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Luminescence properties of rare earth (Eu^{3+} and Tb^{3+}) complexes with conjugated carboxylic acids and 1,10-phenanthroline incorporated in silica matrix

Bing Yan, Hong-jie Zhang *, Shu-bin Wang, Jia-zuan Ni

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 13022, China

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Abstract

Binary and ternary complexes of europium and terbium with conjugated carboxylic acid (nicotinic acid and 3,4-furandicarboxylic acid) and 1,10-phenanthroline were introduced into silica gel by the sol–gel method. The luminescence behavior of the complexes in silica gels was studied compared with the corresponding solid state complexes by means of emission, excitation spectra and lifetimes. The result indicated that the rare earth ions (Eu^{3+} and Tb^{3+}) showed fewer emission lines and slightly lower emission intensities in the silica gel than those in pure rare earth complexes. The lifetimes of rare earth ions (Eu^{3+} and Tb^{3+}) in silica gel doped with rare earth complexes became longer than those in pure rare earth complexes. © 1998 Elsevier Science S.A.

Keywords: Rare earth complexes; Conjugated carboxylic acid; Luminescence properties; Sol–gel method

1. Introduction

The sol–gel method has been shown to be a suitable approach for the preparation of novel luminescent materials. Much recent work has focused on the development of solid-state tunable dye laser media using organic dye dopants [1–3]. Unfortunately, organic dyes were limited useful application due to their photodecomposing [4]. Some work have been examined the luminescence behavior of $EuCl_3$ and $Eu(NO_3)_3$ salts [5,6] adsorbed into porous glasses and doped into sol–gel derived hosts. $EuCl_3$-doped silica gels produced highly quenched luminescence. Thus, it is of great interest to modify the local environment of Eu^{3+} and Tb^{3+} ions to improve their absorptive characteristics and to reduce nonradiative decay mechanisms from the excited state.

Since some of lanthanide ions, e.g., Eu^{3+} and Tb^{3+}, possess good luminescence characteristics (high color purity) based on the electronic transitions between the 4f energy levels, a series of compounds activated by Eu^{3+} and Tb^{3+} have been studied for practical applications as phosphors [7,8]. However, since the f–f transitions of these ions are inhibited, they absorb very little excitation energy. Photoactive lanthanide organic coordinate compounds, such as europium and terbium chelates with β-diketones, aromatic carboxylic acids and heterocyclic ligands exhibit intense narrow band emissions via an energy transfer from the ligands to the metal ions under near UV excitation [9–11]. In the recent years, some work were reported on the luminescence behavior of Eu^{3+} and Tb^{3+} complexes with β-diketone [12], aromatic carboxylic acids [13] and bipyridyl [14] in sol–gel derived host materials. But little attention has been paid to the binary and ternary rare earth complexes with conjugated acid and organic base. In the context, the conjugated carboxylic acid: nicotinic acid and 3,4-furandicarboxylic acid, whose low triplet state energies are suitable for the luminescence of Eu^{3+} and Tb^{3+} ion, respectively.[1] So europium complexes with nicotinic acid (terbium with 3,4-furandicarboxylic acid) and 1,10-phenanthroline were synthesized and were incorporated in silica matrix by sol–gel method, the luminescence properties of the host material were also discussed in details. The result will provide a new path for developing organic–inorganic hybrid luminescent material.

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* Corresponding author.

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2. Experimental details

2.1. The synthesis of rare earth complexes

The binary europium complex with nicotinic acid and terbium complex with 3,4-furandicarboxylic acid were prepared according to Refs. [15,16]. The rare earth ternary complexes with nicotinic acid and 1,10-phenanthroline were prepared as described in Ref. [17]. The ternary complexes with 3,4-furandicarboxylic acid and 1,10-phenanthroline were synthesized as follows: Excess 3,4-furandicarboxylic acids (about 3 mmol) and excess 1,10-phenanthroline (over 1 mmol) were soluted by absolute ethanol and mixed together, the pH value of the mixture was adjusted to 6.3 by adding aqueous sodium hydroxide with stirring. Then an alcoholic solution of rare earth chloride (1 mmol) was added to the mixed alcoholic solution above. Heating and stirring for 3 h, the precipitate was filtered off, washed with water and ethanol, dried first at room temperature, and was stored over silica-gel drier. The final products were dissolved in *N,N*-dimethyl formide (DMF) for future use. Whose compositions were confirmed by the elemental analysis with a CARIO-ERBA 1106 elemental analyzer.

2.2. The incorporation of the rare earth complexes into silica gels

Silica gels were prepared by the hydrolysis and condensation of tetraethoxysilane $Si(OC_2H_5)_4$(TEOS) as described in Ref. [18]. A 4.2:1 H_2O to $Si(OC_2H_5)_4$ mole ratio was used with proper amount of alcohol (C_2H_5OH) or DMF as solvent. The DMF solution of rare earth complexes were added to the silica precursor solution. After refluxing some hours at 338 K in water bathing, the transparent gel was placed for 3 days or so and then dried at 373 K. The weight ratios of rare earth complexes ($Eu(NIA)_3 \cdot 2H_2O$, $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$, $TbH(FRA)_2 \cdot 3H_2O$ and $TbH(FRA)_2 \cdot phen \cdot 4H_2O$) to the silica gels are 2.56%, 2.74%, 2.63% and 2.72%, respectively.

2.3. The spectroscopy measurements

Infrared (IR) spectra were measured on a Perkin-Elmer infrared spectrophotometer (Model 580B) with Kbr pellet technique. Excitation and Emission spectra were recorded on a Spex Fluorolog-II spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Lifetimes were measured with a Spex 1934D phosphorimeter using a 450-W flash lamp as the excitation source (pulse width = 3 μs).

3. Results and discussions

The compositions of europium and terbium complexes with conjugated carboxylic acid and 1,10-phenanthroline were confirmed in the following by the elemental analysis. For $Eu(NIA)_3 \cdot 2H_2O$, calculated: C(38.97), H(2.87), N(7.58) and Eu(28.31); found: C(38.75), H(2.63), N(7.40) and Eu(27.64). For $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$, calculated: C(54.06), H(3.65), N(10.51) and Eu(16.30); found: C(54.48), H(3.34), N(10.24) and Eu(16.94). For $TbH(FRA)_2 \cdot 3H_2O$, calculated: C(27.58), H(2.04) and Tb(30.44); found: C(27.82), H(2.04), N(3.89) and Tb(30.04). For $TbH(FRA)_2 \cdot phen \cdot 4H_2O$, calculated: C(39.99), H(2.92), and Tb(19.57); found: C(39.47), H(2.49), N(4.09) and Tb(22.61). Where HNIA = nicotinic acid, and H_2FRA = 3,4-furandicarboxylic acid and phen = 1,10-phenanthroline, respectively.

Fig. 1 shows the excitation and emission spectra of pure $Eu(NIA)_3 \cdot 2H_2O$ (A) and $Eu(NIA)_3 \cdot 2H_2O$ in silica gel (B), respectively. Obvious differences can be found in these spectra. For pure $Eu(NIA)_3 \cdot 2H_2O$, the excitation spectrum consist of a symmetric and broad band ranging from 200 to 450 nm ($\lambda ex = 308.8$ nm) with some small peaks superimposed on the band; the corresponding emission spectrum contains $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transition lines of Eu^{3+}, with hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ red emission as the most prominent group. The observed number of $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions, is 1, 2, 2, 1, 2, respectively. However, for $Eu(NIA)_3 \cdot 2H_2O$ in silica gel, the excitation spectrum becomes an asymmetric but smooth band ($\lambda ex = 327$ nm) ranging from 200–450 nm; the corresponding emission spectrum shows slightly lower intensity than that of pure $Eu(NIA)_3 \cdot 2H_2O$ and fewer emission lines of Eu^{3+}, i.e., one $^5D_0 \rightarrow {}^7F_0$, one $^5D_0 \rightarrow {}^7F_1$, one $^5D_0 \rightarrow {}^7F_2$, one $^5D_0 \rightarrow {}^7F_3$, one $^5D_0 \rightarrow {}^7F_4$. The same feature holds for the excitation and emission spectra of $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$, as shown in Fig. 2. The excitation spectra of pure $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ in silica gel show maximum wavelength at 308 nm and 296 nm, respectively. The emission spectrum of pure $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ one, two, two, one and two lines, but these numbers are 1, 1, 1, 1, and 2, respectively for $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ in silica gel.

Fig. 3 shows the excitation and emission spectra of pure $TbH(FRA)_2 \cdot 3H_2O$ (A) and $TbH(FRA)_2 \cdot 3H_2O$ (B) in silica gel, respectively. The same phenomenon of the differences in these spectra. For pure $TbH(FRA)_2 \cdot 3H_2O$, the excitation spectrum is a symmetric and broad band ranging from 200 to 350 nm ($\lambda ex = 277.5$ nm) with some small peaks superimposed on the band; the corresponding emission spectrum contains $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transition lines of Tb^{3+}, with the transition $^5D_4 \rightarrow {}^7F_5$ green emission as the most prominent group. The observed number of $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ transitions is 1, 2, 2, 2, respectively. However, for $TbH(FRA)_2 \cdot 3H_2O$ in silica gel, the excitation spectrum becomes an asymmetric but smooth band ($\lambda ex = 294$ nm) ranging from 250–450 nm; the corresponding emission spectrum shows little lower intensity than that of pure $TbH(FRA)_2 \cdot 3H_2O$ and fewer emission lines of Tb^{3+}, i.e., one $^5D_4 \rightarrow {}^7F_6$, one $^5D_4 \rightarrow {}^7F_5$, one $^5D_4 \rightarrow {}^7F_4$, and one $^5D_4 \rightarrow {}^7F_3$. The same feature holds for the emission spec-

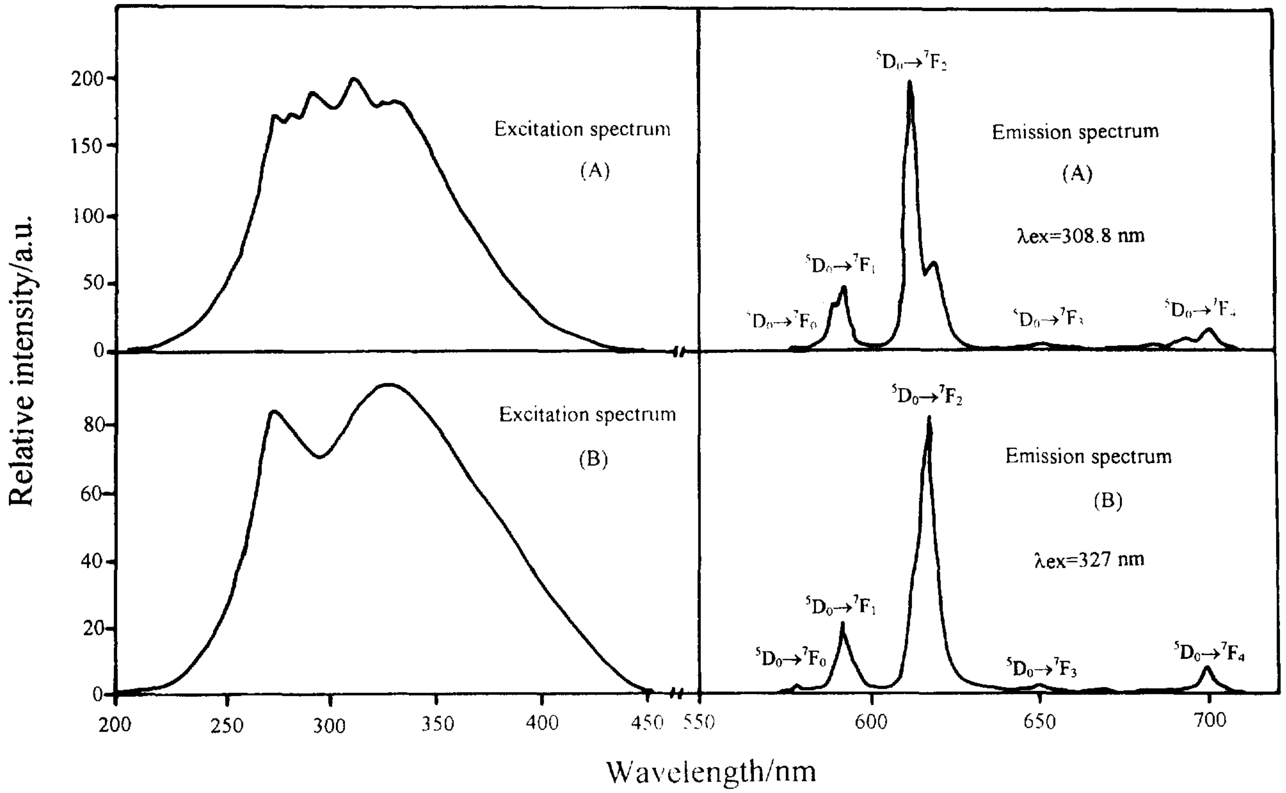

Fig. 1. The excitation and emission spectra of pure Eu(NIA)$_3$·2H$_2$O (A) (λex = 308.8 nm) and Eu(NIA)$_3$·2H$_2$O in silica gel (B) (λex = 327 nm).

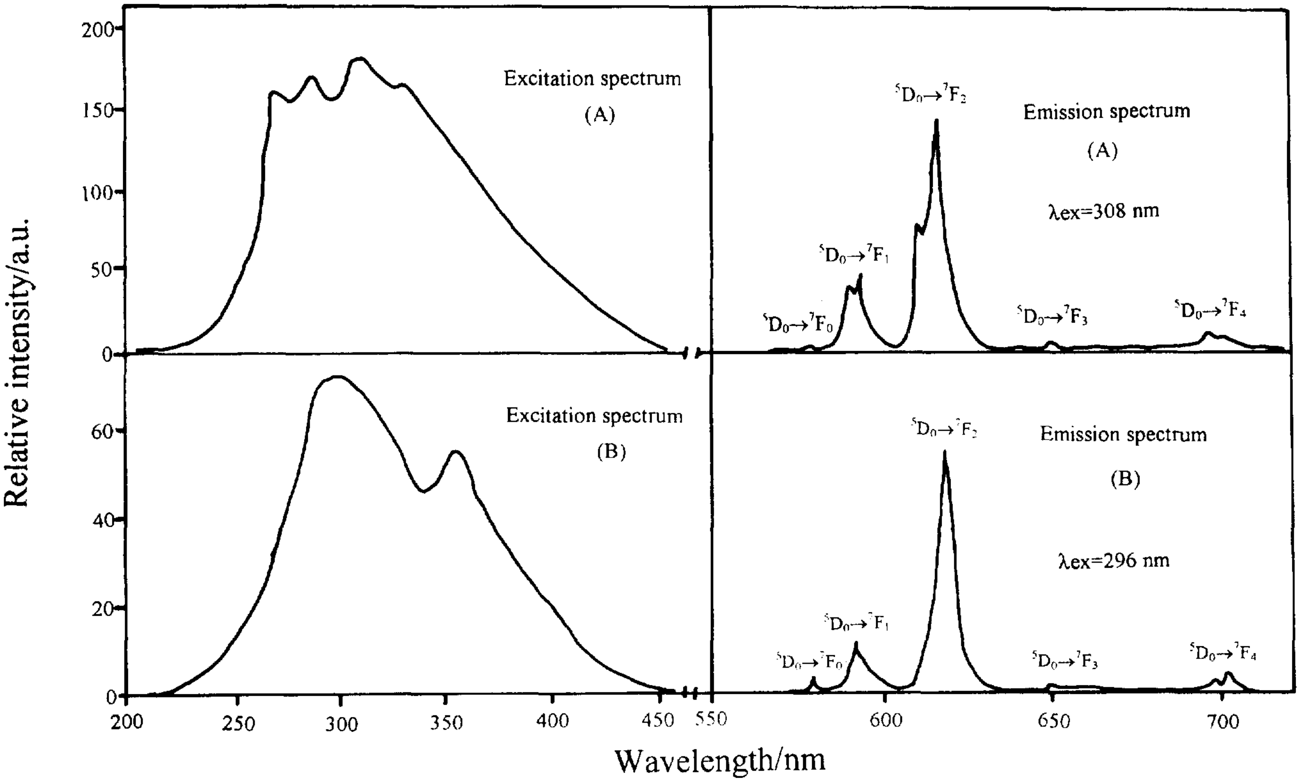

Fig. 2. The excitation and emission spectra of pure Eu(NIA)$_3$·(phen)$_2$·3H$_2$O (A) (λex = 308 nm) and Eu(NIA)$_3$·(phen)$_2$·3H$_2$O in silica gel (B) (λex = 296 nm).

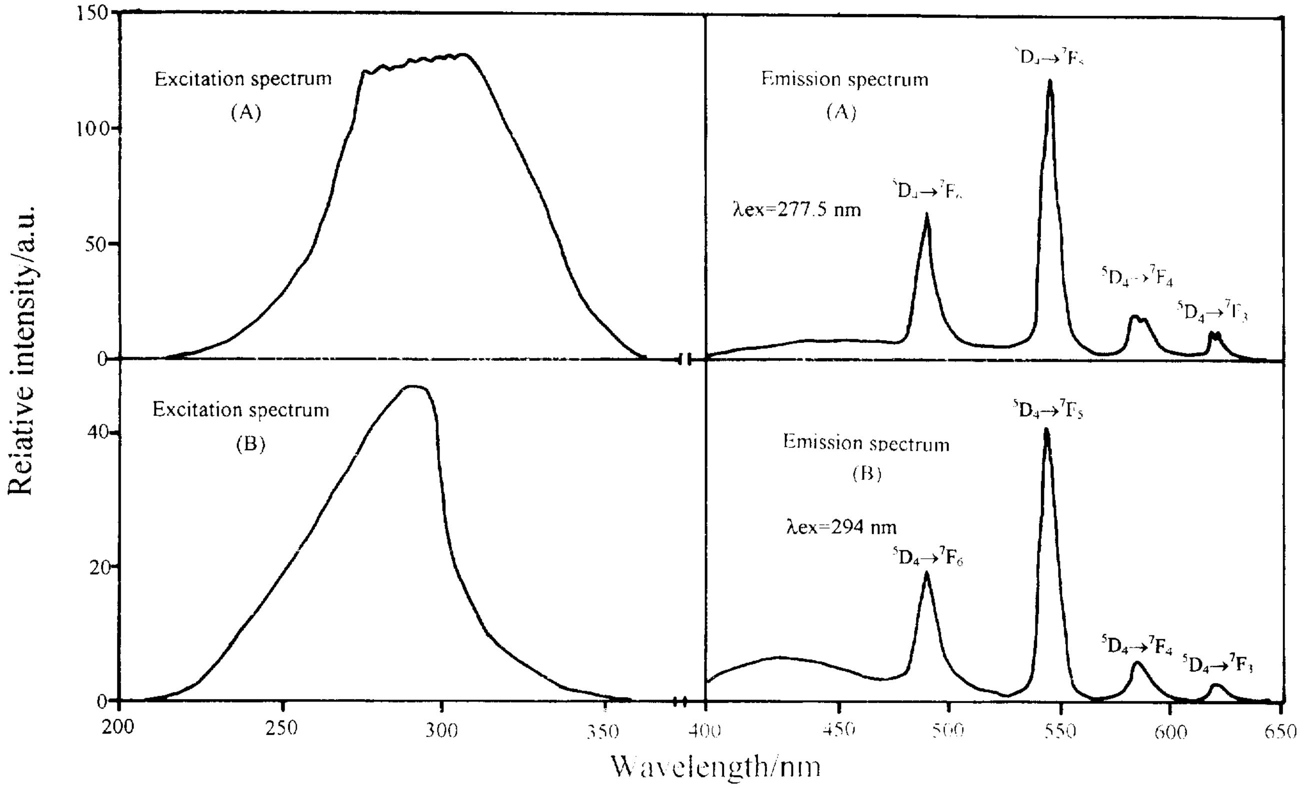

Fig. 3. The excitation and emission spectra of pure $TbH(FRA)_2\cdot 3H_2O$ (A) (λex = 277.5 nm) and $TbH(FRA)_2\cdot 3H_2O$ in silica gel (B) (λex = 294 nm).

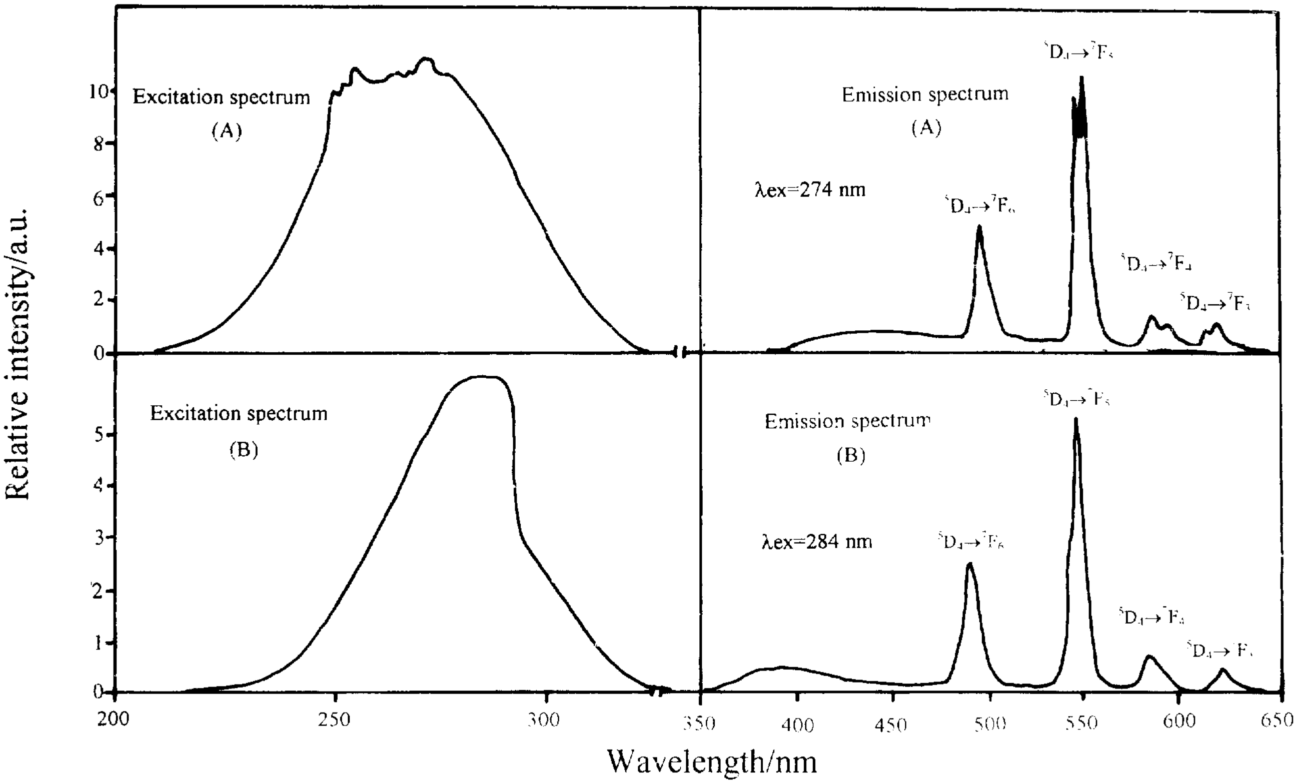

Fig. 4. The excitation and emission spectra of pure $TbH(FRA)_2$ phen$\cdot 4H_2O$ (A) (λex = 274 nm) and $TbH(FRA)_2$ phen$\cdot 4H_2O$ in silica gel (B) (λex = 284 nm).

Table 1
The luminescence properties of pure rare earth complexes (solid samples) and them in silica gel

Matter	λex/nm	λem/nm [a]	Relative intensities/a.u.	Lifetimes/μs
$Eu(NIA)_3 \cdot 2H_2O$ (pure)	308.8	612.5,620	29.7	737
$Eu(NIA)_3 \cdot 2H_2O$ (sol–gel)	327	614	11.8	1104
$Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (pure)	308	612,620	26.9	759
$Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (sol–gel)	296	619	10.3	1345
$TbH(FRA)_2 \cdot 3H_2O$ (pure)	277.5	546	20.7	403
$TbH(FRA)_2 \cdot 3H_2O$ (sol–gel)	294	546	7.4	613
$TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (pure)	274	543.5,547	1.9	782
$TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (sol–gel)	284	549	0.9	964

[a] For Eu(III) complexes: ${}^5D_0 \rightarrow {}^7F_2$ transition and for Tb(III) complexes: ${}^5D_4 \rightarrow {}^7F_5$ transition.

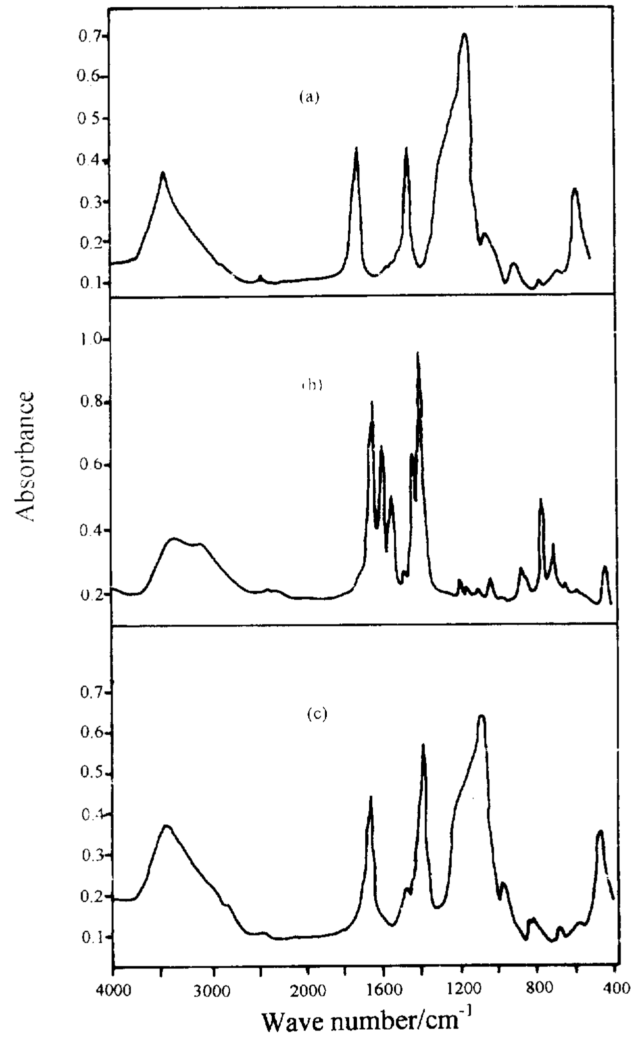

Fig. 5. The IR spectra of silica gel (a), silica gel containing $Eu(NIA)_3 \cdot 2H_2O$ (b) pure $Eu(NIA)_3 \cdot 2H_2O$ (c).

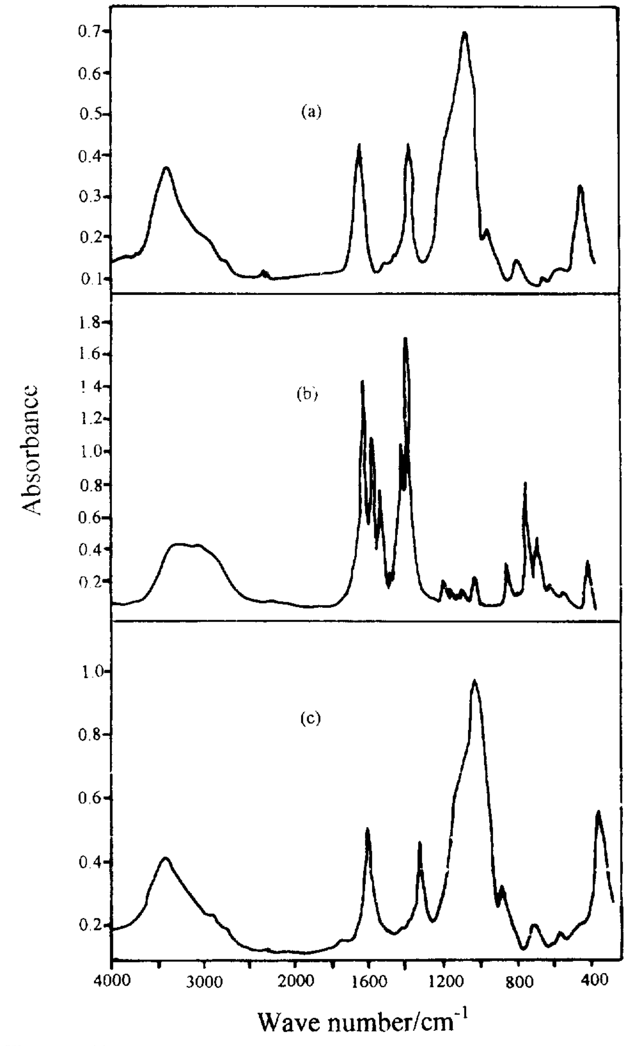

Fig. 6. The IR spectra of silica gel (a), silica gel containing $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (b) and pure $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (c).

tra of $TbH(FRA)_2 \cdot phen \cdot 4H_2O$, as shown in Fig. 4. The emission spectrum of pure $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ one, two, two and two lines and its excitation wavelength is 274 nm, but these numbers are 1, 1, 1, 2, respectively for $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ in silica gel and its excitation wavelength is 284 nm. Table 1 shows the data of luminescence properties.

The excitation spectra of pure binary (or ternary) europium and terbium complexes with conjugated carboxylic acid with 1,10-phenanthroline, and they in silica gel are both due to the absorption of the organic ligands. The lowest triplet state energies of HNIA and H_2FRA are suitable for the sensitization of the resonant emission energies of Eu^{3+} and Tb^{3+}, respectively. Excitation into the absorption of ligands results in the strong luminescence of Eu^{3+} and Tb^{3+}, indicating that an efficient intramolecular energy transfer occurs from the conjugated carboxylic acid (or phen) to Eu^{3+}. The differences in the excitation and emission spectra between pure complexes and these complexes in silica gel can be accounted in the following way. For pure rare earth complexes, the surrounding environments of the Eu^{3+} and Tb^{3+} are homogeneous. so their excitation bands are symmetric and the emission lines split into several ones under the ligands field. The small peaks on the excitation bands may be due to the vibration absorptions of the ligands. silica gel is a kind of non-crystalline substance with porous macrostructure. The size of the pores is different in a certain range. Therefore, rare earth complexes incorporated in the pores of silica gel will exhibit some disorders in a certain range. This will bring about the excitation bands to be asymmetric and the emission peaks to be broad. So fewer emission lines of Eu^{3+} and Tb^{3+} are observed in silica gel doped with europium and terbium complexes than in their pure complexes.

The decay curves of $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) for $^5D_0 \rightarrow {}^7F_2$ emission in pure Eu(III) complexes and Eu(III) complexes incorporated in silica gel were measured. Both of the decay curves are singly exponential, and the lifetimes of them were shown in Table 1. From the data, it can be seen that the lifetimes of Eu(III) in silica gel become much longer than those of pure Eu(III) complexes. The lifetimes of Eu(III) complexes depends strongly on the vibrations of its nearest ligands. The excitation energy of Eu(III) can be absorbed by the vibration of the ligands, which decreases the lifetime of Eu(III). The relatively rigid structure of silica gel restricts the vibration of the ligands of Eu(III), resulting in decreasing the non-radiative transitions caused by vibration and thus increasing the lifetime of Eu(III). This description can be confirmed by the IR spectra of silica gel (a), pure $Eu(NIA)_3 \cdot 2H_2O$ (b), silica gel containing $Eu(NIA)_3 \cdot 2H_2O$ (c); IR spectra of silica gel (a), pure $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (b) and silica gel containing $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (c), as shown in Figs. 5 and 6. From Figs. 5 and 6, it can be seen that the silica gel containing $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) exhibits the same absorption peaks as the pure silica gel, and the characteristic absorption peaks belonging to $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) are not present in the silica gel. This implies that the vibration of the ligands of Eu(III) has been hindered by the surrounding gel matrix. So the lifetime of Eu(III) in silica gel doped with $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) becomes longer than that in pure $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$). The above mentioned phenomenon that the excitation band of pure $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) shows some small peaks (vibration lines) while the excitation band of silica gel doped with $Eu(NIA)_3 \cdot 2H_2O$ (and $Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$) does not show these small peaks can be explained in the same way. Figs. 7 and 8 give the IR spectra of silica gel (a), pure $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (b), silica gel containing $TbH(FRA)_2 \cdot 3H_2O$ (c); the IR spectra of silica gel (a), pure $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (b) and silica gel containing $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (c). The same result can be obtained from the two figures. Table 2 gives the assignments of the main absorption peaks in these figures.

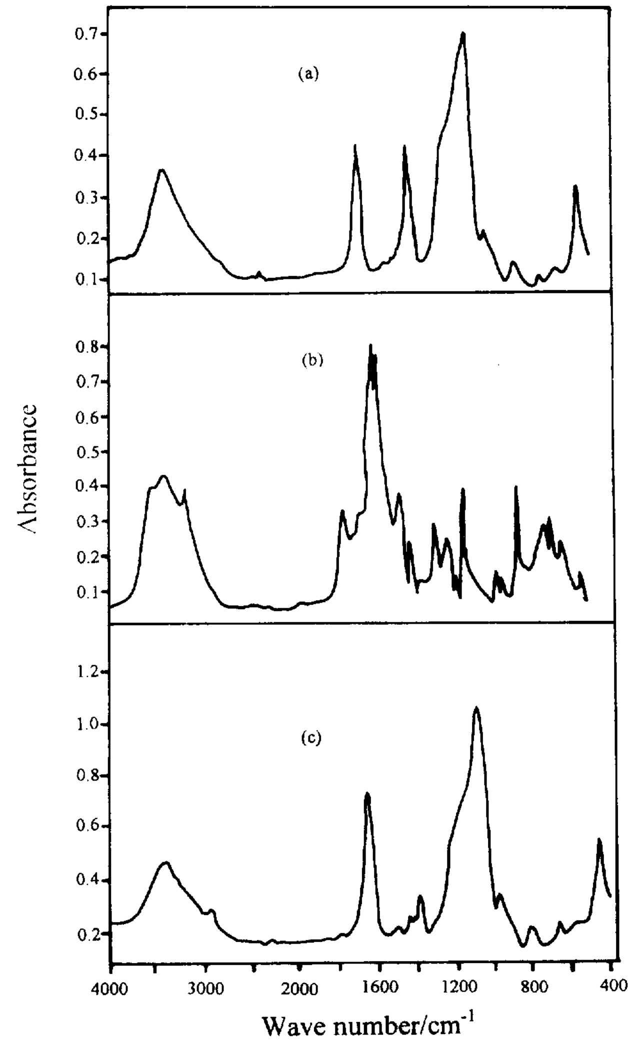

Fig. 7. The IR spectra of silica gel (a), silica gel containing $TbH(FRA)_2 \cdot 3H_2O$ (b), pure $TbH(FRA)_2 \cdot 3H_2O$ (c).

4. Conclusions

(1) Silica gel is a suitable host matrix for the luminescence of rare earth complexes. The rare earth ions (Eu^{3+} and Tb^{3+}) show fewer emission lines and the slightly weaker emission intensities in the silica gel than in pure rare earth complexes.

Table 2
The absorption bands of IR spectra for europium and terbium complexes

Compounds	Main absorption bands and their assignments, intensities
Pure silica–gel	3424.6 (ν OH, 0.8743) 1656.7 (δ OH, 1.0423) 1385.1 (δs C–H, 1.3405) 1082.0 (νs Si–O–Si, 1.6549) 960.5 (νas Si–OH, 0.4398) 800.0 (δ Si–O–Si, 0.4317) 461.7 (δ O–Si–O, 0.8971)
$Eu(NIA)_3 \cdot 2H_2O$ (sol–gel)	3418.5 (ν OH, 0.8914) 1655.3 (δ OH, 1.0356) 1384.2 (δs C–H, 1.2906) 1093.8 (νs Si–O–Si, 1.4136) 964.4 (νas Si–OH, 0.4346) 800.0 (δ Si–O–Si, 0.4419) 462.1 (δ O–Si–O, 0.8630)
$Eu(NIA)_3 \cdot (phen)_2 \cdot 3H_2O$ (sol–gel)	3437.0 (ν OH, 0.6837) 1660.2 (δ OH, 0.7930) 1384.5 (δs C–H, 0.7389) 1096.9 (νs Si–O–Si, 1.3551) 968.6 (νas Si–OH, 0.5640) 798.3 (δ Si–O–Si, 0.4256) 466.3 (δ O–Si–O, 0.8440)
$TbH(FRA)_2 \cdot 3H_2O$ (sol–gel)	3419.0 (ν OH, 0.5638) 1660.0 (δ OH, 1.0106) 1389.9 (δs C–H, 0.5251) 1097.3 (νs Si–O–Si, 1.4126) 967.4 (νas Si–OH, 0.5171) 798.3 (δ Si–O–Si, 0.3739) 462.6 (δ O–Si–O, 0.7946)
$TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (sol–gel)	3424.1 (ν OH, 0.4951) 1656.1 (δ OH, 0.5217) 1384.0 (δs C–H, 0.8345) 1079.2 (νs Si–O–Si, 0.9266) 964.5 (νas Si–OH, 0.3237) 798.8 (δ Si–O–Si, 0.2114) 462.6 (δ O–Si–O, 0.4644)

νs (νas): Symmetrical (asymmetrical) stretching vibration.
δ: In-plane bending vibration.

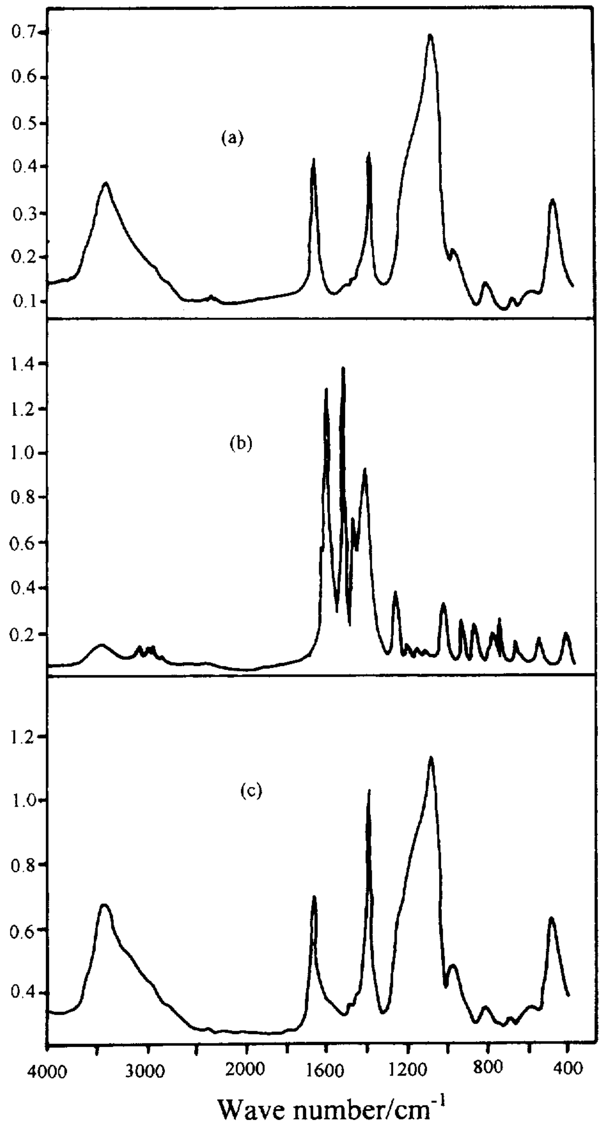

Fig. 8. The IR spectra of silica gel (a), silica gel containing $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (b) and pure $TbH(FRA)_2 \cdot phen \cdot 4H_2O$ (c).

(2) The lifetimes of rare ions in silica gel (Tb^{3+} and Eu^{3+}) doped with europium and terbium complexes become longer than that in pure ones.

(3) From the data, The excellent luminescence properties of rare earth complexes incorporated in silica gel by sol–gel method can make them promising candidates for potential use as luminescent material. The silica gel incorporated with little amount of rare earth complexes can obtain the excellent luminescent material. Which can provide sufficient experimental data for further application and development.

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