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**Luminescent ionogel based on europium (III)-coordinated carboxyl
–functionalized ionic liquid and gelatin**

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Abstract

In this work, we report the preparation and luminescent properties of a novel luminescent ionogel consisting of carboxyl-functionalized ionic liquid, Eu^{3+} ions and gelatin. The obtained ionogel was investigated by FT-IR, SEM and photoluminescence spectroscopy. FT-IR spectra show that both the ionic liquid and the gelatin are coordinated to Eu^{3+} ions through oxygen atoms. Luminescence data confirms that Eu^{3+} ions are well-protected by the ionic liquid and gelatin from deleterious quenching interactions with water molecules.

Introduction

Ionic liquids (ILs) have been attracting intensive attentions due to their unique properties such as low volatility, thermal stability, non-flammability, high ionic conductivity, electrochemical stability, and so on.¹⁻³ These attractive properties make ILs suitable for a wide range of electrical energy generation and storage applications⁴⁻⁶. Furthermore, the use of ILs in the preparation of materials is becoming more and more important.⁷⁻¹³ In order to make ILs more suitable for materials applications, there is currently a challenging need for immobilizing them in solid devices and simultaneously keeping the main properties of ILs except flow. The

immobilization of ILs within solid matrices such as inorganic materials or polymers leads to a new class of organic-inorganic hybrid materials, which also is known as a new class of solid state electrolytes or ionogels.^{5, 14-24} They have already found applications in electrochemical devices.²⁵⁻²⁸ Furthermore, ionogels have also been used as the matrices for developing luminescent organic-inorganic hybrid materials.^{23, 29-35, 36-38, 39-41} We have previously reported luminescent ionogels prepared by doping carboxyl-functionalized IL coordinated with Eu^{3+} ions³⁶⁻³⁸ into the organosilica.³⁹ The study revealed that the presence of ILs can significantly increase the lifetime and quantum efficiency of Eu^{3+} ions.^{39, 42} To date, the reported luminescent ionogels mainly employ silica or PMMA as the matrices although ionogels combining IL and biopolymer such as gelatin have appears frequently.^{17, 43, 44}

In this study, we report a novel luminescent ionogel by doping europium (III) ion-containing carboxyl-functionalized IL ($\text{Eu}[\text{Carb-C}_1\text{mim}]\text{Br}^{38}$) into gelatin. Gelatin is an inexpensive, nontoxic and natural biocompatible biopolymers derived from collagens that are a mixture of many single- or multi- stranded polypeptides predominantly, glycine, proline and 4-hydroxyproline⁴⁵, which possesses large variety of functional groups that can coordinate to europium (III) ions.

Experimental

Materials: 1-Methylimidazole (99%, Aldrich), 3-Bromopropionic ($\geq 98\%$, Aldrich), Eu_2O_3 (99%, Aldrich), Gelatin (97.78%, Tianjin Fengchuan Chemical Reagent Science And Technology Co., Ltd.) were used as received without further purification. The carboxyl-functionalized IL was synthesized according to the reported method.⁴⁶ ($\text{Eu}[\text{Carb-C}_1\text{mim}]\text{Br}$) was prepared as discribed previously.³⁸ The molar ratio of Eu^{3+} : [$\text{Carb-C}_1\text{mim}]\text{Br}$ is 1:3. The obtained $\text{Eu}[\text{Carb-C}_1\text{mim}]\text{Br}$ shows good solubility in water.

Preparation of ionogel: Gelatin (1 g) was dissolved in 5 mL of deionized water, 1 g of Eu-[Carb-C₁mim]Br dissolved in 5 mL of water was then added and a homogenous solution was obtained, which was then heated at 40 °C overnight. Evaporation of waters at 60 °C for one week resulted in the luminescent ionogels.

Characterization: Infrared (IR) spectra were obtained on a Bruker Vector 22 spectrometer in the range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹. SEM images were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV. The steady-state luminescence spectra and the lifetimes were measured on an Edinburgh Instrument FS920P spectrometer, with a 450W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm⁻¹), an emission monochromator (600 lines mm⁻¹), and a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Results and discussion

Gelatin shows perfect solubility in water, water-soluble europium (III) compounds should be employed to prepare the biopolymer based-luminescent ionogels. We therefore choose a Eu³⁺-coordinated IL which is derived from reaction of Eu₂O₃ with a carboxyl-functionalized IL and is soluble in water³⁸. The luminescent ionogels were easily obtained by mixing the aqueous solutions of gelatin and the Eu³⁺-coordinated IL in flask and followed by evaporation some of the waters at 60° C for several days. The obtained ionogels show red emission color under UV irradiation (Figure 1).

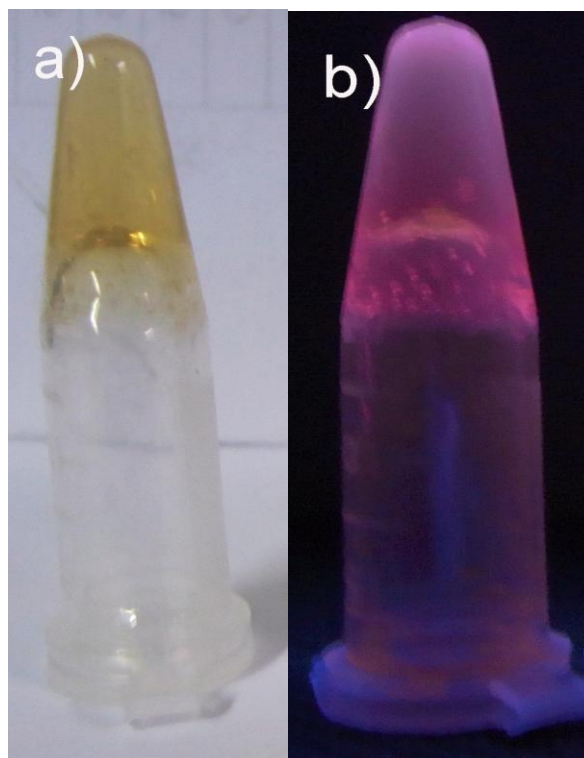


Figure 1 Digital photo graphs of the luminescent ionogel. Under day light (left) and under UV light (right)

Figure 2 shows the FT-IR spectra of the gelatin, Eu-[Carb-C₁mim]Br and the luminescent ionogel. Several absorption bands at 3289 cm⁻¹ (N-H stretching vibration), 2965 cm⁻¹ (C-H stretching vibration), 1650 cm⁻¹ (amide I C=O stretching vibration), 1541cm⁻¹ (amide II, N-H bending vibration) are observed in the FT-IR spectrum of the gelatin (Figure 2a). Bands at 1556 and 1445 cm⁻¹ can be observed in the FT-IR spectrum of Eu-[Carb-C₁mim]Br, which can be assigned to the asymmetric and the symmetric stretch of the caboxylate group, respectively (Figure 2b). No absorption band at 1726 cm⁻¹ from the -COOH group can be observed in Figure 1b, indicating that all the carboxyl-functionalized ILs are coordinated to Eu³⁺ ions. In the FT-IR spectrum of ionogel (Figure 2c), the absorption band corresponding to amide I C=O stretching vibration shifts to 1641cm⁻¹, the coordination of Eu³⁺ to the oxygen

atoms of C=O groups can be responsible for the shifting. The morphology of the luminescent ionogels was investigated by scanning electron microscope (SEM), and the SEM image is shown in Figure 3, which reveals that the ionogels are composed of nanoparticles with diameter of 30 nm. The nanoparticles are aggregated to form the monolith.

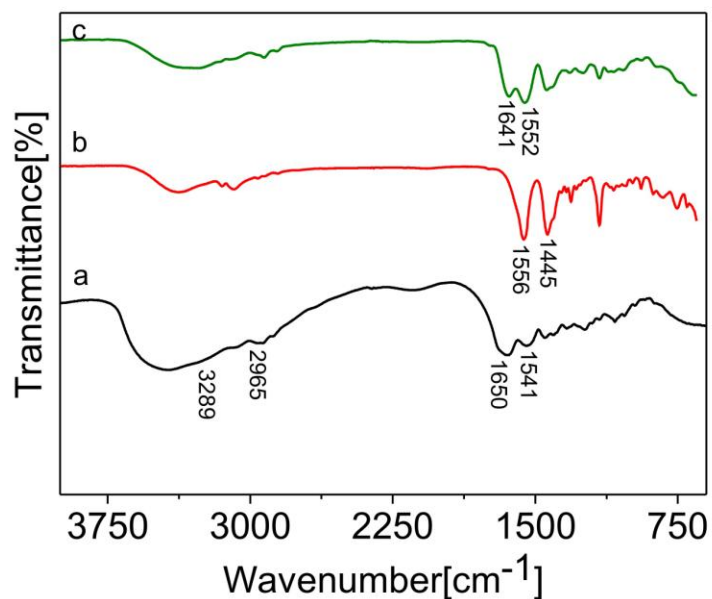


Figure 2 FT-IR spectra of a) gelatin, b) Eu-[Carb-C₁mim]Br and c) the luminescent ionogel.

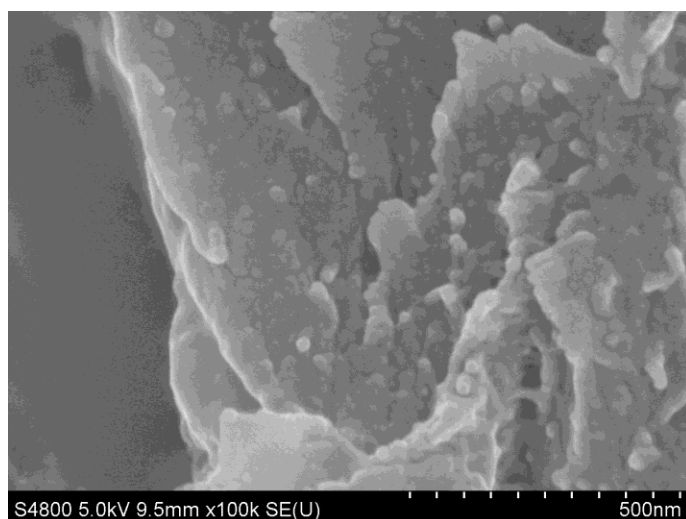


Figure 3 SEM image of the luminescent ionogel.

The excitation and emission spectra of Eu-[Carb-C₁mim]Br are shown in Figure 4. The excitation spectrum obtained by monitoring the $^5D_0 \rightarrow ^7F_2$ line at 617 nm shows several discrete line-like absorption bands at 318, 262, 380, 395, 415 and 465 nm, which can be attributed to the transition of $^7F_0 \rightarrow ^5H_6$, $^7F_0 \rightarrow ^5D_4$, $^7F_0 \rightarrow ^5G_2$, $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_2$, respectively. The absorption band at 395 nm dominates the excitation spectrum. Upon excitation at 395 nm leads to line-like emission bands arising from the transition between $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) peaking at 579, 592, 617, 650, 696 nm, respectively, with the hypersensitive transition at $^5D_0 \rightarrow ^7F_2$ as the most prominent line, which indicates that Eu³⁺ sites are indeed without a center of inversion.²⁹ The luminescence decay curve is found to be mono-exponential, indicating the presence of only one type of Eu³⁺ symmetry site. The luminescence time of the 5D_0 level is 0.579 ms.

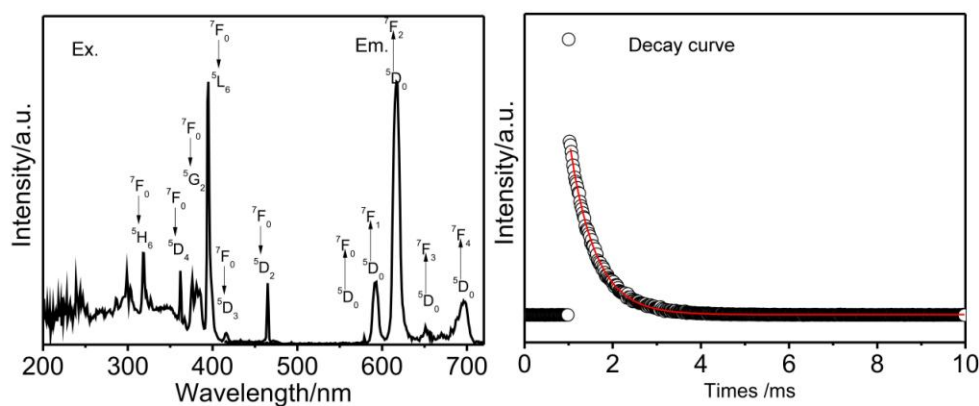


Figure 4 Luminescent data of Eu-[Carb-C₁mim]Br. Excitation spectrum was observed at 617 nm for both samples. Emission spectrum was obtained upon excitation at 395nm. The decay curve was obtained by excitation at 395 nm.

The excitation and emission spectra of the luminescent iongel are shown in Figure 5. Unlike that of Eu-[Carb-C₁mim]Br, in addition to the line-like absorption bands attributed to the f-f transitions, a broad band in the range of 200-450 nm can be also observed, the origin of this broad band is unclear now. The emission spectrum excited with a wavelength of 395 nm shows similar emission bands composed of five line-like emission lines. Similarly, the decay curve of Eu³⁺ ions in the luminescent iongel can also be well-fitted with one exponential function. The decay time is determined to be 0.810 ms, which is longer than that of Eu³⁺ ions in Eu-[Carb-C₁mim]Br. The prolonged lifetime indicates the repulsion of water molecules from the coordination sphere due to the coordination of C=O groups to Eu³⁺ ions. We recently observed a remarkable luminescence enhancement upon the addition of a imidazolium based molecule in the Eu³⁺ β-diketonate complexes confined within zeolite due to the decreased proton strength in the channels of zeolite L. The obtained photophysical data in the current work inspires us to try the use of the carboxyl-functionalized IL in the system described in ref⁴⁷ in further investigations.

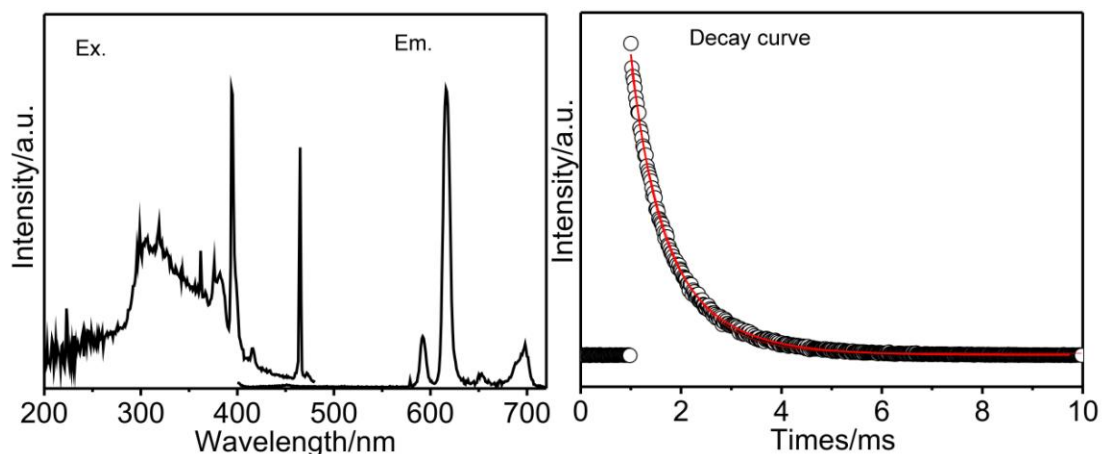


Figure 5 Luminescent data of the luminescent iongel. Excitation spectrum was observed at 617 nm for both samples. Emission spectrum was obtained upon

excitation at 395nm. The decay curve was obtained by excitation at 395 nm.

On the basis of the empirical formula suggested by Supkowski and De Horrocks Jr,⁴⁸ we can estimate the number of water molecules (n_w) coordinated to the metal ions in the material, which can be written as:⁴⁸

$$n_w = 1.1(k_{\text{exp}} - k_r - 0.31) \quad (1)$$

Where k_{exp} is the reciprocal value of the $^5\text{D}_0$ lifetime, and k_r is the radiative probabilities.

The radiative contribution maybe calculated from the relative intensities of the $^5\text{D}_0 - ^7\text{F}_J$ ($J = 0 - 4$) transitions (the transitions $^5\text{D}_0 - ^7\text{F}_J$ with $J = 5$ and 6 are either not observed or are very weak) and can be expressed as:

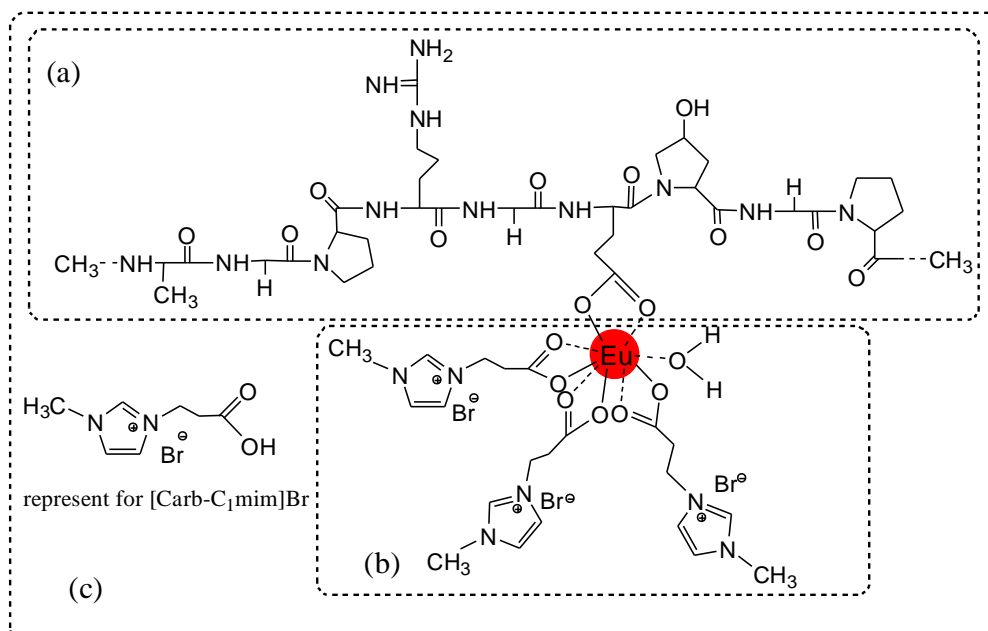
$$k_r = \frac{A_{0-1}E_{0-1}}{S_{0-1}} \sum_{J=0}^4 \frac{S_{0-J}}{E_{0-J}} \quad (2)$$

Where A_{0-1} is the Einstein coefficient of spontaneous emission between the $^5\text{D}_0$ and $^7\text{F}_1$ level, usually considered to be equal to 50 s^{-1} , and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $^5\text{D}_0 - ^7\text{F}_J$ transitions, respectively.

The data obtained are summarized in Table 1. From the result, it is reasonable to assume that much more water molecules have been expelled from the first coordination sphere of Eu^{3+} ions from the luminescent ionogel than the coordination complex. The possible chemical structure of samples could be seen in Scheme 1.

Table 1 Experimental $^5\text{D}_0$ lifetime, calculated radiative $^5\text{D}_0$ decay rate, number of waters coordinated to Eu^{3+} ion in $\text{Eu}[\text{Carb-C}_1\text{mim}]\text{Br}$ and the luminescent ionogel.

samples	τ /ms	k_r /ms ⁻¹	k_{exp} /ms ⁻¹	n_w
Eu-[Carb-C ₁ mim]Br	0.579	0.332	1.727	1.194
ionogel	0.810	0.413	1.235	0.563



Scheme 1 Possible chemical structure of a) Gelatin b) Eu-[Carb-C₁mim]Br c) the luminescent ionogel

Conclusions

In summary, we have reported a novel luminescent ionogel via the doping of water-soluble europium (III)-coordinated ILs into the bio-degradable gelatin. The ratio between the areas of the $^5D_0 / ^7F_2$ and $^5D_0 / ^7F_1$ transition bands as well as the value of decay time of Eu^{3+} ions in the ionogel are larger than that in the europium (III)-coordinated ILs, the coordination of gelatin to Eu^{3+} ions has been believed to be responsible for the larger values. The luminescent ionogel can be effectively excited by 395 nm wavelength and can emit bright red emission, which make this novel

luminescent ionogel be suited to cooperation with UV emitting LEDs.

Acknowledgements

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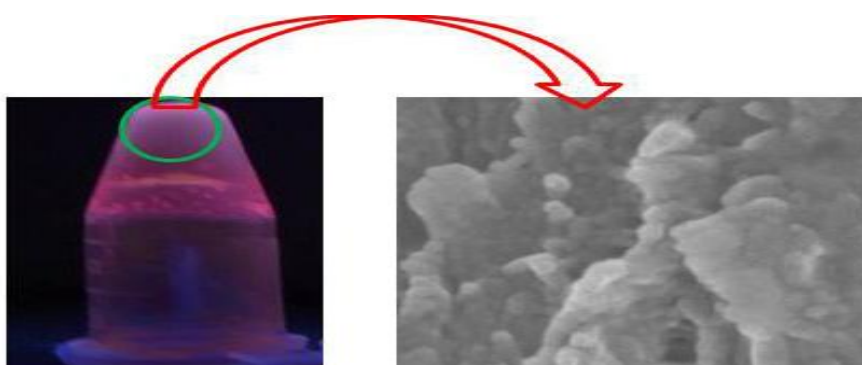
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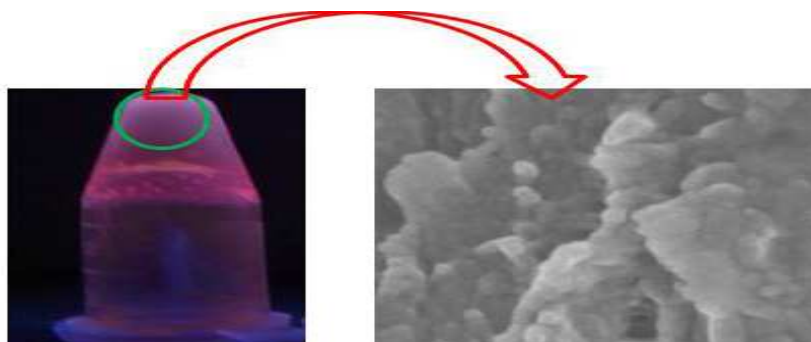
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