化学键合制备得到了基于镧系配合物修饰的分子印迹聚合物探针(Eu-MIPs)。利用FT-IR、XPS、UV-Vis、PL等表征方法对探针分子的结构和性能进行分析。研究表明, Eu-MIPs荧光聚合物具有优异的荧光性能。此外, 通过进一步研究 Eu-MIPs对血红蛋白(Hb)的荧光传感性能发现, Hb能够对 Eu-MIPs的荧光产生明显的猝灭效果, 这可能是由于Hb和离子液配体对紫外光具有竞争性吸收, 进而使配体-稀土之间的能量传递过程受到影响, 从而造成Eu-MIPs的荧光猝灭。同时, Eu-MIPs对Hb具有较强的选择性和抗干扰能力, 有望用作特异性检测Hb的荧光探针。

关键词: 分子印迹; 镧系配合物; 荧光探针; 传感检测

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1 Introduction

Molecular imprinting technology can be used to prepare polymers that can specifically bind to template molecules^[1]. Molecularly imprinted polymers (MIPs) have the advantages of good thermal stability, excellent selectivity, and structural predictability^[2-3]. MIPs have attracted great attention by their various applications in various application fields such as purification, catalysis and detection^[4-6].

Hemoglobin (Hb) is an extremely important protein in the human blood. It can be used as a blood buffer substance to regulate it, and the change in its concentration is a signal produced by many diseases^[7-8]. In recent years, fluorescent molecularly imprinted polymer materials using hemoglobin as the template molecule have become a research hot-spot^[9-13]. Among all the lanthanide complexes, Eu^{3+} complexes have been intensively studied due to their inherent sharp emission peaks and high quantum efficiency. Eu^{3+} can respectively emit pure red light in almost any environment and free of the influence of external factors due to the light emission is originated from the electron redistribution of 4f orbitals, which are effectively shielded by the overlying 5s2 and 5p6 orbitals. In addition, lanthanide poly(ionic liquid) has extremely low volatility, better thermal and chemical stability, and good dissolution and extraction capabilities^[14-17]. The new fluorescent MIPs sensor obtained by imprinting and polymerizing based on lanthanide poly(ionic liquid) can effectively improve the reaction efficiency to realize the sensitive detection of the target substance^[18-22].

Therefore, in this work, we report the synthesis of molecularly imprinted polymer probes (Eu-MIPs) consisting of MIPs and β -diketonate lanthanide complex through sol-gel method. Moreover, Eu-MIPs have different fluorescence responses to aqueous solutions of different metal ions (K^+ , Mg^{2+} , Na^+ , Ca^{2+} , Zn^{2+} , Cl^-) and Hb. The results show that the prepared samples can effectively monitor Hb with high sensitivity and selectivity, and the detection limit of Eu-MIPs to Hb is 0.048 $\mu\text{mol/L}$, indicating the hybrid probe is feasible and reliable for hemoglobin sensing.

2 Experiment

2.1 Preparation of Eu-MIPs

2.1.1 Experimental Reagents

SiO_2 , absolute ethanol, hemoglobin, anhydrous ether, europium chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BFA), 2,6-pyridinedicarboxylic acid (DPA), ethyl orthosilicate (TEOS), phosphate buffer solution (PBS), 3-aminopropyl triethoxy silane (APTES), sodium dodecyl sulfate (SDS), glacial acetic acid (HAc), 1-ethyl-(3-dimethylaminopropyl) carbodiimide (EDC), N-Hydroxy succinimide (NHS).

2.1.2 Preparation Process

(1) Preparation of molecularly imprinted polymers (MIPs)

Using the sol-gel method, SiO_2 were dissolved in the mixture of absolute ethanol (20 mL) and phosphate buffer solution (20 mL). And then hemoglobin (100 mg), APTES monomer (20 mL) and TEOS (6 mL) were added to the above solution to obtain MIPs after magnetic stirring for 20 h.

(2) Synthesis of lanthanide Eu^{3+} complex-functionalized ionic liquid ($[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$)

A certain amount of 2, 6-pyridinedicarboxylic acid (DPA) and 4-bromophenylacetic acid (PA) was added into ethanol (10 mL) slowly and was stirred at 65 °C for 24 h under a nitrogen atmosphere. Finally, the sample was repeatedly washed with ether for 3 to 4 times and dried in a vacuum oven for 20 h to obtain a white powdery ionic liquid (DPA-PA). And then add europium ion complex ($\text{Eu}(\text{BFA})_3$) via stirring magnetically at 65 °C for 24 h to obtain $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$.

(3) Synthesis of Eu^{3+} -functionalized Molecularly Imprinted Polymers (Eu-MIPs)

First, a certain amount of $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ was dissolved in 5 mL H_2O , and the pH was adjusted to 8. Then, 0.003 g EDC and 0.001 g NHS were sequentially added to the above solution under ice bath, in which $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}:\text{NHS}=1:1$, EDC is in slight excess. The mixed solution was magnetically stirred for one hour in an ice bath to obtain $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA-NHS}$, which was stored in a

refrigerator for later use. 10 mL PBS buffer and 0.568 g MIPs were added to a 25 mL one-neck flask, followed by $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA-NHS}$ (1.265 g) and deionized water (10 mL), and the mixed solution was stirred for 12 h to obtain non-molecularly imprint-

ed polymers (Eu-NIPs). The mixed solution prepared in (3) was centrifuged for 20 min, then the supernatant was discarded, and the template molecules on the Eu-NIPs were eluted with 10% SDS + 10% HAc eluent, and dried to obtain Eu-MIPs (Fig. 1).

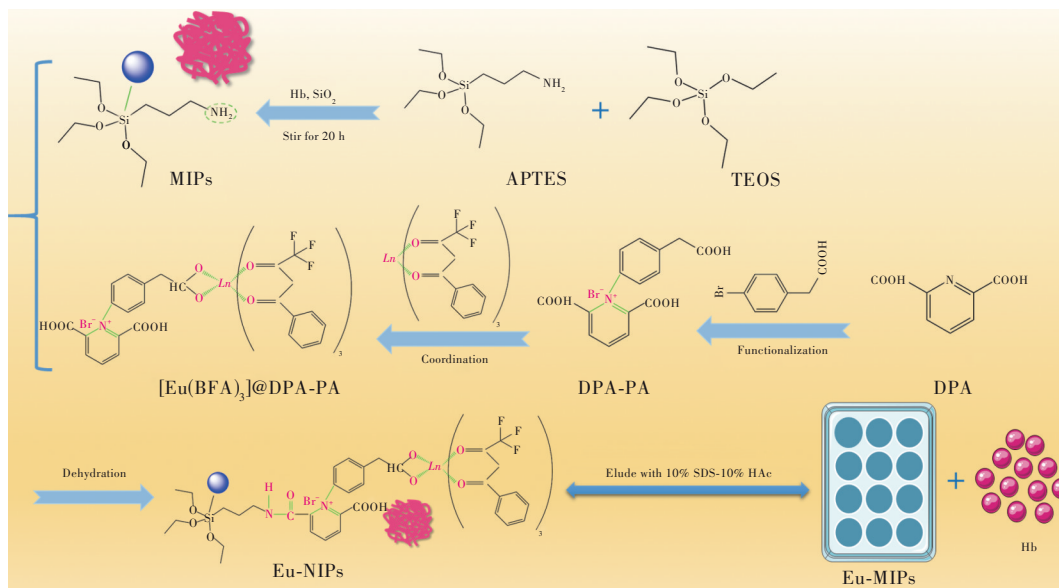


Fig.1 Experimental process and schematic diagram of Eu-MIPs

(4) Sensing detection of hemoglobin

The supersaturated aqueous solution of Eu-MIPs was ultrasonicated and the supernatant was collected as detection probe. Hemoglobin powder (100 mg) was dissolved in deionized water, and the volume was adjusted to 100 mL as the test substance. And then, different concentrations of hemoglobin detection solution were added to an equal volume of the probe solution. The test solutions were mixed well before recording their excitation and emission spectra.

2.2 Performance and Characterization of Samples

The Fourier Transform Infrared Spectroscopy (FT-IR) was analyzed and measured by the American Nexus 912 A0446 spectrometer, and the solid samples were prepared by KBr tablet technology. The fluorescence intensity was measured by the Japanese RF-5301PC spectrophotometer, and the xenon lamp was used as the excitation light source. X-ray photoelectric spectrometry (XPS) was analyzed and measured by the American Thermo Scientific K-Alpha spectrometer. The ultraviolet-visible (UV-Vis)

spectrum was measured by the American Lambda 750 spectrometer, and the sample was deionized water as the solvent. All instrument tests are performed at room temperature.

3 Results and Discussion

3.1 Structural Characterization of DPA-PA, $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs

Fig. 2 shows the infrared spectra of DPA-PA, $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs. It can be seen from Fig. 2 that the peak at 1700 cm^{-1} in the infrared spectrum of DPA-PA is related to the characteristic stretching vibration of the ionic liquid monomer $-\text{COOH}$, and the vibration peak is in $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$. It moves to 1731 cm^{-1} , which indicates that the carboxyl group has coordinated chelation with Eu^{3+} in the presence of $\text{Eu}(\text{BFA})_3$. In addition, the absorption peaks at 3085 cm^{-1} were attributed to the stretching vibration of the methylene group. These characteristic peaks indicate that the lanthanide complex $\text{Eu}(\text{BFA})_3$ has been successfully immobilized on the ionic liquid^[23-24]. The absorption band at 1633 cm^{-1} $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ is caused

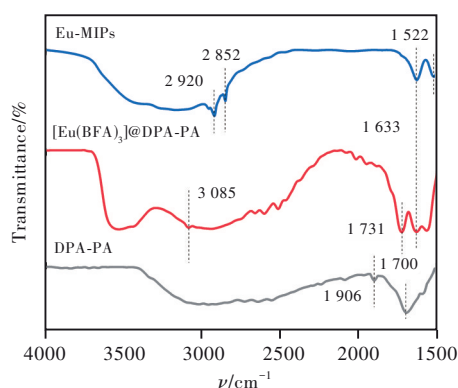


Fig.2 FT-IR spectrum of DPA-PA, $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs.

by the stretching vibration of the C=O double bond on the carbonyl group. The new peaks at 2852 cm^{-1} and 2920 cm^{-1} can be attributed to the O—H bond on the carboxyl group and the C—H bond on the benzene ring, respectively, indicating that the rare earth-based ionic liquids have been successfully modified on MIPs. It can be observed from the figure that Eu-MIPs has a strong absorption band at 1522 cm^{-1} , which is formed by the stretching vibration of the C=N bond, and 3085 cm^{-1} due to the stretching vibration of the methylene group. These results indicate that the amidation reaction has been taken by the carboxyl group ($[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$) and the amino group (MIPs) to synthesize Eu-MIPs.

From XPS survey spectra illustrated in Fig. 3(a), it can be seen that both $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs contain C, N, O and Eu elements, while Si elements only appear on the surface of Eu-MIPs, indicating that MIPs have been modified by lanthanide complex to obtain the hybrid materials Eu-MIPs.

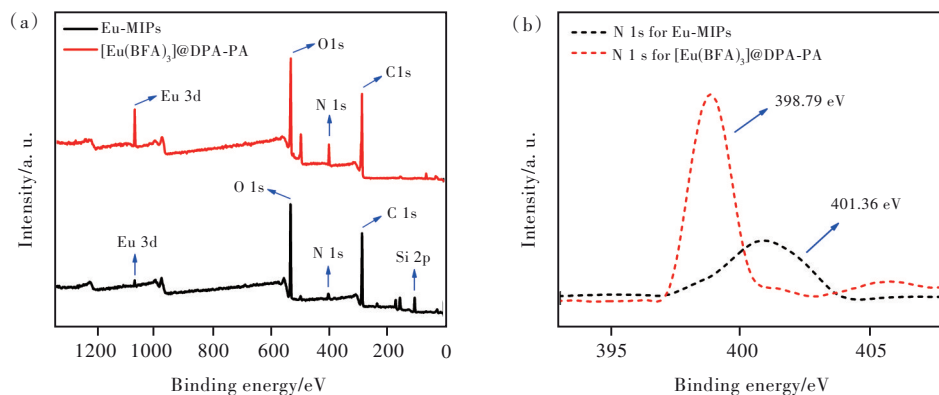


Fig.3 (a) XPS spectrum of $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs. (b) N 1s spectrum of $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ and Eu-MIPs.

Furthermore, Fig. 3 (b) shows that the diffraction peak of N has shifted, and the binding energy has increased from 398.79 eV to 401.36 eV . This may be due to the amidation reaction between the N atom on the amino group of MIPs and the carboxyl group on the Eu^{3+} -based ionic liquid^[25-28]. The FTIR and XPS characterization illuminated the successful synthesis of the Eu-MIPs by coordinating BFA sensitized Eu^{3+} with $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$.

3.2 Photoluminescence Properties of Hybrids Eu-MIPs

The emission spectra of Eu-MIPs (black line) and Eu-MIPs-Hb (red line) exhibited four sharp lines at $\lambda = 593, 613, 651, 697\text{ nm}$, which could be attributed to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions, respectively (Fig. 4). Of which, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition dominated the whole spectrum and was responsible for the luminescence emission of Eu^{3+} in red. It can be used to study the sensing properties of hemoglobin due to the excellent fluorescence properties of Eu-MIPs. In consideration of the excellent luminescent properties of Eu-MIPs, its potential sensing application for various metal cations and hemoglobin has been examined in detail. In addition, with the increasing of quenching effect, the emission intensity at 613 nm (the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+}) is decreasing gradually when excited at 248 nm (slit: $5.0/5.0\text{ nm}$; PMT voltage: 350 V). In addition, after adding Hb, the coordinate values of the CIE chromaticity diagram changed from $(0.6599, 0.3398)$ to $(0.6123, 0.3855)$, and the red luminescence color was significantly lighter under the ultraviolet light of 248 nm , which further confirmed

that Hb can effectively weaken the fluorescence intensity of Eu-MIPs. Therefore, Eu-MIPs can selectively recognize Hb through its fluorescence quenching effect, which is not common in previous reports^[29-30].

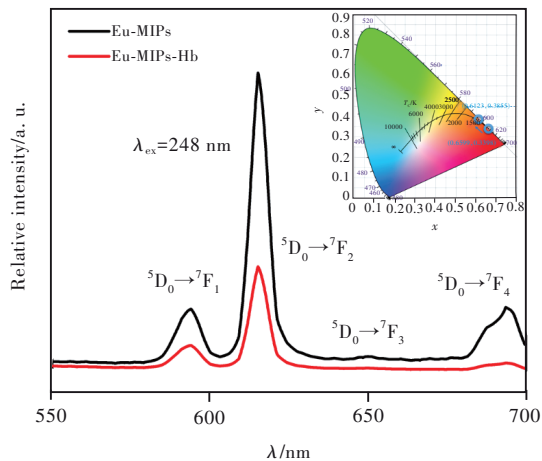


Fig.4 The emission spectra of Eu-MIPs (black line) and Eu-MIPs-Hb (red line). Inset shows the corresponding CIE coordinates.

For further investigation on the photoluminescence sensing properties of Eu-MIPs, we selected a series of ions (K^+ , Mg^{2+} , Na^+ , Ca^{2+} , Zn^{2+} , Cl^-) and took a small amount of the samples to ultrasonically disperse them in aqueous solutions of different ions, the concentration of the solution was 10 mmol. The results are given in Fig. 5, which suggests that the high selectivity of the Eu-MIPs to Hb. As shown in Fig. 5 (a), (b), the characteristic red emission of Eu^{3+} gradually weakened after adding different substances in the sample aqueous solution. Notably, it can be seen from the histogram in Fig. 5 (b) that compared with other ions, Hb can significantly quench the fluorescence intensity of Eu-MIPs. The fluorescence intensity of Eu-MIPs dropped sharply immediately after the addition of Hb and remained stable after about 5 min, indicating that Eu-MIPs responds very quickly to Hb. These results suggest that Eu-MIPs are specific for detecting Hb in aqueous solution. Furthermore, the interfering experiments were performed to investigate the selectivity of the proposed method toward Hb. The anti-interference ability of Eu-MIPs to Hb with the interference of other ions is given in Fig. 5(c). The results indicate that

these ions do not pose any serious interference in the determination of Hb. Therefore, Eu-MIPs have excellent selectivity and anti-interference ability for Hb in aqueous solution.

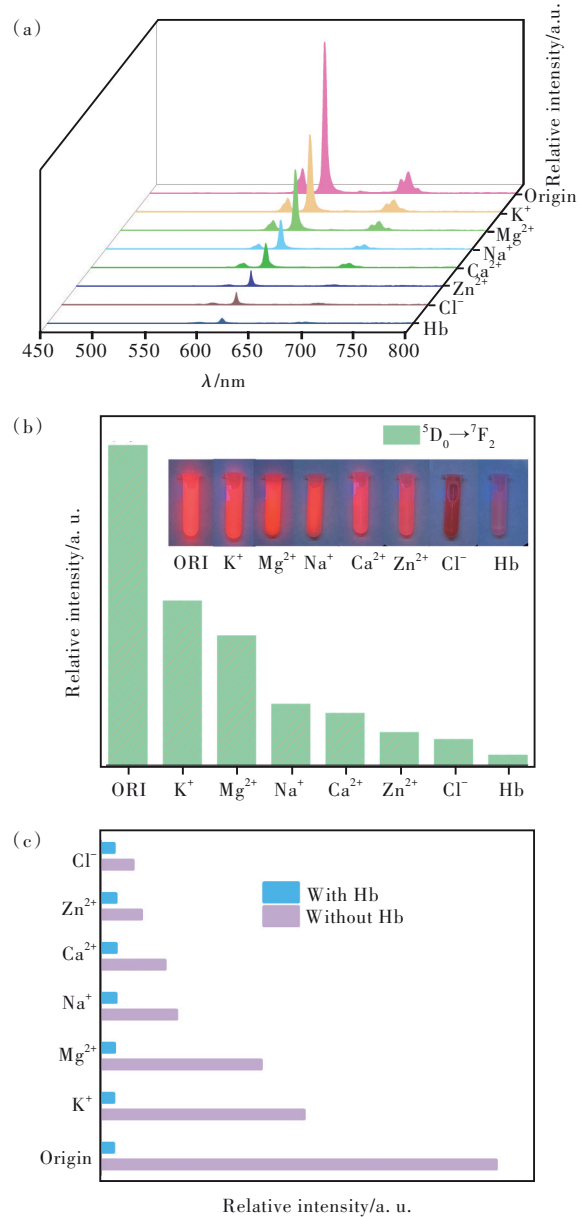


Fig.5 Fluorescence spectra (a) and luminescence intensities (b) of Eu-MIPs for different substances in aqueous solution under excitation at 248 nm. (c) The selectivity and anti-interference ability of Eu-MIPs to Hb under the interference of other substances ($\lambda_{ex}=248$ nm).

To further explore the accuracy of fluorescence detection of Hb by Eu-MIPs, we investigated the effect of Hb concentration on fluorescence quenching. As shown in Fig. 6(a), in the concentration-response luminescence spectrum of Eu-MIPs aqueous solution, the fluorescence intensity in aqueous solution

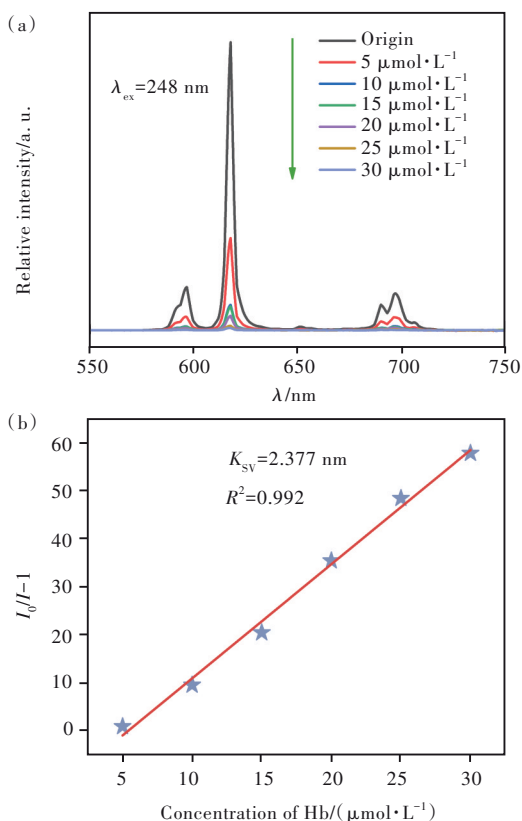


Fig.6 (a) Emission spectra of Eu-MIPs in the presence of 5–30 $\mu\text{mol/L}$ Hb in aqueous solution ($\lambda_{\text{ex}}=248$ nm). (b) Corresponding calibration curves between I_0/I with the concentration of Hb ($\lambda_{\text{em}}=612$ nm).

gradually decreased as the concentration of Hb increased from 5 $\mu\text{mol/L}$ to 30 $\mu\text{mol/L}$. Fig. 6(b) is the fitting curve of the linear relationship between I_0/I and Hb concentration ($R^2=0.992$). The calculated K_{SV} is 2.377, indicating that Hb has a good fluorescence quenching effect on Eu-MIPs. According to the standard of IUPAC 3σ ($\text{LOD}=3\sigma/k$, σ represents the standard deviation obtained by multiple tests on the blank, and k is the slope of the calibration curve), it can be also calculated the detection limit of Hb in water by K_{SV} and σ , which is 0.048 $\mu\text{mol/L}$. Thus, these results further demonstrate that the Hb has strong quenching effect on the fluorescence of Eu-MIPs.

3.3 Possible Mechanism of Fluorescence Quenching of Eu-MIPs

To explain a possible sensing mechanism of Eu-MIPs toward Hb, their luminescence quenching effects were analyzed further. The luminescence intensity of lanthanide elements mainly depends on the

energy transfer efficiency from the ligand to the central ion. As shown in Fig. 7, in the same wavelength range, there is a competitive absorption of light between the ligand and hemoglobin, which inhibits the ligand. The process of energy absorption by the body affects the energy transfer between the rare earth element and the ionic liquid ligand, so that the fluorescence of Eu-MIPs is quenched in the presence of Hb^[31-33].

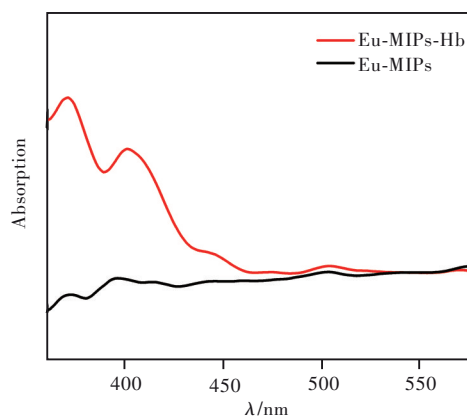


Fig.7 UV-Vis spectroscopic of Eu-MIPs and Eu-MIPs-Hb

4 Conclusion

In summary, MIPs were prepared by adding Hb to the mixed solution of SiO_2 , APTES and TEOS by the sol-gel method, which was then subjected to the amidation reaction with $[\text{Eu}(\text{BFA})_3]@\text{DPA-PA}$ to prepare Eu-MIPs. The structure and properties of Eu-MIPs were characterized, and the results indicated that the prepared polymer had excellent luminescence properties. Under UV excitation, by comparing the fluorescence intensities of Eu-MIPs before and after exposure to Hb, it is found that Hb has a significant quenching effect on the fluorescence of Eu-MIPs, which may be due to the competitive absorption of UV light by Hb and ionic liquid ligands. In turn, the energy transfer process between ligands and rare earths is affected, resulting in the fluorescence quenching of Eu-MIPs. Therefore, Eu-MIPs will be expected to be used as excellent fluorescent probes for the specific detection of Hb.

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