# Photophysical Properties of Lanthanide (Eu<sup>3+</sup>, Tb<sup>3+</sup>) Hybrid Soft Gels of Double Functional Linker of Ionic Liquid–Modified Silane

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### ABSTRACT

Four kinds of luminescent hybrid soft gels have been assembled by introducing the lanthanide (Eu<sup>3+</sup>, Tb<sup>3+</sup>) tetrakis  $\beta$ -diketonate into the covalently bonded imidazolium-based silica through electrostatic interactions. Here, the imidazoliumbased silica matrices are prepared from imidazolium-derived organotriethoxysilanes by the sol-gel process, in which the imidazolium cations are strongly anchored within the silica matrices while anions can still be exchanged following application for functionalization of lanthanide complexes. The photoluminescence measurements indicated that these hybrid soft gels exhibit characteristic red and green luminescence originating from the corresponding ternary lanthanide ions (Eu<sup>3+</sup>, Tb<sup>3+</sup>). Further investigation of photophysical properties reveals that these soft gels have inherited the outstanding luminescent properties from the lanthanide tetrakis  $\beta$ -diketonate complexes such as strong luminescence intensities, long lifetimes and high luminescence quantum efficiencies.

#### INTRODUCTION

It has long been well recognized that trivalent lanthanide elements have excellent luminescent properties, which is due to the shielding of the inner 4f orbital by the filled  $5p^{6}6s^{2}$  subshells and the abundant transition energy level (1). As a result, the photophysical properties of trivalent lanthanide ions have attracted much attention due to their potential applications in the field of light-emitting devices, optical amplifiers, laser materials, functional probes for chemical or biological systems and biological imaging techniques (2-8). However, the wide application of lanthanide ions themselves to luminescent materials has been limited for a long period, which is mainly due to their low molar absorption coefficients as the f-f transitions are Laporte forbidden (9), so that it is difficult to generate efficient luminescence by direct excitation of the lanthanide ion. To resolve this problem, the lanthanide ions are usually either doped into some special matrices such as oxides and oxysalts or chelated with an adjacent strongly absorbing chromophore in the UV region (10). For the latter, the usually used sensitizing ligands mainly comprise  $\beta$ -diketones, aromatic carboxylic acids and heterocyclic ligands (11). Among these molecular systems, the lanthanide  $\beta$ -diketonate complexes are the most intensely studied ones due to their intense emission bands, long luminescent lifetime and high luminescence quantum efficiency (12,13). However, for practical

applications, such lanthanide complexes still have poor thermal stability and low mechanical strength (14). To overcome these, the organic–inorganic hybrid matrix materials have attracted considerable attention because of the ability to integrate the photophysical properties of the organic components and the favorable thermal and mechanical properties of the inorganic networks (15–17).

Room-temperature ionic liquids (RTILs) are salts which have melting points below room temperature and compose entirely of ions (18). Over the past decades, RTILs have received numerous attentions for their potential application due to their low melting points, negligible volatility, nonflammability, increased thermal stability, high electrochemical window and ease of recycling, etc. (19). For material field applications, one of the important strategies for using ionic liquids is by confining them into some porous solids to obtain so-called "ionogels" (20). By confining the lanthanide-doped ionic liquid mixtures into porous silica network, Binnemans et al. have prepared some highly luminescent inorganic-organic hybrid ionogels (21,22). And they also prepared a kind of flexible luminescent polymer film by confining europium complexes-doped ionic liquid into the PMMA membrane (23). Vioux et al. has been conscious of the applications of ionogels early and discussed its properties, preparation and potential applications in great details (24-26). An alternative approach is to covalently immobilize the ionic liquids on silica supports via bridged silsesquioxanes formation for constructing functional materials (27,28). Here, an N'-alkyl imidazolium-based silylated ionic liquid, which contains the trialkoxysilyl groups, is mostly used (29). Carlos et al. have successfully prepared several kinds of imidazolium salt-immobilized silica-supported materials with europium tetrakis( $\beta$ -diketonate) complex anion counterions assembled through electrostatic interactions, which emit intense luminescence of the trivalent europium ions (30). We have also successfully prepared some kinds of luminescent materials using the imidazoliumbased silvlated ionic liquid as building blocks (31,32).

Here, we synthesized and performed characterization of a set of luminescent soft gels by immobilizing the imidazolium-based silylated ionic liquid to silica-based matrix followed by an anion metathesis assembly. Finally, all the resulting materials have been investigated in detail with respect to their characteristic and photoluminescent properties.

#### MATERIALS AND METHODS

*Materials.* The EuCl<sub>3</sub>·6H<sub>2</sub>O and TbCl<sub>3</sub>·6H<sub>2</sub>O were prepared by dissolving their corresponding oxides in concentrated hydrochloric acid followed by evaporation. 1-Chlorohexane (98%), lithium bis(trifluoromethanesulfonyl)

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imide (98%), 3-(Chloropropyl)triethoxysilane (98%, (OEt)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>Cl), 1-Methylimidazole (99%), Thenoyltrifluoroacetone (98%, TTA), 1,1,1-Trifluoroacetylacetone (98%, TFA), hexafluoroacetylacetone (98%, HFA) and 2-Naphthoyltrifluoroacetone (98%, NTA) are purchased from Adamas reagent company and used as received. Formic acid (97%, FA), Tetramethoxysilane (98%, TMOS) and Sodium hydroxide (98%, NaOH) are purchased from Alfa Aesar and generally used as received. All the other reagents were analytical pure and purchased from China National Medicines Group.

Synthesis procedures of 1-methyl-3-[3-(triethoxysilyl)propyl]-imidazolium chloride. The 1-methyl-3-[3-(triethoxysilyl)propyl]imidazolium chloride [Mtespim][Cl] was prepared using a previous reported method (33) as following: the (OEt)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>Cl was mixed with the same equivalent 1-methylimidazole and added to a two-necked, round-bottomed flask equipped with a magnetic stirrer. Then, the mixture was kept at 70°C for 72 h under argon protection with vigorous stirring. The resulting pale yellow viscous liquid was then cooled to room temperature and washed with anhydrous cyclohexane. The upper cyclohexane was decanted directly and the procedure was repeated three times. Finally, the residual cyclohexane was removed by reduced pressure distillation using a rotary evaporator.

Synthesis procedures of 1-hexyl-3-mexylimidazolium bis[(trifluoromethyl)sulfonyl]imide. The ionic liquid 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide [C6mim][Tf<sub>2</sub>N] was synthesized from [C6mim][C1] by a metathesis reaction between lithium bis(trifluoromethylsulfonyl)imide Li[Tf2N]2 and [C6mim][Cl] according to the previous literatures (34-36). Firstly, the 1-hexyl-3-methylimidazolium chloride ([HMIM][Cl]) was prepared as follows: 4 mmol of 1-methylimidazole and 4 mmol 1-chlorohexane were added to a two-necked, roundbottomed flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was heated under argon protection at 80°C with stirring for 1 week. The resulting viscous liquid was then cooled to room temperature and washed with ethyl acetate by thorough mixing. The upper ethyl acetate was decanted directly and the procedure was repeated three times. Finally, the residual ethyl acetate was removed with the rotary vacuum distillation apparatus by heating at 80°C. Subsequently, an aqueous solution of 4.5 mmol lithium bis(trifluoromethanesulfonyl)imide was added to [HMIM][Cl] with thorough mixing. Then, the mixture was washed several times with aliquots of deionized water until no longer chloride residues were detected by the AgNO<sub>3</sub> test. The product was dried at 80°C overnight under vacuum condition to afford an oil-like [C6mim][Tf<sub>2</sub>N] at room temperature.

Synthesis of lanthanide complexes  $NEt_4Ln(L)_4$  (for Ln = Eu, L = TTAor NTA; while Ln = Tb, L = HFA or TFA). The lanthanide complexes NEt<sub>4</sub>Eu(TTA)<sub>4</sub> were synthesized by a method previously described by us (32). Typically, in a two-necked, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer, 4 mmol of TTA was dissolved in ethanol and this ligand was deprotonated with 4 mmol NaOH at 60°C for 2 h. Subsequently, a portion of EuCl<sub>3</sub>·6H<sub>2</sub>O solution (1 mmol in ethanol) was added to it dropwise, followed by the addition of 1 mmol NEt<sub>4</sub>Cl in ethanol. The solution was reflexed at 60°C for another 1 h. Then, the mixture was filtered to remove the white precipitate, sodium chloride. The resulted filtrate was the ethanol solution of NEt<sub>4</sub>Eu(TTA)<sub>4</sub> and was transferred into a flask for anion exchange. For NEt<sub>4</sub>Eu(NTA)<sub>4</sub>, the same procedure was used except that the TTA was replaced by NTA. The synthesis procedures for NEt<sub>4</sub>Tb(TFA)<sub>4</sub> and NEt<sub>4</sub>Tb(HFA)<sub>4</sub> are similar to that of NEt<sub>4</sub>Eu(TTA)<sub>4</sub> except that the ligand TTA was replaced by TFA and HFA and the EuCl<sub>3</sub>·6H<sub>2</sub>O was replaced by TbCl<sub>3</sub>·6H<sub>2</sub>O.

Synthesis procedures of the lanthanide complexes-functionalized soft gel. The ionogel was prepared according to a modified published method using a nonhydrolytic sol-gel route (37). In a Teflon vial, 1 mmol [C6mim][Tf<sub>2</sub>N] and 26 mmol FA were stirred well at room temperature, and then a mixture of [Mtespim][Cl] and TMOS was added to the solution (molar ratio FA/TMOS/[Mtespim][Cl]/[C6mim][Tf<sub>2</sub>N] = 7.8/0.9/0.1/ 0.3). After stirring well, the mixture was exposed at ambient temperature for 2 weeks and then a transparent monolith bulk ionogel was obtained. Unfortunately, the monolithic ionogels fragmentized during the following experimentation. After a 48 h extraction in Soxhlet extractor with refluxing acetonitrile, the entrapped ionic liquid [C6mim][Tf2N] was removed. Then, the gel material was dried at 50°C overnight under vacuum condition to remove the residual acetonitrile. After that, the gel material was directly immersed into the previous solution of NEt<sub>4</sub>Ln(L)<sub>4</sub> for anion exchange at room temperature. After a week, the gel material was taken out and transferred into Soxhlet extractor with refluxing ethanol to remove the excess NEt<sub>4</sub>Ln(L)<sub>4</sub>. As before, the lanthanide complexes– functionalized gel material was dried at 50°C overnight under vacuum condition to remove the residual ethanol. Subsequently, a series of fragmented luminescent soft gels: Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup>, Gel-Im<sup>+</sup>[Eu (NTA)<sub>4</sub>]<sup>-</sup>, Gel-Im<sup>+</sup>[Tb(TFA)<sub>4</sub>]<sup>-</sup> and Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup> were obtained.

*Physicochemical characterization.* Fourier transform infrared spectra (FTIR) were measured within KBr slices from 4000 to 400 cm<sup>-1</sup> using a Nexus 912 AO446 infrared spectrum radiometer. X-ray powder diffraction patterns (XRD) were acquired on Rigaku D/max-Rb diffractometer equipped with Cu anode; the data were collected within the  $2\theta$  range  $10^{\circ}$ - $70^{\circ}$ . Scanning electronic microscope (SEM) images were obtained with a Philips XL-30. Transmission electron microscope (TEM) experiments were performed using a JEOL2011 microscope operated at 200 kV. Thermogravimetric analysis (TG) was carried out using a Netzsch STA 449C system at a heating rate of 5°C/min under the nitrogen protection. The diffuse reflectance UV–vis spectra of the powdered samples were recorded by a BWS003 spectrophotometer. Luminescence excitation spectra, emission spectra, lifetimes and quantum efficiencies are measured on an Edinburgh Instruments FLS 920 fluorescence spectrometer.

#### **RESULTS AND DISCUSSION**

The silica-based matrix is prepared through an ionic liquidmediated nonhydrolytic sol-gel route, using a mixture of TMOS, FA, 1-hexyl-3-mexylimidazolium bis[(trifluoromethyl) sulfonyl]imide and 1-methyl-3-[3-(triethoxysilyl)propyl]-imidazolium chloride. The formic acid used here serves as a solvent, water source and catalyst for both hydrolysis and condensation. After the completion of gelation, the confined ionic liquid was removed by Soxhlet extraction. Then, different lanthanide tetrakis( $\beta$ -diketonate) complex anions are assembled into the matrix through electrostatic interactions after a simple anion metathesis reaction. The synthetic route is shown in the Scheme 1 and the detailed synthetic procedures are given in the following experimental section.

The FTIR spectra of lanthanide complexes-functionalized soft gels are shown in Fig. 1. As shown in the FTIR spectra, a weak characteristic absorbance for the ring stretching of imidazolium moiety is found at 1578 cm<sup>-1</sup>, suggesting that the ionic liquid [Mtespim][Cl] has been successfully immobilized onto the framework of silica matrix (38). The imidazolium moiety also exhibits the characteristic bands (39) of aromatic C-H stretching at 3162, 2953 and 2882  $\text{cm}^{-1}$ . The absorptions at 1690  $\text{cm}^{-1}$  are assignable to the stretching vibration of carbonyl groups, which come from the residual formic acid confined deeply in the soft gels. For the lanthanide complexes moieties, there are only very weak absorption peaks that appear at about 1626  $\text{cm}^{-1}$ , which could be assigned to the carbonyl stretching band of the  $\beta$ -diketone ligands coordinated to the lanthanide ions. Meanwhile, the band appearing at 1459 cm<sup>-1</sup> can be ascribed to the scissoring vibration of -(CH<sub>2</sub>)<sub>3</sub>- groups originated from 3-(chloropropyl)triethoxysilane (40), which further evidences the immobilization of [Mtespim] [Cl]. The asymmetric stretching of Si-O-Si appears as a very strong band at 1067 cm<sup>-1</sup>, whereas the bending stretching vibration of it appears at 798 and 451 cm<sup>-1</sup>. The medium intensity band at 950 cm<sup>-1</sup> and the shoulder at about 570 cm<sup>-1</sup> are associated with the Si-O stretching vibrations of the silanol (Si-OH) of surface groups (41). Moreover, the broad band around 3600 cm<sup>-</sup> and the weak band at 1630  $\text{cm}^{-1}$  can be assigned to the bending and stretching vibrations of -OH of the physical adsorbed water. It was worth noticing that the Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup> shows a relatively stronger band than the other ones, which may be owing to the higher content of fluorine for the HFA ligand.

Figure 2 shows the room-temperature XRD patterns of the all lanthanide complexes-functionalized soft gels from 10° to 70°. All curves exhibit a similar single broad hump centered at 23.4°, which demonstrates the amorphous nature of the soft gels. According to the literatures (42,43), these broad peaks can be associated with the presence of amorphous siliceous domains in soft gels. Furthermore, the absence of any sharp and strong peak in the diffraction curve of these samples correlates well with the absence of a large crystalline region. In addition, none of the hybrid materials contains measurable amounts of phases corresponding to the pure lanthanide tetrakis( $\beta$ -diketonate) complexes, which is an indication of the formation of true homogeneous lanthanide complexes-functionalized soft gels. SEM and TEM of the most efficient luminescent hybrid soft gel Gel-Im<sup>+</sup>[Eu (TTA)<sub>4</sub>]<sup>-</sup>, which demonstrate a homogeneous materials were shown in Fig. 3. As clearly shown in the SEM images (A, B), a relatively homogeneous fine porous structure is observed on the surface of this material. The main reason for the porosity property is probably the confinement and extraction effect of the ionic liquid [C6mim][Tf<sub>2</sub>N] through the sol-gel processes and Soxhlet extraction. Accordingly, this kind of fine porous structure also can be seen in other hybrid soft gels. As we discussed above, however, the hybrid soft gels discussed in this study are a kind of noncrystalline state materials with amorphous nature. Therefore, there exists no exact long-range ordered microstructure that we can see from its TEM images (Fig. 3C,D), which is also a coincidence with the results of XRD analysis.

To investigate the thermal stability of the obtained hybrid materials, the TG and differential thermogravimetric trace (DTG) are performed on the most efficient luminescent hybrid soft gel Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup> as a representative example under a nitrogen atmosphere at a heating rate of 5°C/min. As shown in the Fig. 4, the TG curve could be divided into four main weight loss procedures with the help of DTG curve analysis. The first weight loss procedure before 175°C can be attributed to the loss of physically absorbed water and residual solvent. When we continue heating, the gel material may further crack and release those deeply wrapped solvent confined during the sol–gel processes, which is associated with to the second step (ranging from 175°C to 258°C) of weight loss. While the third procedure of weight loss between 258°C and 430°C could be associated with

the decomposition of the europium complexes attaching onto the soft gel matrices through electrostatic interactions (30), it is also an evidence for the success of anion exchange. Finally, the last weight loss beyond 430°C is probably caused by the decomposition of imidazolium moieties that covalently bonded to the siliceous matrixes.

Figure 5 shows the diffuse reflectance spectra of different soft gels, which provide an intuitive way for the observation of the absorbance of powdered materials. It is observed that all these materials exhibit a broad absorption band in the ultraviolet region except the Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup> and a similar stable absorption band above 400 nm. These broad absorption bands correspond to the absorbance of the  $\beta$ -diketone ligands, which chelate with the trivalent lanthanide ions. Beside the Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup>, these absorption bands mostly overlap with their corresponding photoluminescence excitation spectra as shown in Figs. 6 and 7. It can be predicted that the hybrid soft gels can absorb abundant energy in the ultraviolet range, this energy can be transferred to the trivalent lanthanide ions through the "antenna effect" and then sensitize them. Thus, we expect that those lanthanide complexes-functionalized soft gels would possess excellent photoluminescence properties under the irradiation of ultraviolet light, which has been confirmed by their corresponding emission spectra as shown in Figs. 6 and 7. Besides, it is worthy pointing out that all the soft gels have a poor absorption to the ultraviolet wave around 250 nm.

The luminescent excitation (A, C) and emission (B, D) spectra of the europium complexes–functionalized soft gels are shown in Fig. 6. The excitation spectra are collected by monitoring the strongest emission band of Eu<sup>3+</sup> ion at 612 nm, which presents a broad band centered at 350 nm for Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup> and 341 nm for Gel-Im<sup>+</sup>[Eu(NTA)<sub>4</sub>]<sup>-</sup>, respectively. These broad excitation spectra in ultraviolet range can be both ascribed to the characteristic absorption of the lanthanide complexes, it is in accordance with the conclusion of the UV–vis diffuse reflectance absorption analysis. For the emission spectra of Gel-Im<sup>+</sup>[Eu (TTA)<sub>4</sub>]<sup>-</sup> and Gel-Im<sup>+</sup>[Eu(NTA)<sub>4</sub>]<sup>-</sup>, the emission lines located at 579, 591, 612, 652 and 703 nm can be assigned to the characteristic  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ,  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions, respectively. As we know that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is a typical electric dipole transition, which is strongly relying on



Scheme 1. Synthesis of hybrid soft gels with silica-supported imidazolium salt bridge and lanthanide tetrakis( $\beta$ -diketonate) luminescence center.



Figure 1. The Fourier transform infrared spectra for the lanthanide complexes-functionalized soft gels.



Figure 2. The XRD patterns of different lanthanide complexesfunctionalized soft gels.



Figure 3. Scanning electronic microscope (A, B) and Transmission electron microscope (C, D) images of the hybrid soft gel Gel-Im<sup>+</sup>[Eu (TTA)<sub>4</sub>]<sup>-</sup>.



Figure 4. TG and differential thermogravimetric trace analysis curves for the Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup>.

the local symmetry environment of Eu<sup>3+</sup> ions, therefore, the most predominant transition at 612 nm can be seen as a sign of low symmetry environment around the Eu<sup>3+</sup> ions. As the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is a parity-allowed magnetic dipole type which is practically independent of the surroundings of Eu<sup>3+</sup> ions, the integration ratio of transition  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I({}^{5}D_{0} \rightarrow {}^{7}F_{1})$  (red/orange ratio) has been widely taken as an indicator of Eu<sup>3+</sup> ions site symmetry. The intensity ratio of the two emission peaks are about 14.8 and 9.5 for Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup> and Gel-Im<sup>+</sup>[Eu(NTA)<sub>4</sub>]<sup>-</sup>, respectively, suggesting that the Eu<sup>3+</sup> is not at the center of an asymmetric coordination field. This is due to the fact that the strong coordination interactions took place between the  $\beta$ -diketones and the Eu<sup>3+</sup> ions (44). In addition, we have found that the Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup> show better luminescent properties than Gel-Im<sup>+</sup>[Eu(NTA)<sub>4</sub>]<sup>-</sup> under the same test conditions, which is coincidental with the results of luminescent lifetimes and quantum efficiencies as shown in Table 1.

Figure 7 illustrates the typical photoluminescence spectra of the terbium complexes-functionalized soft gels. The excitation spectra of the two hybrid soft gels Gel-Im<sup>+</sup>[Tb(TFA)<sub>4</sub>]<sup>-</sup> and Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup> are similar, which are collected by monitoring the corresponding emission wavelength of the Tb<sup>3+</sup> ions at 545 nm. Both of them are dominated by a broad band, which center at 312 and 314 nm for Gel-Im<sup>+</sup>[Tb(TFA)<sub>4</sub>]<sup>-</sup> and Gel- $Im^{+}[Tb(HFA)_{4}]^{-}$ , respectively. Subsequently, their corresponding emission spectra are collected by choosing the same wavelength (313 nm) to excite the two terbium complexes-functionalized soft gels. As shown in the Fig. 7, four emission peaks are observed at about 489, 545, 588 and 618 nm in the spectrum of Gel-Im<sup>+</sup>[Tb(HFA)<sub>4</sub>]<sup>-</sup>, which can be assigned to  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ ,  ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$  and  ${}^{5}D_{4} \rightarrow {}^{7}F_{3}$  transitions, respectively. Similar pattern can also be found in the emission spectrum of Gel- $\text{Im}^+[\text{Tb}(\text{TFA})_4]^-$ , except the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition that has divided into two shoulder peaks (542 and 548 nm). Besides, the most striking green luminescence  $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$  is observed in Fig. 7 due to the fact that this emission is the most intense one. We also have found that the Gel-Im<sup>+</sup>[Tb(TFA)<sub>4</sub>]<sup>-</sup> shows better luminescent properties than  $\text{Gel-Im}^+[\text{Tb}(\text{HFA})_4]^-$  according to the elevatory baseline in the emission spectrum of Gel-Im<sup>+</sup>[Tb (HFA)<sub>4</sub>]<sup>-</sup>, which is also proved by the results shown in Table 1.



Figure 5. The UV-vis diffuse reflectance absorption spectra of the soft gels.



Figure 6. Excitation (A, C) and emission (B, D) spectra of the europium complexes-functionalized soft gels.

To further investigate the luminescence properties of these hybrid soft gels, we have measured the luminescence decay curves for  ${}^{5}D_{0}$  energy level of Eu<sup>3+</sup> and  ${}^{5}D_{4}$  energy level of Tb<sup>3+</sup> of the resulting materials with the Edinburgh FLS920 phosphorimeter. The resulting lifetimes of the Eu<sup>3+</sup> and Tb<sup>3+</sup> functionalized hybrids are listed in Table 1, which confirms that all

the lanthanide ions occupy the same average local environment within each sample (45).

Moreover, the outer luminescence quantum efficiencies for  ${}^{5}D_{0}$  energy level of Eu<sup>3+</sup> and  ${}^{5}D_{4}$  energy level of Tb<sup>3+</sup> are also determined using an integrating sphere from the Edinburgh FLS920 phosphorimeter. It can be clearly seen from the Table 1



Figure 7. Excitation (A, C) and emission (B, D) spectra of the terbium complexes-functionalized soft gels.

Table 1. Luminescent data for the lanthanide complexes-functionalized soft gels.

Samples	$I_{02}/I_{01}*$	$\tau(\mu s)$ †	$\eta(\%)$ ‡
Gel-Im <sup>+</sup> [Eu(TTA) <sub>4</sub> ] <sup>-</sup>	14.8	784	14.81
Gel-Im <sup>+</sup> [Eu(NTA) <sub>4</sub> ] <sup>-</sup>	9.5	532	7.57
Gel-Im <sup>+</sup> [Tb(TFA) <sub>4</sub> ] <sup>-</sup>	_	543	14.44
Gel-Im <sup>+</sup> [Tb(HFA) <sub>4</sub> ] <sup>-</sup>	-	179	8.83

\*The emission intensity ratios of the  $5D_0 \rightarrow 7F_1$  transition (I<sub>01</sub>) and the  $5D_0 \rightarrow 7F_2$  transition (I<sub>02</sub>) for europium complexes–functionalized soft gels; †lifetimes ( $\tau$ ) of  $5D_0$  energy level and  $5D_4$  energy level for Eu<sup>3+</sup> and Tb<sup>3+</sup> excited state, respectively, error  $\pm 10\%$ ; ‡the luminescent quantum efficiency ( $\eta$ ) value of  $5D_0$  Eu<sup>3+</sup> and  $5D_4$  Tb<sup>3+</sup> excited state determined by an integrating sphere from the Edinburgh FLS920 phosphorimeter, error  $\pm 10\%$ .

that the luminescent quantum efficiency of Gel-Im<sup>+</sup>[Eu(TTA)<sub>4</sub>]<sup>-</sup> is higher than those of Gel-Im<sup>+</sup>[Eu(NTA)<sub>4</sub>]<sup>-</sup>, which coincide with the values of integration ratio of transition red/orange ratio and luminescence lifetimes. Meanwhile, we have noticed that both the europium complexes–functionalized soft gels show longer lifetimes than the terbium-containing materials, suggesting that the method used in this study is better suited to prepare europium-functionalized luminescent materials. Besides, the table also indicates that the resulted soft gels possess some of the outstanding luminescent properties of lanthanide complexes: relatively high quantum efficiency and long luminescent lifetime.

## CONCLUSIONS

In summary, ternary lanthanide luminescent hybrid soft gels Gel-Im<sup>+</sup>[LnL<sub>4</sub>]<sup>-</sup> (for Ln = Eu<sup>3+</sup>, L = TTA or NTA; while for Ln = Tb<sup>3+</sup>, L = TFA or HFA) were successfully prepared by linking the europium/terbium tetrakis  $\beta$ -diketonate complexes into the silicon framework, which provides a representative method for assembling lanthanide-functionalized porous materials with chemical bonds. During the synthesized process, silica-based matrix is prepared through an ionic liquid-mediated nonhydrolytic sol-gel route in advance, and then the lanthanide complexes anion are assembled into the matrix through electrostatic interactions after a simple anion metathesis reaction. The properties of these hybrid soft gels are characterized in detail. Further investigation on the luminescence properties show that all hybrid soft gels present strong luminescence intensities, long lifetimes and high luminescence quantum efficiencies. The outstanding luminescent properties of these hybrid soft gels inherit from the lanthanide complexes, suggesting that the method used here can be copied across the other lanthanide complexes functional materials. Ultimately, this work not only enriches the types of lanthanide-functionalized luminescent hybrid materials but also extends the method for preparing lanthanide composite materials.

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