

Preparation and Luminescence Properties of Hybrid Materials Containing Europium(III) Complexes Covalently Bonded to a Silica Matrix

H. R. Li, J. Lin, H. J. Zhang,* L. S. Fu, Q. G. Meng, and S. B. Wang

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

Received December 10, 2001. Revised Manuscript Received June 10, 2002

A new kind of luminescent organic–inorganic hybrid material (denoted Hybrid I) consisting of europium 1,10-phenanthroline complexes covalently attached to a silica-based network was prepared by a sol–gel process. 1,10-Phenanthroline grafted to 3-(triethoxysilyl)propyl isocyanate was used as one of the precursors for the preparation of an organic–inorganic hybrid materials. For comparison purposes, the hybrid material (denoted Hybrid II) in which phenanthroline was not grafted onto the silica backbone of the frameworks was also prepared. Elemental analysis; NMR, FT-IR, UV/vis absorption, and luminescence spectroscopies, and luminescence decay analysis were used to characterize the obtained hybrid materials. It is shown that the homogeneity of Hybrid I is superior to that of Hybrid II, and a higher concentration europium can be incorporated into Hybrid I than Hybrid II. Excitation at the ligand absorption wavelength (283 nm) resulted in the strong emission of the Eu^{3+} $^5\text{D}_0 - ^7\text{F}_J$ ($J = 0-4$) transition lines as a result of the efficient energy transfer from the ligands to the Eu^{3+} in Hybrid I. The number of water molecules coordinated to the europium ion was estimated, and the structure of the as-synthesized Hybrid I was predicted on the basis of the experimental results.

1. Introduction

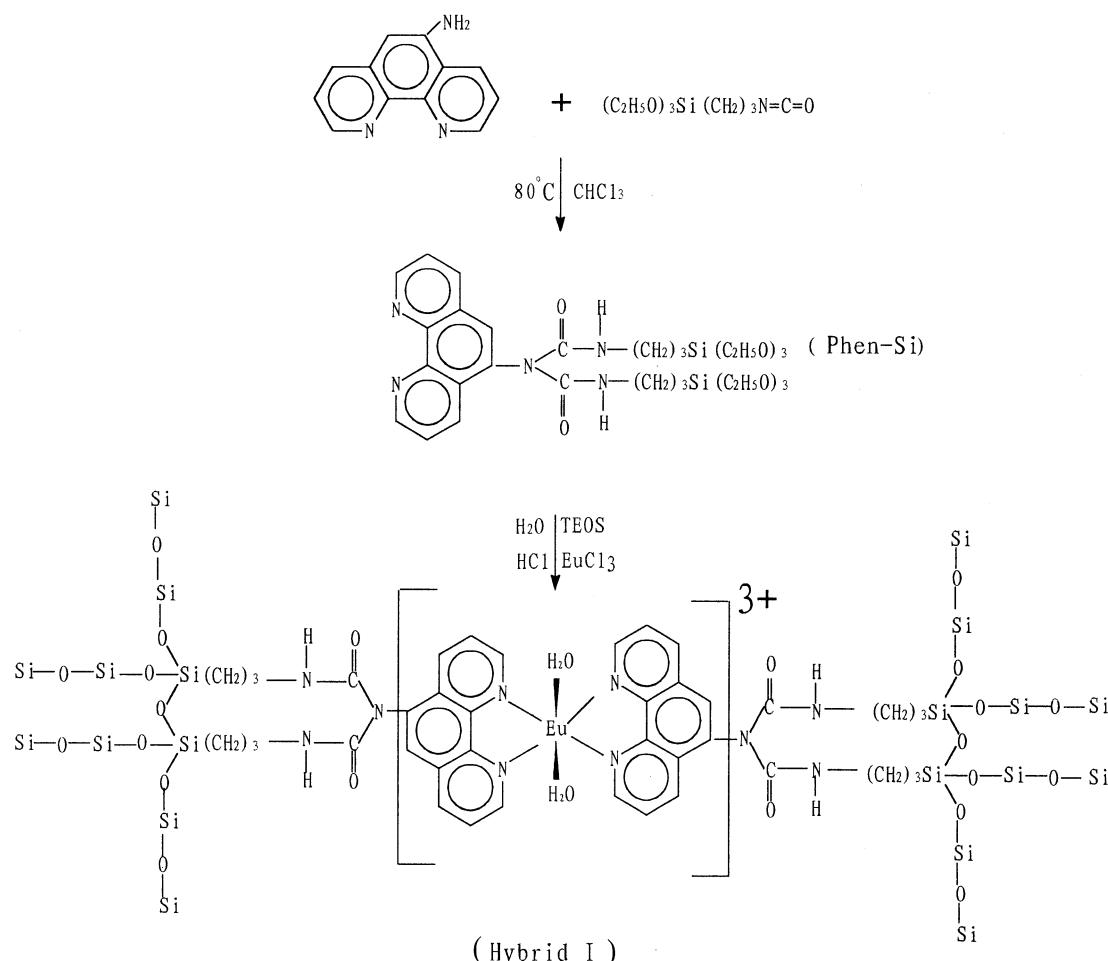
The sol–gel process is a well-known technique for preparing inorganic–organic hybrid materials.^{1–3} The substitution of the alkoxyde group at the silane by an alkyl or aryl group allows for the modification of the inorganic network with organic groups. The very large range of choices for the two components offers the possibility of obtaining materials with attractive properties such as mechanical, thermal, and other physical and chemical properties.⁴ These properties can be further tailored by modifying the sol–gel processing conditions to allow, for example, for control of the microstructure, shape, and degree of connection between the two networks.^{5,6} Another possibility for establishing unprecedented material properties is the incorporation of a filler such as titanium dioxide⁷ or the doping of the composites with molecules such as dyes^{8–10} or lanthanide complexes.^{11–22} In fact, the incorporation of rare earth complexes with β -diketones, aromatic carboxylic

acids, and heterocyclic ligands into sol–gel-derived host structures has been extensively described in recent studies.^{11–22} These studies indicate that the thermal stabilities and mechanical properties of the rare earth complexes were improved by the matrixes. Typically, such materials are obtained by doping silica gels with lanthanide complexes, in which only weak physical interactions exist between the silica gel and the complexes. Hence, many problems, including clustering of the emitters, inhomogeneous dispersion of both components, leaching of dopants, and limited concentration of organic species, occur. Covalent grafting of the ligands to the backbone of networks via Si–C bonds can overcome the above-mentioned problems.^{23–28}

The rigid framework of 1,10-phenanthroline and its high affinity toward various cations are attractive features for the construction of tunable chromophores.²⁹

* Corresponding author. E-mail: hongjie@ns.ciac.jl.cn.
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Scheme 1. Synthesis Procedure for Phen-Si and Predicted Structure of Hybrid I

1,10-Phenanthroline can form complexes with lanthanide ions such as Tb^{3+} and Eu^{3+} . In such cases, the organic ligand absorbs exciting radiation and transfers the excitation energy to the lanthanide emitter. Furthermore, the successful preparation of complexes with light-harvesting ligands such as 1,10-phenanthroline and 2,2-bipyridine has opened up vast vistas for extensive photophysical applications. Actually, both of these heterocyclic ligands are antennas of near-UV radiations because of their efficient ligand-to-metal intracomplex energy transfer.^{30–32}

In this paper, a new kind of compound (denoted Phen-Si) containing 1,10-phenanthroline that plays a double role, i.e., as a ligand of the lanthanide ions and as a

precursor of the sol–gel process, was synthesized. The hybrid luminescent material (denoted Hybrid I) was prepared using Phen-Si as one of the precursors, which was reacted with tetraethoxysilane (TEOS) by hydrolysis and condensation in the presence of lanthanide ion Eu^{3+} . For comparison, a hybrid material consisting of a simple mixture of 5-amino-1,10-phenanthroline, Eu^{3+} , and the silica gel (denoted Hybrid II) was also prepared. A comparative study on the luminescence properties of Hybrid I and Hybrid II was performed.

2. Experimental Section

Tetraethoxysilane (TEOS, Aldrich) and 3-(triethoxysilyl)-propyl isocyanate (Aldrich) were used as received. The solvent DMF (dimethylformamide) was used after distillation in a vacuum. Europium chloride ($EuCl_3$) was obtained by dissolving Eu_2O_3 (99.99%, Shanghai yuelong) in hydrochloric acid.

The key material, 5-amino-1,10-phenanthroline (denoted Phen-NH₂) was prepared as described previously.³³ Hydrazine hydrate (1 mL) diluted in ethanol (20 mL) was added dropwise to a suspension of 5-nitro-1,10-phenanthroline (1 g) with 5% Pd/C (200 mg) in ethanol. The mixture was stirred at 70 °C for 5 h. After filtration, the solution was concentrated until the formation of a green-yellow precipitate. The yellow solid was filtered off and washed with water. Phen-Si was prepared according to the procedure depicted in Scheme 1 using Phen-NH₂ as the starting reagent.³⁴ Phen-NH₂ (0.212 g, 1 mmol) was dissolved in 20 mL of $CHCl_3$ in a round-bottom flask. The

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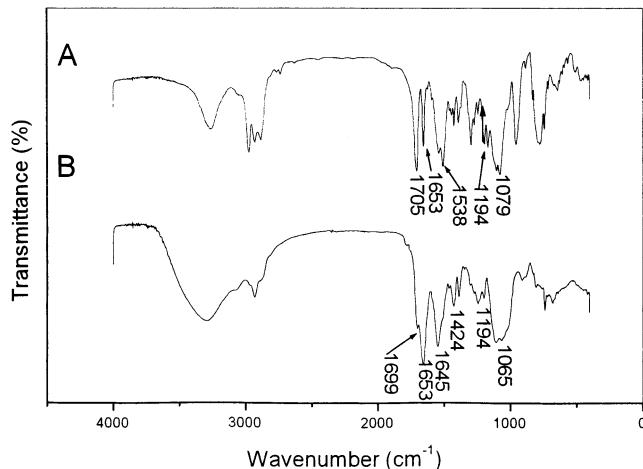


Figure 1. FT-IR spectra for (A) Phen-Si and (B) Hybrid I.

solution was stirred while 2 mL of 3-(triethoxysilyl)propyl isocyanate was added dropwise. The chloroform was evaporated at atmospheric pressure, and the resulting mixture was heated at 80 °C in a covered flask for 12 h. Cold hexane was then added to precipitate the white powder. The powder was collected by filtration, purified in methanol, and dried in a vacuum. Anal. Calcd for $C_{32}H_{51}N_5O_8Si_2$: C, 55.5; H, 7.4; N, 10.0. Found: C, 54.9; H, 7.0; N, 10.8. NMR ($CDCl_3$): δ 0.522 (4H, m), 1.13 (18H, t), 1.60 (4H, m), 3.21 (4H, q), 3.68 (12H, q), 7.26 (2H, brs), 7.69 (2H, m), 7.87 (1H, s), 8.25 (2H, m), 9.23 (2H, m). IR (BrK): $-CONH-$ (1653 cm^{-1} , 1538 cm^{-1}), C-Si (1194 cm^{-1}).

A sol-gel-derived hybrid material doped with lanthanide (Hybrid I) was prepared as follows: Phen-Si was dissolved in methanol, and TEOS and H_2O (pH 2) were then added under stirring. An appropriate amount of $EuCl_3$ mixed with 2 mL of DMF was added to the resulting mixture. The mixture was agitated magnetically to achieve a single phase and then transferred into a cuvette. Thermal curing was performed at 60 °C and continued until the sample solidified. The molar ratio of Phen-Si/TEOS/ H_2O/Eu^{3+} was 1:1:4:0.5. Hybrid II was prepared by using the same procedure except that Phen-Si was replaced by Phen-NH₂. For the leaching experiments, Hybrid I and Hybrid II were soaked in DMF solutions at 60 °C in a sealed cuvette containing a magnetic stirring bar. The DMF was removed and the emission spectra of the hybrid materials were recorded periodically.

All measurements were performed at room temperature. The fluorescence excitation and emission spectra were recorded on a SPEX Fluorolog-2T2 spectrofluorometer equipped with a 450-W xenon lamp as the excitation source. The UV-vis absorption spectra were taken with a TU-1901 spectrophotometer. Luminescence lifetime measurements were carried out on a SPEX 1934D phosphorimeter using a 7-W pulse xenon lamp as the excitation source with a pulse width of 3 μs . FT-IR spectra were measured within the $4000\text{--}400\text{ cm}^{-1}$ region on a Perkin-Elmer model 580B infrared spectrophotometer with the KBr pellet technique. 1H and ^{13}C NMR spectra were recorded on a Bruker AC 400 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were carried out on a 240 Perkin-Elmer analyzer.

3. Results and Discussion

Figure 1 shows the FT-IR spectra of (A) Phen-Si and (B) Hybrid I. The occurrence of the grafting reaction is evidenced by the bands located at 1653 and 1645 cm^{-1} , which originate from the $-CONH-$ amide group. The addition of Eu^{3+} , TEOS, and water to Phen-Si is responsible for some changes in the IR spectrum, as

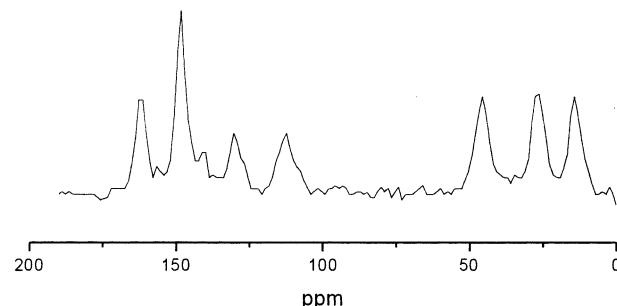


Figure 2. Solid-state ^{13}C CPMS NMR spectrum of Hybrid I.

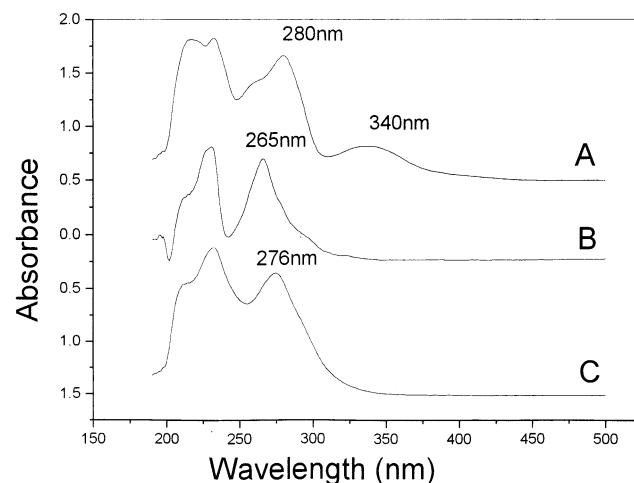


Figure 3. Absorption spectra for (A) 5-amino-1,10-phenanthroline, (B) Phen-Si, and (C) Phen-Si with excess Eu^{3+} ions.

shown in Figure 1B. This is due to the hydrolysis/condensation of TEOS and Phen-Si and the formation of a complex between Eu^{3+} and Phen-Si (A). The $\nu(Si-C)$ vibration located in the $1188\text{--}1193\text{ cm}^{-1}$ wavelength range and the $-CONH-$ amide group vibration can still be observed in Figure 1B. The presence of the organic groups in Hybrid I can be further confirmed by ^{13}C CPMS NMR spectroscopy (Figure 2). Peaks located at 43, 26, and 13 ppm can be attributed to the $(CH_2)_3$ chains. Other signals observed in the range 110–150 ppm can be assigned to aromatic carbons, and the peak at 161 ppm originating from the $C=O$ amide functions is also clearly evidenced.

Figure 3 shows the UV-vis absorption spectra of (A) 5-amino-1,10-phenanthroline, (B) Phen-Si and (C) Phen-Si with excess Eu^{3+} ions. Comparing the absorption spectrum of Phen-Si (B) with that of 5-amino-1,10-phenanthroline (A), we can see a blue shift of the major electronic transitions (from 280 to 265 nm) and the disappearance of the peak centered at 340 nm. Furthermore, a red shift (from 265 nm in Figure 3B to 276 nm in Figure 3C) is observed upon addition of excess Eu^{3+} ions to Phen-Si, indicating the formation of a complex between Eu^{3+} and Phen-Si.

The excitation spectrum of Hybrid I ($Phen-Si/Eu^{3+} = 2:1$) and the absorption spectrum of the ligand (Phen-Si) are shown in Figure 4 together. The observed overlap between these two spectra clearly indicates the typical sensitization of the Eu^{3+} by the heterocycle ligand, an antenna effect,^{30–32} and thus confirms that Eu^{3+} ions are surrounded by Phen-Si.³⁵ In addition, the overlap between the emission spectrum of the donor and the

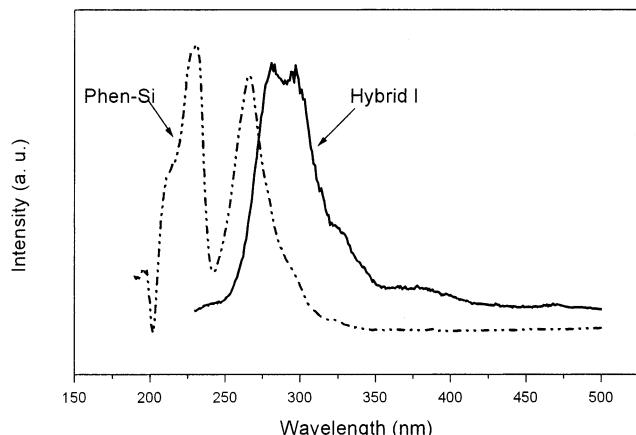


Figure 4. Excitation spectrum of Hybrid I and UV/vis absorption spectrum of Phen-Si.

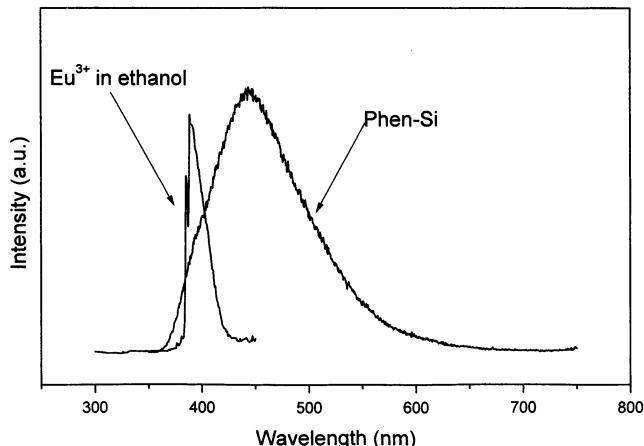


Figure 5. Absorption spectrum of Eu^{3+} ions in ethanol and emission spectrum of Phen-Si.

absorption spectrum of the acceptor (the Förster model³²) is essential for energy transfer. Figure 5 displays the overlap between the emission spectrum of Phen-Si and the absorption spectrum of EuCl_3 in ethanol. Hence, we can come to the conclusion that the phenanthroline group covalently bonded to the silica can sensitize the Eu^{3+} ion.

The excitation and emission spectra of (A) Hybrid I and (B) Hybrid II are shown in Figure 6. The excitation spectra of the materials were obtained by monitoring the emission of the Eu^{3+} ions at 618 nm. For Hybrid I, the excitation spectrum is dominated by a broad band centered at 282 nm, which is the characteristic absorption of the lanthanide complexes arising from the efficient transition based on the conjugated double bonds of the heterocyclic ligand. However, a broad noisy band of the ligand ranging from 250 to 500 nm superimposed by some f-f transition lines of Eu^{3+} (394 and 465 nm) is observed in the excitation spectrum of Hybrid II. When the emission spectrum of Hybrid I was obtained by excitation at 282 nm, only the emission lines of Eu^{3+} ${}^5\text{D}_0-{}^7\text{F}_J$ ($J = 0-4$) were observed, with the hypersensitive transition ${}^5\text{D}_0-{}^7\text{F}_2$ as the most prominent group; no emission from the ligands was detected. This indicates that energy transfer could take place from the ligands (Phen-Si) to the central metal ion (Eu^{3+}). A

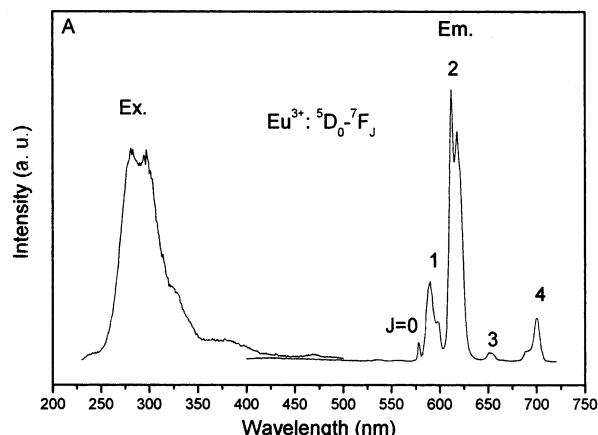


Figure 6. Excitation and emission spectra of (A) Hybrid I and (B) Hybrid II.

symmetric and broad band ranging from 500 to 650 nm with some sharp peaks superimposed (transition from ${}^5\text{D}_0$ to ${}^7\text{F}_J$ states of Eu^{3+}) can be observed in the emission spectrum of Hybrid II, but the intensity of the corresponding emission spectrum is much weaker than that of Eu^{3+} in Hybrid I. These results indicate that the energy transfer from the ligand to Eu^{3+} is far from efficient in Hybrid II. The decreased luminescence intensity for Hybrid II compared to Hybrid I is probably related to the vibration of N-H from $-\text{NH}_2$ group, which induces nonradiative transitions of Eu^{3+} via N-H vibrations. Other factors such as the triplet state level, however, can not be excluded.³⁶ It is worth noting that the great difference between the ${}^5\text{D}_0-{}^7\text{F}_0$ emission of Hybrid I and that of Hybrid II. The pattern of the ${}^5\text{D}_0-{}^7\text{F}_0$ emission can provide a better diagnostic probe for Eu^{3+} coordination homogeneity.³⁷ The homogeneity of Hybrid I is shown well in Figure 5A, which displays only one line for the ${}^5\text{D}_0-{}^7\text{F}_0$ emission. In contrast, Figure 5B shows that Hybrid II is far from homogeneous. In Figure 5B, splitting of the ${}^5\text{D}_0-{}^7\text{F}_0$ emission can be observed.

Leaching experiments on Hybrid I and Hybrid II were also carried out. Figure 7 displays the dependence of the integrated intensities of the Eu^{3+} ${}^5\text{D}_0-{}^7\text{F}_2$ transitions of Hybrid I and Hybrid II on the extraction time in DMF. From Figure 7, we can see that Hybrid I is much more stable than Hybrid II under the same extraction conditions. This indicates that the covalent

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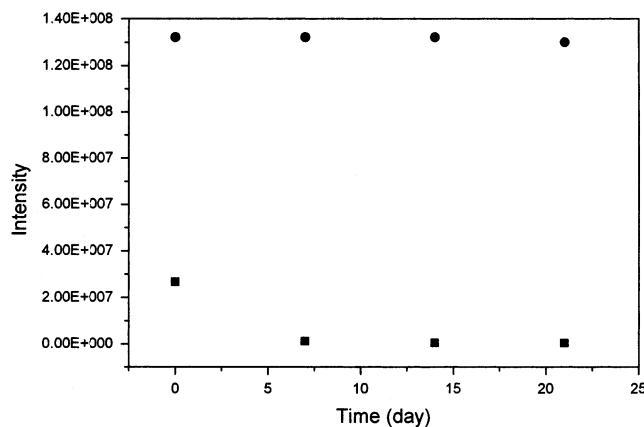


Figure 7. Dependence of the integrated intensity of the $\text{Eu}^{3+} 5\text{D}_0 - 7\text{F}_2$ transition of Hybrid I (circles) and Hybrid II (squares) on the extraction time in DMF.

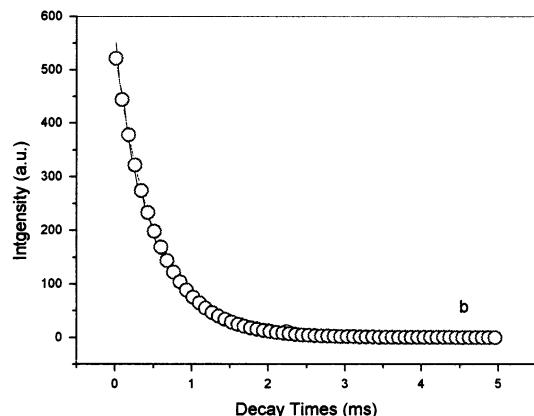


Figure 8. Decay curves of Hybrid I (open circles, experimental data; solid line, fitted according to $I = I_0 + A \exp[-(t - t_0)/\tau]$).

bond between the complexes and the sol–gel matrix can effectively prevent the leaching of the dopants.

The decay curve (Figure 8) of the Eu^{3+} in Hybrid I is singly exponential, confirming that all Eu^{3+} ions lie in the same average environment, from which the luminescence lifetime was determined. Moreover, Horrocks^{38,39} suggested that the number of the water molecules, n_w , coordinated to the Eu^{3+} ion could be evaluated from the experimental decay time by the empirical formula

$$n_w = 1.05(k_{\text{exp}} - k_r) \quad (1)$$

$$k_{\text{exp}} = \tau_{\text{exp}} - 1 = k_r + k_{\text{nr}} \quad (2)$$

where k_r and k_{nr} are the radiative and nonradiative probabilities, respectively. The radiative contribution, k_r , can be calculated from the relative intensities of the $5\text{D}_0 - 7\text{F}_J$ ($J = 0 - 4$) transitions, and it can be expressed as⁴⁰

$$k_r = (A_{0-1}E_{0-1}/S_{0-1}) \sum (S_{0-J}/E_{0-J}) \quad (3)$$

where A_{0-1} is Einstein's coefficient of spontaneous emission between 5D_0 and 7F_1 levels (usually considered to be equal to 50 s^{-1})^{41,42} and E_{0-J} and S_{0-J} are the energy and the integrated intensity of the $5\text{D}_0 - 7\text{F}_J$ transition, respectively. Using eqs 1–3, the parameters

Table 1. Experimental (k_{exp}) and Calculated Radiative (k_r) and Nonradiative (k_{nr}) 5D_0 Decay Rates (ms^{-1}), Decay Time (τ , ms), and the Number of Water Molecules Coordinated to Eu^{3+} Ions, n_w , for Hybrid I

sample	Hybrid I
τ (ms)	0.524
k_{exp} (ms^{-1})	1.908
k_r (ms^{-1})	0.255
k_{nr} (ms^{-1})	1.643
n_w	2

k_r and k_{nr} and the number of the coordinated water molecules, n_w , can be obtained, as reported in Table 1.

Our experimental results can be explained by the concept of site isolation proposed by Sen and co-workers,⁴³ who believe that specific entities (e.g., the anchored heterocycle group) can be considered as the binding sites for the metal ions. Here, the trifunctional sol–gel monomer plays a double role, i.e., as a precursor for the sol–gel and as the binding site for the lanthanide ions, confining the migration of the lanthanide ions and the aggregation to large particles (Scheme 1). Upon hydrolysis and condensation, the ligands form a preliminary network, which further restricts aggregation of the lanthanide ions. Therefore, the leaching and aggregation of the lanthanide ions are well controlled. Furthermore, the heterocycle group from Phen-Si makes it possible to dope lanthanide ions instead of their organometallic complexes into the sol–gel system, which guarantees that the lanthanide ions can be loaded at a maximum concentration.

4. Conclusions

We have shown that the method of covalently grafting organometallic complexes to the silica backbone via covalent bonds is more effective than the conventional method of doping silica gels with organometallic complexes. A remarkable increase in the europium complex concentration and a homogeneous incorporation can be realized by the covalent attachment of the complexes to the inorganic network during the sol–gel process. Hybrid I produced a strong, nearly monochromatic emission of Eu^{3+} ions, whereas Hybrid II displayed a broad emission when excited at the ligand absorption wavelength. Moreover, no leaching effects of the europium complexes can be observed in this system. Furthermore, the current synthesis method can be easily applied to other ligands and to different modified alkoxy silanes, and the desired properties can be tailored by an appropriate choice of the precursors.

Acknowledgment. This work is supported by “973”, the National Key Project for Fundamental Research of Rare Earth Functional Materials; the National Natural Science Foundation of China (Grants 29971030, 20131010); and the National Noble Youth Sciences Foundation of China (Grant 29225102).

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