

Synthesis and photophysical study of luminescent ionogels prepared through the confinement of ionic liquid within the $\text{Eu}^{3+}/\text{Tb}^{3+}$ complex covalently bonded polymer networks

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Rare earth complex hybrid ionogel is an emerging functional material that can combine the unique properties of ionic liquids with the luminescent properties of rare earth elements. Here, we report a synthesis of novel luminescent ionogels via a simple and convenient method of basing on the thermal curing method. The luminescent ionogels were prepared by confining the ionic liquid within a cross-linked polymer networks which the $\text{Eu}^{3+}/\text{Tb}^{3+}$ complex covalently bonded onto. The ionogel reported here shows outstanding luminescence properties that originated from the corresponding rare earth complexes: broad excitation spectra, line-like emission spectra, long luminescence lifetimes and so on.

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1. Introduction

Rare earth hybrid materials have been widely studied because of their great potential application in sensing [1], signal amplifier [2], light emitting device [3] and so on. A large part of the rare earth hybrid materials were constructed from the rare earth complexes which are noted for the intense luminescence emission, high quantum efficiency, sharp emission peak and long luminescent lifetime properties [4]. The organic ligands were initially used to increase the light absorption of rare earth ions through the so-called “antenna effect”, but recent researches had shown that some ligands could further act as a bridge molecular for grafting the rare earth ions to various substrates [5]. Carlos *et al.* had done many groundbreaking researches in this respect during the past decades; They had succeeded in immobilizing rare earth complexes in a series of silicon matrix through the couple agent modified organic ligands [6,7]. Zhang’s group had synthesized many kinds of sol-gel hybrid materials based on the rare earth complexes, including visible or near-infrared light emitting materials [8-10]. Yan *et al.* had developed many modification methods of basing on a molecular-bridge moiety for constructing rare earth hybrid materials, such as rare earth complexes functionalized quantum-dot loaded zeolites hybrids, rare earth complexes functionalized MCM-41/SBA-15/SBA-16 hybrids, rare earth complexes modified GaN-based hybrids and so on [11-14].

Ionic liquid is a new emerging solvent which exhibits unique properties such as electric conductivity, dissolution capacity, negligible vapor pressure and high thermal and electrochemical stability [15-17]. Besides as a solvent, the

ionic liquid was also demonstrated to be very useful matrix for preparing luminescent soft materials. Typically, immobilization of ionic liquids by some matrices could form a so-called ionogel materials. Binne mans *et al.* firstly reported the luminescent ionogels which prepared by confining the rare earth complexes in silica and polymer matrices [18-20]. Yan [21] *et al.* had reported luminescent hybrid ionogels that was synthesized by dispersing some rare earth compounds in an confined ionic liquid system, which exhibits the up-conversion photoluminescence property. Li [22] *et al.* had reported some interesting ionogel materials which was synthesized with the carboxyl-functionalized ionic liquids, the resulted materials were proved to be a vapor-sensitive luminescent sensors. As novel soft luminescent materials, the rare earth hybrid ionogels have ability to combine the rare earth compounds with ionic liquids organically, and then present unique optical/electrical properties, therefore, the research of it would draw more attention in the future.

Here, we report a simple and convenient method for preparing the europium/terbium complex functionalized ionogel basing on a thermal curing method. The ionic liquid was confined inside a cross-linked PMMA matrices where the rare earth complexes covalently bonded onto, and finally two transparent rare earth hybrid ionogels were obtained. The photophysical properties of the resulted materials have been investigated in details.

2. Materials and methods

2.1. Materials

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf₂], 99%) was purchased from Shanghai Cheng Jie Chemical Co.; methyl methacrylate (MMA, 99%), methacrylic acid (MAA, 98%), 2-thenoyltrifluoroacetone (TTA, 98%), benzoyl peroxide (BPO, AR) and trifluoroacetylacetone (TFA, 98%) were provided by Aladdin Reagent Co. and used as received. LnCl₃·6H₂O (Ln=Eu/Tb) were prepared by dissolving the corresponding Eu₂O₃/Tb₄O₇ in concentrated hydrochloric acid. All other reagents are analytically pure and purchased from Sinopharm Chemical Reagent Co.

2.2. Physical measurements

The photoluminescent excitation and emission spectra were measured on a Hitachi F-4600 spectrophotometer, while the luminescence lifetime measurements were carried out on an Edinburgh Instrument FLS920. Thermogravimetric analysis (TGA) was performed on the Netzsch TG209F at a heating rate of 10 °C/min under the nitrogen protection. Fourier transform infrared spectra (FTIR) were measured on Shimadzu FTIR-8400S within a KBr slices supporter from 4000-400 cm⁻¹.

2.3. Synthesis of polymerizable rare earth complexes: Eu(TTA)₃MAA and Tb(TFA)₃MAA

The Eu(TTA)₃MAA was prepared as following: a portion of EuCl₃·6H₂O (1 mmol) was dissolved in ethanol at first, the solution was then transferred into a round-bottomed flask which was kept at 60 °C. Then, an appropriate amount of TTA (3 mmol) ethanol solution and MAA (1 mmol) ethanol solution were added into the solution successively while stirring. The mixture was kept at 60 °C for 3 h and then the pH was adjusted to 7-8 with sodium ethoxide. The mixture was stirred at 60 °C for another 5 h, and then was poured into an appropriate amount of deionized water to promote the precipitation of the resulted rare earth complex. The precipitation was collected by filtration and washed with enough cyclohexane. The resulted Eu(TTA)₃MAA was dried at 50 °C overnight in a vacuum oven.

The Tb(TFA)₃MAA was synthesized with the similar method.

2.4. Synthesis of rare earth complexes hybrid ionogels

The rare earth complex hybrid ionogels were prepared by an *in situ* thermal polymerization method: Firstly, 1/100 mmol Eu(TTA)₃MAA was dissolved in 2 mL [Bmim][NTf₂] ionic liquid, followed by the addition of 6

mmol MMA and 1% BPO by weight under nitrogen atmosphere protection. The mixture was stirred and treated by ultrasonic together at 70 °C until a uniform solution formed. After that, the mixture was transferred into a glass sample tube and then polymerized at 70 °C for 8 h under nitrogen atmosphere protection, until a transparent bulky-gel was obtained, the resulted material was denoted as Eu-ionogel.

The synthetic process of Tb-ionogel was similar except that the Eu(TTA)₃MAA were replaced by the corresponding Tb(TFA)₃MAA.

3. Results and discussion

The rare earth complexes functionalized ionogels were prepared by *in situ* thermal polymerizing MMA with the polymerizable rare earth complexes within an ionic liquid solution. The rare earth compounds used here are ternary complexes, whose primary ligands are a typical β-diketone molecular (TTA or TFA) which were used to enhance the luminescent properties of rare earth ions via the “antenna effect”. While the MMA is a coupling molecular which acts both as the second ligand and polymerizable units used for connecting the rare earth ions to the polymer backbone covalently. The ionic liquid [Bmim][NTf₂] used here not only acts as the solvent of reagents but also the main functional filler of the resulted materials. The final products are transparent bulky-gels, Fig. 1 gives the photographs of Eu-ionogel and Tb-ionogel that were taken under daylight and UV lamp, respectively. As shown in the figure, the Eu-ionogel shows a strong red luminescence under the irradiation of 365 nm lights while the Tb-ionogel shows a strong green luminescence under the 254 nm UV Lamp, which proved the method reported here is viable way for constructing novel luminescent materials. The photoluminescent properties of the ionogels have been investigated and discussed in details in the following sections.

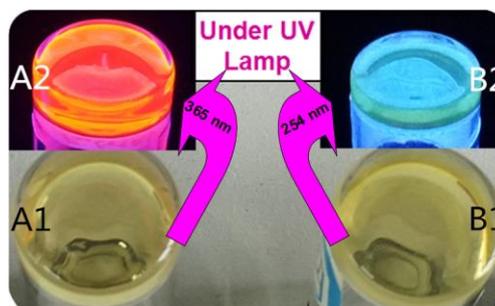


Fig. 1. Photograph of Eu-ionogel and Tb-ionogel: (1) under daylight (A1 and B1); (2) under 365 nm UV Lamp (A1) and 254 nm UV Lamp (B2)

3.1. Fourier transform infrared spectroscopy and thermal gravimetric analysis

In order to verify whether the rare earth complexes were bonded to the polymer networks, a comparative

analysis of Fourier transform infrared spectroscopy (FTIR) was carried out between the ionogels before and after Soxlet extraction treatment that aimed to remove the confined ionic liquids, the results were shown in Fig. 2a. Because of the content of $[\text{Bmim}][\text{NTf}_2]$ is very high while the one of rare earth complexes is at relatively low level, there is not obvious absorption signal that could be assigned to the rare earth complexes within the FTIR spectra of ionogels as shown in Fig. 2a A. The peak around 1731 cm^{-1} can be related to the characteristic vibration band of $\text{C}=\text{O}$ at the PMMA framework. After treated with the Soxlet extraction for removing the embedded ionic liquids, three weak peaks appear at 1596 cm^{-1} , 1560 cm^{-1} and 1533 cm^{-1} (Fig. 2a B and C), which could be assigned to the delocalization effect of the π -electron in the chelate ring moieties formed in the rare earth complexes. Which can be seen as a hard evidence of

that the rare earth complex units have connected to the PMMA framework covalently. In order to investigate the formation and thermal stability of the resulted materials, the Eu-ionogel was chosen as an example for thermal gravimetric (TG) analysis, the result was shown in Fig. 2b. As shown in the TG curve, the major weigh loss procedure appears between $275\text{ }^\circ\text{C}$ and $475\text{ }^\circ\text{C}$ which accounts for nearly 90% of the sample can be associated with the decomposition of the PMMA networks and the embedded ionic liquids. While the minor weigh loss procedure before $275\text{ }^\circ\text{C}$ is probably caused by the physically absorbed water or the residual small molecular. The content beyond $475\text{ }^\circ\text{C}$ probably comes from the residual lithium and europium compounds. It's obviously that the content of ionic liquids confined in the resulted ionogels is up to about 80%.

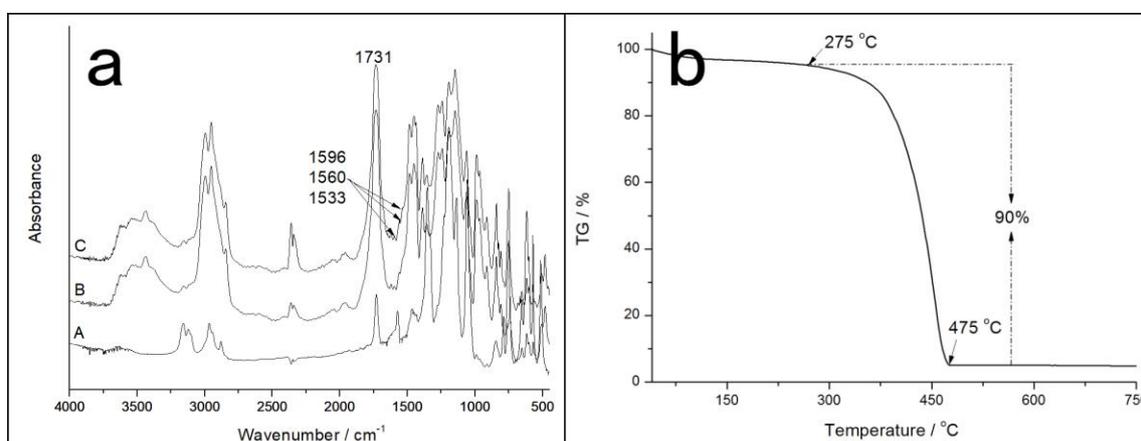


Fig. 2. (a) FTIR spectra of ionogels before (A) and after (B = Eu-ionogel; C = Tb-ionogel) Soxlet extraction; (b) TG analysis curve of Eu-ionogel

3.2. Photophysical properties analysis

The luminescent excitation and emission spectra of Eu-ionogel had been investigated and shown in Fig. 3a and 3b, respectively. The excitation spectra was collected by monitoring the strongest emission band of europium(III) ions at 613 nm, showing a wide adsorption peak which centers at about 350 nm. It suggests that the resulted material has higher ability to absorb ultraviolet lights and then sensitizes the emission of europium(III) ions. Basing on this, the excitation wavelength was set at 350 nm when measuring the luminescent emission spectrum. The result was recorded at room temperature subsequently. As shown in Fig. 3b, the emission peaks at 578, 592, 613, 651 and 702 nm correspond to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions of europium(III) ions, respectively. The

emission spectrum is dominated by an intense peak at 613 nm which corresponds to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition. It is well-known that ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition belongs to the electric dipole transition which strongly depends on the local symmetry of europium(III) ions, while the parity-allowed magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is independent of the ion's surroundings [23]. Thus, the intensity ratio $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2) / I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ is widely used to be the indicator of local environmental symmetry of europium(III) ions. Based on the results, the value of $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2) / I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$ is up to 19.2, indicating that europium(III) ions are surrounded by asymmetric environment. In addition, the strong red luminescence also indicates that the intramolecular energy transfer has took place efficiently between the europium(III) ions and its surroundings when the Eu-ionogel was exposed to the specific ultraviolet lights.

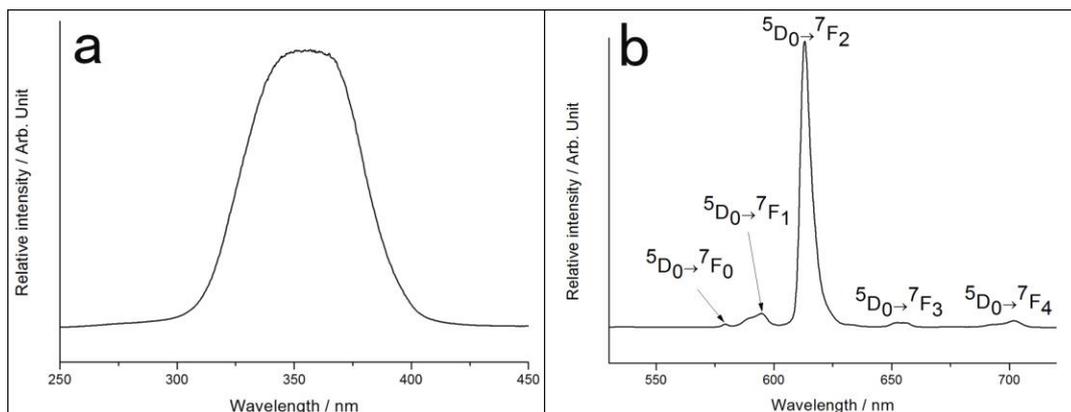


Fig. 3. Excitation (a) and Emission (b) spectra of the Eu-ionogel

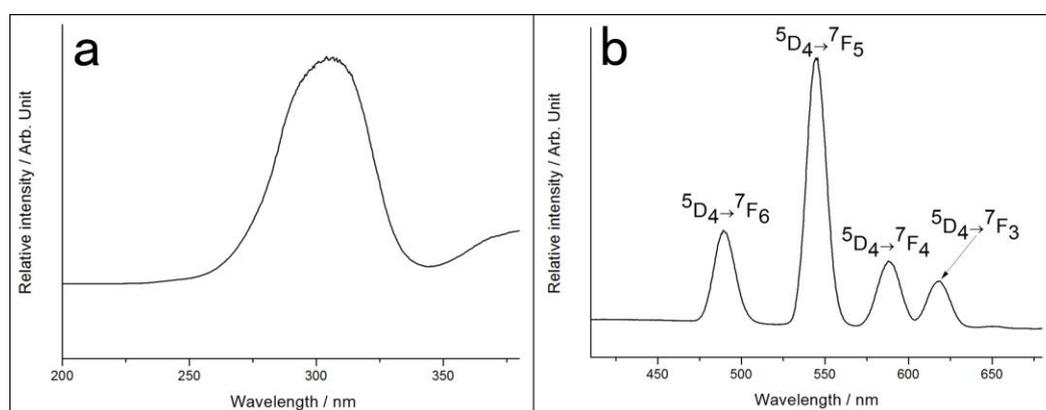


Fig. 4. Excitation (a) and Emission (b) spectra of the Tb-ionogel

In the same way, the luminescent excitation and emission spectra of the Tb-ionogel were measured and presented in Fig. 4a and 4b, respectively. Typically, the excitation spectrum was collected in room temperature by monitoring the strongest emission of terbium(III) ions at 545 nm. As shown in Fig. 4a, the terbium hybrid ionogel possesses a broad excitation band within the ultraviolet region which centers at about 306 nm. Therefore, the 306 nm wavelength was chosen as the excitation source for the luminescent emission measurement. The luminescent

spectrum of Tb-ionogel was also measured at room temperature and shown in Fig. 4b, consisting of four characteristic transition peaks of terbium(III) ions between 450 nm and 650 nm. As shown in the figure, the emission bands center at about 489, 545, 588 and 618 nm could be assigned to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transition of terbium(III) ions, respectively. Among them, the $^5D_4 \rightarrow ^7F_5$ transition is the most intense one which makes the Tb-ionogel striking green luminescence under ultraviolet lights.

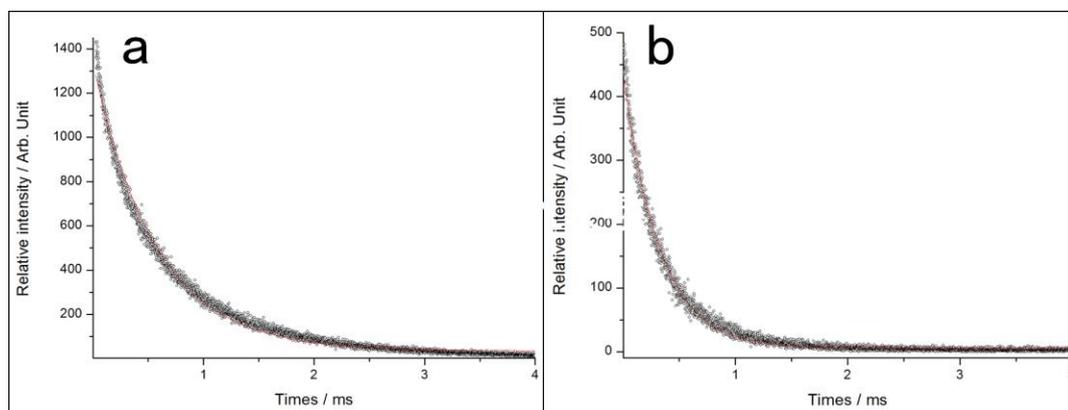


Fig. 5. Luminescence decay curve of Eu-ionogel (a) and Tb-ionogel (b)

Moreover, the luminescent lifetimes for ⁵D₀ energy level of europium(III) ions and ⁵D₄ energy level of terbium(III) ions were measured by the FLS920 fluorescence spectrometer. Fig. 5a and 5b has presented the corresponding luminescence decay curves. Both of the decay curves can be fitted into a single exponential function, and the lifetime values were calculated as 566 ms and 321 ms for Eu-ionogel and Tb-ionogel, respectively. Besides, the theoretical luminescence quantum efficiency (η) of Eu-ionogel was calculated basing on its luminescence lifetime value (τ) and the corresponding emission intensity, according to Judd-Ofelt theory [24]. The detailed methods are listed below:

$$A_{0J} = A_{01} \times \frac{I_{0J}}{I_{01}} \times \frac{\nu_{01}}{\nu_{0J}} \quad (1)$$

$$A_r = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04} \quad (2)$$

$$\frac{1}{\tau} = A_r + A_{nr} \quad (3)$$

$$\eta = \frac{A_r}{A_r + A_{nr}} \quad (4)$$

I_{0J} is the corresponding integrated intensities of ⁵D₀→⁷F_J(J=0~4) transition peaks of europium(III) ions. ν_{0J} (J=0~4) is the energy barycenter of each peak. And the A_{01} refers to the Einstein's coefficient of spontaneous emission between ⁵D₀ and ⁷F₁, whose value was determined to be 50 s⁻¹ theoretically and can be seen as a reference when calculating the values of the other A_{0J} (J=0~4). A_r is the rate of radiative transition of material while A_{nr} is the one of non-radiative. The luminescence quantum efficiency for a specified material can be measured by the rate of radiative transition (A_r) to the total radiation rate ($A_r + A_{nr}$). It is clearly that the value of luminescence quantum efficiency (η) depends strongly on the so-called red/orange ratio (I_{02}/I_{01}) and the lifetime value. Ultimately, the η value of Eu-ionogel was determined to be 58.39%.

4. Conclusions

In summary, we had designed and synthesized two rare earth hybrid ionogels by thermal curing method, which has been proven to be a simple and convenient way for constructing novel luminescent hybrid materials. The photoluminescent properties of Eu-ionogel and Tb-ionogel had been characterized in details, results show that the ionogels possess well luminescent properties such as broad excitation spectrum, line-like emission spectrum, long luminescent lifetime and so on. Thereinto, the luminescent quantum efficiency of Eu-ionogel is up to 58.39% according to the theoretical calculation and the analysis of luminescence properties. The results show that the ionogels reported here could act as a favorable carrier

for rare earth complexes when preparing novel luminescent materials. Further efforts on rare earth hybrid ionogels will be put on its conductivity and applied potential for assembling photoelectric devices.

Acknowledgments

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