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In situ synthesis and luminescence characteristics of complexes of europium(III) with 4,6-diacetylresorcinol

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Abstract

The complexes of europium(III) with 4,6-diacetylresorcinol (H₂DAR) and a co-ligand (phen, bpy or 2,2'-bipyridine *N*,*N*'-dioxide (2,2'-bpyO₂)) were *in situ* synthesized in silica matrix via a two-step gel process. The formation of complexes in silica gel was confirmed by the luminescence excitation spectra. The silica gels that contain *in situ* synthesized europium complexes exhibit the characteristic emission bands of the Eu(III). The results show that there are two ways to enhance the emission intensity of the Eu(III): (i) synthesize the complex in silica matrix and (ii) synthesize the complex with a co-ligand, which coordinates with Eu(III) in the composite system and can efficiently transfer the energy from 4,6-diacetylresorcinol to the Eu(III). The order of the luminescence intensities of the complexes is: Eu₂(DAR)₃(phen)₂-(sol–gel) > Eu₂(DAR)₃(2,2'-bpyO₂)₂-(sol–gel) > Eu₂(DAR)₃ (bpy)₂-(sol–gel) > Eu₂(DAR)₃-(sol–gel) > pure Eu₂(DAR)₃·4H₂O. © 2007 Published by Elsevier Ltd.

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1. Introduction

Materials containing lanthanide ions have been used as phosphors and laser materials because of their sharp, intensely luminescent f–f electronic transitions. In particular, a number of lanthanide complexes display a bright and narrow lanthanide ion emission.

In such a process, the quantities that contribute to the luminescence intensity are as follows: (i) the intensity of the ligand absorption, (ii) the efficiency of the ligand-to-metal energy transfer, and (iii) the efficiency of the metal luminescence [1].

There are several ways to increase the intensity of the lanthanide luminescence exploiting the antenna effect: (i) Find a suitable ligand that can transfer the energy to the metal ion efficiently. (ii) Synthesize the complex with a co-ligands, e.g., phen, bpy, or 2,2'-bipyridine N,N'-dioxide, which shows intense absorption band in the UV region due to π - π * transition. In order to eliminate O–H oscillators in the short range and reduce the nonradiative decay from the excited state of Ln(III), the coordination sphere should be supplemented with a co-ligand such as phen, bpy, or

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Fig. 1. Schematic presentation of H₂DAR, phen, bpy, and 2,2'-bpyO₂.

2,2'-bipyridine *N*,*N*'-dioxide. Quenching water molecules in the coordination sphere of lanthanide ion can be removed and therefore the luminescence intensity of the complex be enhanced. Moreover, the co-ligand coordinating with Ln(III) in the composite system might play an important role in the process of energy absorption and efficient transfer to the chelated Ln(III). And (iii) synthesize the complex by *in situ* technique via silica gel process, this process being a potentially attractive means of synthesizing novel luminescent materials. The incorporation of lanthanide complexes, particularly europium(III) complexes [2–5], has been investigated in detail. Xerogels doped with europium(III) complexes have been shown to exhibit substantially improved luminescence characteristics with respect to comparable materials containing the simple metal.

In this paper, the complexes of europium(III) with 4,6-diacetylresorcinol (H₂DAR), whose low triplet state energies are suitable for the luminescence of Eu(III), and phen, bpy or 2,2'-bipyridine N,N'-dioxide (2,2'-bpyO₂), whose structures were shown in Fig. 1, were synthesized and incorporated in silica matrix by *in situ* technique via a gel process, and the luminescence properties of the complexes in silica matrix were also discussed in detail.

2. Experimental

2.1. Synthesis

Tetraethyloxysilane (TEOS, AR, Kermel), Eu_2O_3 (Eu_2O_3 /TREO = 99.99, Rknerc), phen (AR, Kermel), bpy (AR, Kermel); H₂DAR and 2,2'-bpyO₂ were synthesized after Refs. [6,7], the others reagents used were of analytical grade.

Europium(III) chloride solution was prepared as follows: 0.5 mmol of europium(III) oxide was added into 4 ml of concentrated hydrochloric acid (36%) in a beaker and digested on a steam bath until it was completely dissolved. Surplus HCl was removed by evaporation and the resulting europium(III) chloride was dissolved in 10 ml anhydrous alcohol.

2.1.1. Synthesis of $Eu_2DAR_3 \cdot 4H_2O$

Eu₂DAR₃·4H₂O was prepared as follows: 3 mmol of H₂DAR was dissolved in 95% ethanol and a proper NaOH solution with ethanol (0.5 mol/l) was added to the above solution. EuCl₃ solution (2 mmol) was added dropwise to the solution of H₂DAR with stirring at 50–60 °C. The deposit appeared obviously in the solution. After that, the reactant solution was stirred for 4 h at the same temperature, then filtered and washed with 80% ethanol solution ($V_{(H_2O)}$: $V_{(EtOH)}$ = 1:4) until no Cl⁻ was found in the washed solution. The product was vacuum dried for 6 h at 80 °C, and the complex was obtained. Anal. Calcd. for Eu₂(DAR)₃·4H₂O: C, 37.83; H, 3.39; Eu, 31.91; found: C, 37.80; H, 3.19; Eu, 31.86.

2.1.2. Synthesis of the complexes in silica matrix

The solution used to prepare the silica xerogel consists of 1 mol of TEOS, 4 mol of ethanol and 4 mol of distilled water. A small amount of HCl is added to the solution to promote hydrolysis. H₂DAR and phen with a proper proportion of EuCl₃ (n_{Eu} : n_{H_2DAR} : n_{phen} = 1:1.5:1) were added. pH was controlled within the acid region (about 2–3).

The mixture was stirred at room temperature for several hours in order to ensure the full hydrolysis of TEOS. Finally, a proper amount of hexamethylenetetramine ($(CH_2)_6N_4$) was added to accelerate the polycondensation reaction and the mixture was stirred for another 10 min. The resulting transparent solution was poured into a plastic

box and sealed, and then placed in a drying oven at a temperature of 40 °C. Several hours later, transparent monolithic wet gel was obtained and aged for 1 day and then dried at 60 °C for 2 days followed by perforating the cap of the plastic box [4]. The Eu₂(DAR)₃phen₂ gel (the nominal doped concentration is 0.14 mol%) was stored in a desiccator for further measurements. Other gels (Eu₂DAR₃, Eu₂DAR₃(bpy)₂ and Eu₂DAR₃(2,2'-bpyO₂)₂) were prepared by a method similar to the above process.

2.2. Spectroscopy measurements

The fluorescence excitation and emission spectra were recorded at room temperature on a Hitach F4500 Spectrofluorometer; IR spectra were obtained in 4000–400 cm⁻¹ region using a Perkin-Elmer Spectrum One Spectrophotometer with KBr pellet technique. Fluorescence lifetimes were measured using an EMG 201 MSC quasimolecular 308 nm laser by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission line of Eu(III) at room temperature.

3. Results and discussion

 $(CH_2)_6N_4$ was used as a generator of hydroxyl groups to adjust the pH value for the formation of gelation and the complexes. Hydroxyl groups are gradually released through the reaction between water and $(CH_2)_6N_4$ with an increase of temperature [8]. That can provide a suitable environment for the formation of europium complexes.

3.1. FTIR analysis

Table 1 gives the main bands and their assignments of the IR spectra of pure Eu₂DAR₃·4H₂O, pure silica gel, and silica gel containing Eu₂DAR₃. For the pure complex, the broad band in the region 3500-3100 cm⁻¹ is due to the coordination with water. The rocking mode of the coordinated water was observed around 800 cm^{-1} . The bands at 1312 and 1323 cm⁻¹ are assigned to the phenolic C–O stretching mode of the ligand. Compared with the ligand, these shifts to higher frequencies in the spectrum of the chelated complex are due to its coordination to europium(III) through the oxygen atom of the phenolic group and it appeared as a singlet or a doublet [9]. Furthermore, the absorption in the region 1182 cm⁻¹ due to O–H was not observed in the infrared spectrum of the complex, suggesting that the deprotonation of the ligand occurs before their coordination to europium metal. Likewise, carbonyl stretching frequency in the ligand appearing at 1659 cm⁻¹ has a small decrease by 39 cm⁻¹ in the complex. This indicates that the carbonyl oxygen is involved in the coordination with the metal ion. A characteristic feature of the IR spectrum of the complex is the appearance of a prominent band in the region 482 cm^{-1} . From a comparison with the ligand spectrum, we have tentatively attributed this prominent band to the M–O vibrational mode. Such bands have been observed in acetylacetonate complexes [10] and other o-hydroxyarylcarbonyl compounds [11]. Based on these observations the ligand is chelated to the europium(III) via the acetyl and phenolic oxygens, H₂DAR is concluded to be a bis-bidentate donor, a similar structure that coordinated with metal ions had been confirmed by Shyamala and Jayatyagaraju [12] and Takano et al. [13].

From these data, it can be seen that the silica gel containing Eu_2DAR_3 exhibits almost the same absorption peaks as the pure silica gel, and the characteristic absorption peaks belonging to Eu_2DAR_3 are not observed. It may be considered that the dopant concentration of the luminescent complex in the silica gel is too low to be detected. On the other hand, the results probably imply that the vibrations of the ligand of Eu(III) have been restricted to some extent by the surrounding gel matrix. This further indicates that the molecular vibration of organic ligand is limited by the rigid structure of silica gel matrix [14].

Table 1					
Infrared	spectral	bands	in	cm ⁻	- 1

Compound	Main absorption hands and their assignments (cm^{-1})				
Compound	Mani absorption bands and then assignments (cm)				
H ₂ DAR	2850, 2920 (v _{O-H}), 1659 (v _{C=O}), 1312, 1323 (v _{C-O})				
Pure Eu ₂ (DAR) ₃ ·4H ₂ O	1620 (ν _C), 1325 (ν _{C-O}), 482 (δ _{M-O})				
Pure silica gel	3424 (ν _{H-O-H}), 1656 (ν _{O-H}), 1082 (ν _{Si-O-Si}), 960 (ν _{Si-OH}), 800 (ν _{O-Si-O}), 462 (δ _{O-Si-O})				
Eu ₂ (DAR) ₃ -(sol-gel)	3436 (ν_{H-O-H}), 1641 (ν_{O-H}), 1079 ($\nu_{Si-O-Si}$), 956 (ν_{Si-OH}), 797 (ν_{O-Si-O}), 462 (δ_{O-Si-O})				



Fig. 2. The excitation spectra of (a) pure Eu₂DAR₃·4H₂O and (b) Eu₂DAR₃ in silica gel.

3.2. Luminescence properties

Gd(III) complex was selected as a model complex for the determination of the triplet state energies of the organic ligand owing to their high phosphorescence–fluorescence ratio compared to those of other Ln(III) complexes and Gd(III) can sensitize the phosphorescence emission of ligands. The phosphorescence spectrum of the gadolinium complex in ethanol with H₂DAR was measured, and the triplet state of H₂DAR can be determined to be 21,739 cm⁻¹ based on the maximum phosphorescence bands at 460 nm. The energy differences between the triplet state of H₂DAR and the resonance energy level of Eu(III) (${}^{5}D_{0}$, 17,265 cm⁻¹) can be calculated to be 4474 cm⁻¹. They are all indeed sufficient to efficiently populate the ${}^{5}D_{0}$ luminescent state of Eu(III).

Fig. 2 shows the excitation spectra of (a) pure Eu₂DAR₃·4H₂O and (b) Eu₂DAR₃ in silica gel. Either of the excitation spectra consists of a very broad band instead of a characteristic narrow band of Eu(III) (395 nm), which indicates that the europium complex has been synthesized by an *in situ* technique via silica gel process. Compared to that of pure complex, the maximum excitation wavelength of the complex in silica gel shows a small blue-shift changing from 400 to 353 nm, which implies that different compositions may exist in the two samples. For pure Eu₂DAR₃, the surrounding environment of the Eu(III) is homogeneous, so the excitation spectrum consists of a symmetric and broad band ranging from 250 to 450 nm. However, silica gel is a non-crystalline substance with a porous microstructure, so the excitation spectrum becomes an asymmetric band, and the decrease of local symmetry for Eu(III) also should be proved from the increase of the ratio of the emission intensity of the peak at 610 nm (electric dipole ${}^5D_0 \rightarrow {}^7F_1$ transition).

The emission spectra of the complexes consist of four main peaks at 578 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{0}$), 589 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{1}$), 610 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) and 650 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{3}$), and the emission at 610 nm is the strongest. From Fig. 3(1) we can see that the emission intensity of Eu₂DAR₃ in silica gel (the nominal doped concentration is 0.14 mol%) is four times greater than that of pure Eu₂DAR₃·4H₂O. Synthesis of the complexes by an *in situ* technique via silica gel process can replace some or all of the H₂O molecules or OH groups bound to the europium ion, and the emission intensity is thus increased by the more efficient energy transfer from the organic system and the reduction of the OH vibration that can quench the luminescence of Eu(III).

The lifetimes of ${}^{5}D_{0}$ excited state for the complexes were measured by time-resolved spectroscopy, the lifetime valves were calculated through the mono-exponential decay method [15], and the results are given in Table 2.

The emission quantum yield q for the Eu₂(DAR)₃(phen)₂-(sol-gel), Eu₂(DAR)₃(2,2'-bpyO₂)₂-(sol-gel), Eu₂(DAR)₃(bpy)₂-(sol-gel) and Eu₂(DAR)₃-(sol-gel) were obtained following the procedure described in Ref. [16]. The q value is defined as the ratio between the number of photons emitted by the Eu(III) and the number of photons absorbed by the ligands. According to the method developed by Bril [17] at Philips Research Laboratories, the q value for a given sample can be determined by comparison with standard phosphors, whose quantum yields have



Fig. 3. (1) The emission spectra of pure Eu2DAR3·4H2O and Eu2DAR3 in silica gel; (2) the emission spectra of the complexes in silica gel.

been previously determined by absolute measurements. This method provides absolute yields while avoiding absolute measurements, which are in general complicated. The quantum yield q_x of a sample is thus determined as follows:

$$q_{x} = \left(\frac{1 - r_{\rm ST}}{1 - r_{x}}\right) \left(\frac{\Delta\phi_{x}}{\Delta\phi_{\rm ST}}\right) q_{\rm ST}$$

Table 2 The luminescence properties of the pure complex and the complexes in silica gel

Compound	$\lambda_{ex} \ (nm)$	$\lambda_{em} \ (nm)$	Relative emission intensity				Lifetimes (t/ms)	q (%)
			${}^{5}D_{0} \rightarrow {}^{7}F_{0}$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_3$		
Pure Eu ₂ (DAR) ₃ ·4H ₂ O	400	611	1.2	0.5	15.5	0.5	0.269	4.8
Eu ₂ (DAR) ₃ -(sol-gel)	353	609	7.6	4.8	60.6	1.0	0.526	10.2
Eu ₂ (DAR) ₃ phen ₂ -(sol-gel)	364	610	52.3	37.1	544.9	6.3	1.205	15.4
Eu ₂ (DAR) ₃ (bpy) ₂ -(sol-gel)	352	610	11.5	8.5	106.5	1.3	0.635	10.5
$Eu_2(DAR)_3(2,2'-bipyO_2)_2-(sol-gel)$	345	610	25.6	25.1	311.8	4.4	0.758	12.1

where r_{ST} and r_x are the amount of exciting radiation reflected by the standard and by the sample, respectively, and q_{ST} is the quantum yield of the standard phosphor. The terms $\Delta \Phi_x$ and $\Delta \Phi_{ST}$ give the integrated photon flux (photons s⁻¹) for the sample and the standard phosphor, respectively. The standard in our case was sodium salicylate (Aldrich), which has a broad emission band with a maximum at 450 nm and q = 60% at room temperature [17]. But our experiment shows that the best-excited wavelength of the complexes is not the same as that of sodium salicylate, so the q is not an absolutely quantum yield, it only can be used for making a comparison between each other.

When phen (bpy or 2,2'-bpyO₂) was added as a co-ligand, the luminescence intensity of the complex increased, as can be seen in Fig. 3(2). Compared with bpy or 2,2'-bpyO₂, phen is a more suitable co-ligand.

The results imply that phen (bpy or 2,2'-bpyO₂), as a co-ligand, coordinates with Eu(III) in the composite system. The co-ligand can eliminate O–H oscillators in the short range too, reduce the nonradiative decay from the excited state of Eu(III), and enhance the luminescence intensity, the lifetime and the emission quantum yield. The order of the luminescence intensities of the complexes is: $Eu_2(DAR)_3(phen)_2$ -(sol–gel) > $Eu_2(DAR)_3(2,2'-bpyO_2)_2$ -(sol–gel) > $Eu_2(DAR)_3(bpy)_2$ -

The luminescence properties of the complexes are summarized in Table 2.

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