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# Synthesis and luminescence properties of mesophase silica thin films doped with in-situ formed europium complex

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## Abstract

Mesophase silica thin film doped with in-situ formed ternary Eu complex was synthesized by adding ligands (DBM = dibenzoyl-methane, phen = 1,10-phenanthroline), Eu ions ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ), and Pluronic P123 triblock copolymer into hydrolyzed tetramethoxy-silane (TMOS). The structure of this inorganic/organic film was characterized as a 2d-hexagonal structure by X-ray diffraction (XRD) and TEM analysis. The excitation spectra ( $\lambda_{\text{em}} = 612\text{ nm}$ ) and emission spectra ( $\lambda_{\text{ex}} = 325\text{ nm}$ ) indicated that the ternary complex, Eu-DBM-phen, was formed in-situ during the formation of the film. The mesophase silica thin film doped with the in-situ formed Eu complex showed a higher quantum efficiency compared to a pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex and a mesophase silica thin film doped with in-situ formed binary Eu-phen complex.

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**Keywords:** Mesophase thin film; Rare earth complex; Photoluminescence;  $\beta$ -diketone; Quantum efficiency

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## 1. Introduction

Owing to their high surface areas, ordered pore structures (mostly hexagonal and cubic packed pores), and uniformly controlled pore sizes, ordered mesoporous materials using self-assembled molecular aggregates as structure-directing agents [1] have attracted a great deal of attention from the scientific and industrial communities. Mesoporous thin films are of particular interest due to their promising applications in membrane separations, chemical sensors, optical devices, and electronic devices such as low dielectric constant films, as well as nanosized quantum materials [2–7]. In particular, in the field of optical applications, many types of photo-active or functional dopants can be incorporated into mesoporous thin films. These films have several advantages, such as a high surface area for dopants while being capable of a high concentration without aggregation, appropriate mesopore size for

size confinement, and uniformly controlled pore sizes for facile diffusion. For organic doping in mesophase thin films, during film formation by evaporation-induced self-assembly (EISA), a silica/surfactant/organic additive could be co-assembled by inorganic/organic interaction. The components can be combined at the nanoscopic level into a single thin film to prepare organic doped mesophase material [6,7]. With significant development in the design of organic-inorganic hybrid mesophase structures, mesophase thin films doped with many organic dopants have extended the potential applications in scientific and industrial fields.

The unique emission properties of trivalent rare earth (RE) ions originate from the intra-4f transitions, which are shielded by outer shells. Due to the shielding, the RE ions display narrow-line luminescence, and the emission is relatively insensitive to host materials when they are incorporated into other materials. Thus, trivalent RE ions are ideal dopants for forming highly efficient photo-active materials in many optical applications. However, as the transition within the partially filled 4f electrons is in

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principle spin-forbidden, the absorption coefficients of RE ions are low. In order to overcome this problem, RE complexes using organic ligands such as  $\beta$ -diketones were investigated [8]. In an RE complex system, organic ligands can serve as an energy absorption antenna; then, via efficient intramolecular energy transfer, the RE ions obtain energy and exhibit intense characteristic emissions [9]. Moreover, RE complexes have been utilized as good dopants in many sol–gel materials for the fabrication of photo-active materials at low temperatures [10–17]. Organic ligands coordinated with RE ions in complexes shield the ions from impurities in the surrounding matrix and protect them from quenching by high-energy vibrations from sol–gel hosts. However, high concentrations of RE complexes in sol–gel hosts result in their aggregation, limiting the luminescence efficiency of the materials. Mesophase thin films can incorporate high concentrations to provide better optical characteristics compared to typical sol–gel thin films [18–20]. Bartl et al. synthesized mesostructured thin films doped with in-situ formed Eu–phen complex and showed the hydrophobic aspects of the surfactant prevent aggregation of the complexes [21]. In order to utilize this kind of inorganic/organic mesophase thin films in flat panel display systems and lighting field, high luminescence quantum efficiency is necessary. For trivalent europium ions, the luminescence of some ternary complexes is much brighter than the binary complexes. In this paper, we explore the ternary complexes of europium as luminescence dopants to enhance the luminescence intensity and quantum efficiency of the inorganic/organic mesophase thin film.

The transparent silica mesophase thin film doped with highly luminescent ternary europium complex was synthesized by an in-situ method similar to that in the Ref. [21]. Besides 1,10-phenanthroline (phen), another ligand dibenzoylmethane (DBM) was added to form ternary europium complex. In the synthesis, a homogenous mesostructured thin film was formed using Pluronic P123 triblock copolymer as a template, which enhances the solubility of organic ligands and separates the Eu complexes in hydrophobic regions uniformly. For comparison, the similar inorganic/organic mesophase thin film doped with the binary complex was also synthesized according to Ref. [21]. All the thin films had a typical 2d-hexagonal mesostructure and Eu complexes were combined at the nanoscopic level in the hydrophobic core of micelles. Using spectroscopy method, the luminescence properties of the two mesophase thin films were studied. The results show that the inorganic/organic mesophase thin film doped with ternary europium complex has higher luminescence quantum efficiency than that doped with binary europium complex, which means that added another ligand to form ternary complex has improved luminescence properties of the mesophase thin films doped with the RE complex. It meets the requirements of high luminescence quantum efficiency for display and lighting application.

## 2. Experimental section

### 2.1. Sample preparation

The mesophase silica thin film doped with in-situ formed ternary Eu complex was prepared by a one-step synthesis method at room temperature. For this procedure, tetramethylorthosilicate (TMOS, Aldrich, 98%) was hydrolyzed in distilled water containing hydrochloric acid (HCl, Aldrich, 37%) at room temperature. Separately, Pluronic P123 (BASF), europium chloride hexahydrate ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ , Aldrich, 99%), dibenzoylmethane (DBM, Fluka, 98%), and 1,10-phenanthroline (phen, Aldrich, 99%) were dissolved in methanol ( $\text{CH}_3\text{OH}$ , Merck, 99.8%), and this solution was then added into the hydrolyzed TMOS. The final reactant mole ratios were TMOS:H<sub>2</sub>O:HCl:P123:EuCl<sub>3</sub>·6H<sub>2</sub>O:DBM:phen=1:8.33:0.009:0.0105:0.02:0.06:0.02. The transparent solution was stirred for 1 h and filtered through a 0.22  $\mu\text{m}$ -sized Teflon filter to remove impurities and gas bubbles. This solution was then deposited onto p-type Si(1 0 0) wafers by spin coating at 4000 rpm for 40 s. For comparison, the mesophase silica thin film doped with in-situ binary Eu–phen complex was fabricated with same procedure and Eu/Si molar ratio. Additionally, an Eu(DBM)<sub>3</sub>phen complex was synthesized following a procedure in the literature [22].

### 2.2. Characterization of samples

The structural characterization of the mesophase silica thin film doped with in-situ formed ternary Eu–DBM–phen complex was investigated by X-ray diffraction (XRD) measurements with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15417 \text{ nm}$ ) with a  $0.01^\circ$  step width and 1 s step time on a Rigaku D/MAX-RC diffractometer (40 kV, 80 mA). Transmission electron microscope (TEM) images of the calcined films were recorded using a JEOL JEM-2000EX electron microscope operating at 200 kV. A Woollam M-200D ellipsometer was used to quantify the refractive index of the film. Room-temperature emission spectra and luminescence decay were measured using a 325 nm line of a HeCd laser as an excitation source. The emission spectra were measured using an InGaAs(Cs) photomultiplier tube with a standard lock-in technique. The luminescence decay traces were obtained with a mechanical chopper and a digitizing oscilloscope. The excitation spectra were measured at room temperature (Xe 500 W lamp) with a DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea).

## 3. Result and discussion

### 3.1. Structure of mesophase thin films

Fig. 1 shows the XRD peaks of the as-synthesized mesophase thin film doped with in-situ formed ternary

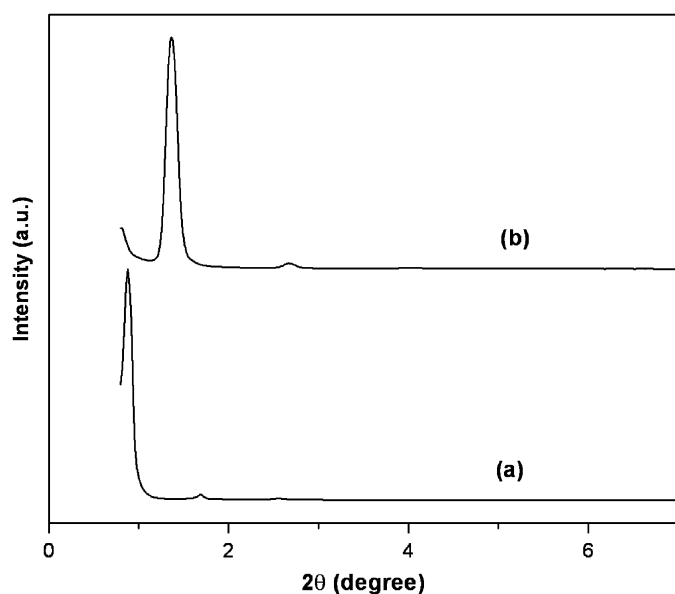


Fig. 1. XRD patterns of (a) the as-synthesized mesophase thin film doped with in-situ formed  $\text{Eu}(\text{DBM})_3\text{phen}$  and (b) the calcined thin film at  $550^\circ\text{C}$ .

$\text{Eu-DBM-phen}$  complex and the same thin film calcined at  $550^\circ\text{C}$ . The XRD pattern of the as-synthesized mesophase film shows two peaks, at  $2\theta = 0.88^\circ$  and  $1.67^\circ$ , which indicate (100) and (200) reflections of a general 2d-hexagonal structure, respectively [23]. The unit cell parameter ( $a_0$ ) can be calculated as follows:  $a_0 = 2d(100)/3^{1/2}$ , where d-spacing of  $d(100) = 10\text{ nm}$  is obtained from the  $2\theta$  value of (100) peak using  $d(100) = \lambda/2 \sin \theta$  [24]. The calculated unit cell parameter including the internal pore diameter and silica wall thickness is  $11.5\text{ nm}$ .

Calcination of the mesophase thin film at  $550^\circ\text{C}$  can circumvent degradation of the organic region. The XRD pattern of the calcined thin film showed a similar structure to the as-synthesized sample. The two peaks still remain in the calcined thin film. However,  $d(100)$  and a unit cell parameter decrease to  $6.4$  and  $7.4\text{ nm}$ , respectively. It suggests the formation of oriented hexagonal mesostructured silica in the as-deposited thin film, because the surfactants and organic dopants were decomposed and only silica framework left after calcinations at  $550^\circ\text{C}$  in air. This structure is also in agreement with the TEM image of the calcined mesoporous thin film, as shown in Fig. 2. The calcined mesoporous thin film has a 2d-hexagonal structure with a unit cell parameter of  $7.2\text{ nm}$ . The XRD patterns and TEM images confirm that even another ligand was added besides the phen, the as-deposited mesophase thin films having a 2-d hexagonal structured silicate framework were formed successfully by using the P123 block copolymer template. The in-situ formed ternary  $\text{Eu-DBM-phen}$  complex was incorporated in the mesophase thin film.

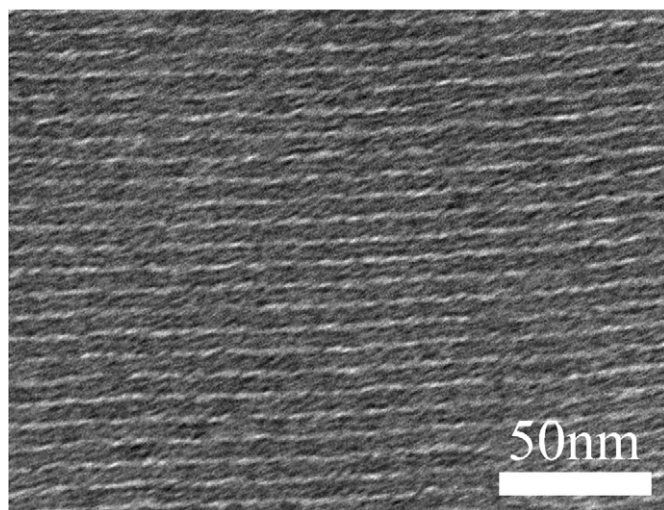


Fig. 2. Top-view TEM image of the calcined mesophase thin film.

### 3.2. Luminescence properties

The excitation spectra of (a) the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, (b) the mesophase thin film doped with the in-situ formed ternary  $\text{Eu-DBM-phen}$  complex, (c) the mesophase thin film doped with in-situ formed binary  $\text{Eu-phen}$  complex at room temperature are compared in Fig. 3. The excitation spectra of the three samples were recorded in a range of  $200\text{--}450\text{ nm}$  by monitoring the  $612\text{ nm}$  emission, which corresponds to the hypersensitive  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition. For the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, the broad band in the range of  $225\text{--}450\text{ nm}$  is attributed to absorption of the organic ligand, which can be assigned to the  $\pi\text{-}\pi^*$  electron transition. In the mesophase thin film doped with ternary  $\text{Eu-DBM-phen}$  complex, an intense band ( $310\text{--}400\text{ nm}$ ) with a relatively weak band (approximately  $250\text{ nm}$ ) on the high-energy side was observed in the excitation spectrum. The strong band ( $310\text{--}400\text{ nm}$ ) corresponds to the absorption band of the DBM ligands, while the weak band (approximately  $250\text{ nm}$ ) corresponds to the absorption band of the phen ligands [25]. Fig. 3(c) is the excitation spectrum of the mesophase thin film doped with in-situ formed binary  $\text{Eu-phen}$  complex. The intense band ( $225\text{--}325\text{ nm}$ ) corresponds to the phen ligands. By monitoring the characteristic emissions of the  $\text{Eu}^{3+}$  ions, the presence of the typical absorption band of the organic ligand in the excitation spectrum indicates that the  $\text{Eu}^{3+}$  ions are coordinated to organic ligands and excited via intramolecular energy transfer from the triplet excited states of the ligands. Compared to the excitation spectrum of the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, the band corresponding to the absorption band of the organic ligand becomes narrower in the mesophase thin film doped with ternary  $\text{Eu-DBM-phen}$  complex. This means that the mesophase framework affects the coordination shell of the  $\text{Eu}^{3+}$  and the energy transfer between ligands and  $\text{Eu}^{3+}$  ions. Compared with excitation spectrum of the mesophase thin

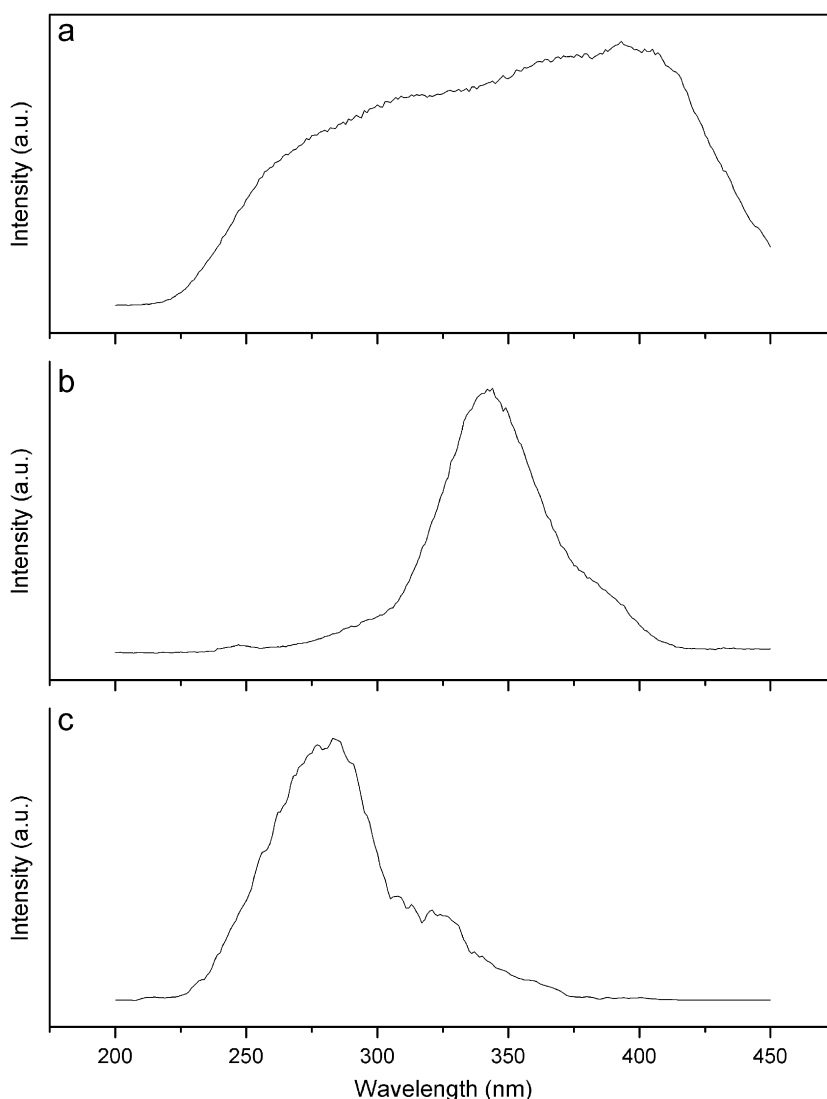


Fig. 3. Excitation spectra of (a) the  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, (b) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, and (c) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{phen})_3$  complex at room temperature by monitoring the emission wavelength of 612 nm.

film doped with in-situ formed binary  $\text{Eu}$ –phen, in the mesophase thin film, after added the DBM ligand, the band corresponding to the absorption band of the DBM ligand is much stronger than that of the phen ligand and the DBM ligand becomes to dominantly sensitize the  $\text{Eu}^{3+}$  ions. The DBM is a more efficient sensitizer for the luminescence of the central  $\text{Eu}^{3+}$  ion compared to the phen, and the intramolecular energy transfer from the DBM ligand is more efficient according to the luminescence theory of trivalent rare earth complexes [26]. Thus, the energy transfer is more efficient in the mesophase thin film doped with ternary  $\text{Eu}$ –DBM–phen complex than that in the mesophase thin film doped with binary  $\text{Eu}$ –phen complex. This is further supported by the observation that the luminescence intensity of  $\text{Eu}^{3+}$  in the mesophase thin film doped with ternary  $\text{Eu}$ –DBM–phen complex is higher than that in the mesophase thin film doped with binary  $\text{Eu}$ –phen complex under the same excitation.

Fig. 4 presents the corrected emission spectra for the preceding samples at room temperature. Under a 325 nm laser excitation, all of the spectra present the characteristic emissions of  $\text{Eu}^{3+}$  ion. It indicates the energy transfer from ligands to  $\text{Eu}^{3+}$  is efficient and the in-situ  $\text{Eu}$  complexes are formed in the mesophase thin films. The peaks near 594 nm derive from the allowed magnetic dipole transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ), which has no electric dipole contribution [27]. This transition is practically independent of the ion's surroundings. The peaks around 620 and 648 nm are due to the induced electric dipole transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{2,4}$ ), which are allowed on condition that the europium ion occupies a site without an inverse center. Their intensities are hypersensitive to crystal environments. Peaks corresponding to the transitions of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0,3}$  appear at approximately 580 and 657 nm. Their intensities depend upon both odd parity–even parity state mixing and J–J' mixing within the 4f-electron state manifold [28–30]. In the emission spectra

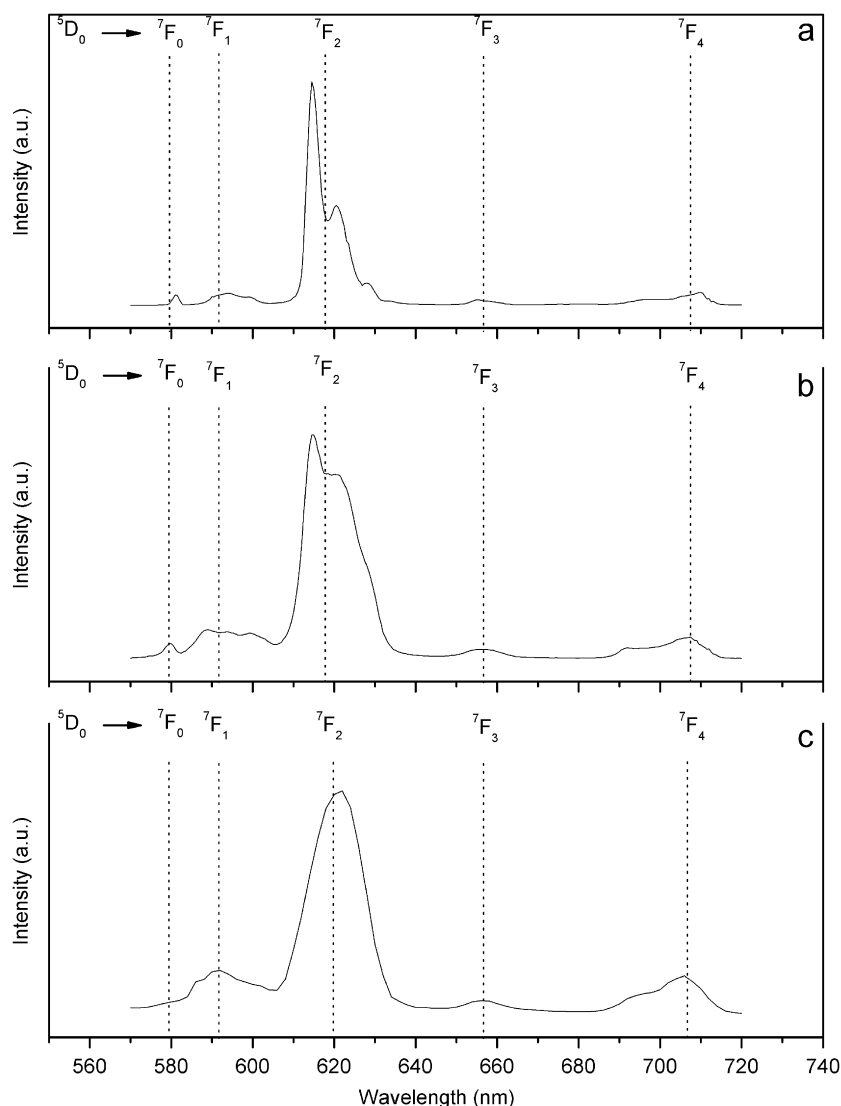


Fig. 4. Corrected emission spectra for (a) the  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, (b) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, and (c) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{phen})_3$  complex at room temperature under 325 nm laser excitation.

of the four samples, the induced electric dipole  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition makes a dominant contribution to the emissions. Compared to the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, the emission peaks of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition in Figs. 4(b) and (c) are relatively broadened, and the number of Stark components is decreased. Together, these results suggest less ordered crystalline environments of  $\text{Eu}^{3+}$  ions in the mesophase thin film compared to the pure complex. However, the distinct splitting of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  europium peak in the mesophase thin film points to a relatively ordered 'crystalline' rare earth ion environment. The excitation and emission spectra also indicate that  $\text{Eu-DBM-phen}$  complex and  $\text{Eu-phen}$  complex are formed in-situ during the synthesis of the composite films.

### 3.3. Luminescence decay time and location of $\text{Eu}^{3+}$

The luminescence lifetime is an important parameter in the photophysical description of europium luminescence.

In Fig. 5, the luminescence decay curves relative to the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, the mesophase thin film doped with ternary  $\text{Eu-DBM-phen}$  complex, and the mesophase thin film doped with binary  $\text{Eu-phen}$  complex can be closely fitted with a single exponential function, and lifetimes of  $318 \pm 1.4$ ,  $815 \pm 1.5$ , and  $330 \pm 0.75 \mu\text{s}$  were obtained. The monoexponential decay processes of the inorganic/organic mesophase thin films are indicative of a single average site distribution for  $\text{Eu}^{3+}$  ions in each sample. These findings indicate that, identical to the well-crystallized pure complex, there exists only one emission center in both the two inorganic/organic mesophase thin films. There are three regions in the inorganic/organic mesophase thin films, the silica framework, the hydrophobic region in micellar interior and ionic interface formed by surfactant charge-groups [7,31,32]. According to the synthesis process of the inorganic/organic mesophase thin films doped with in-situ formed  $\text{Eu}$  complex, the hydrophilic end (PEO) moieties of the P123 were asso-

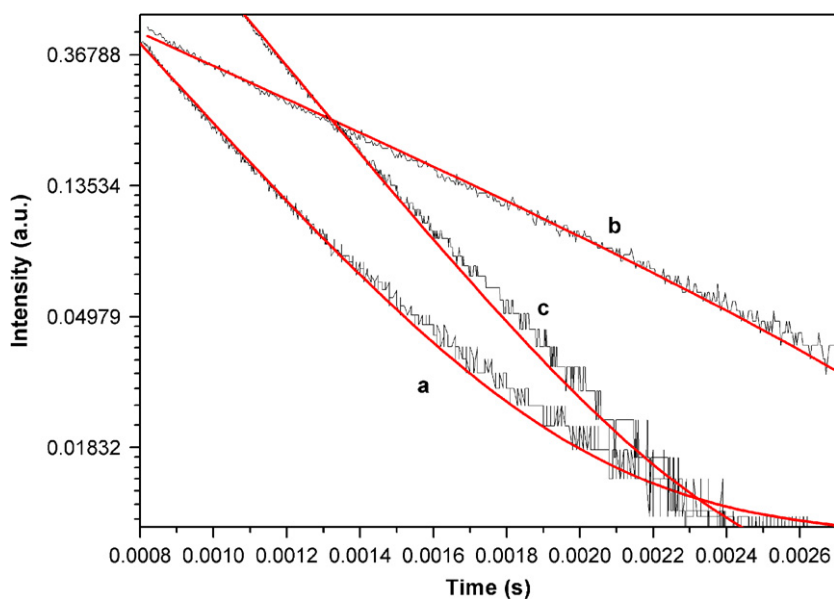


Fig. 5. Luminescence decay curves of (a) the  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, (b) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{DBM})_3\text{phen}$  complex, and (c) the mesophase thin film doped with in-situ formed  $\text{Eu}(\text{phen})_3$  complex at room temperature.

ciated with hydronium ions under acid condition and the cationic silica species were combined with these charge-associated PEO units through noncovalent interactions (electrostatic, hydrogen bonding, van der Waals forces, etc.) [33,34]. When the surfactant micelles were formed, the organic ligands were incorporated into hydrophobic part (PPO) of micellar interiors by hydrophobicity. Associate with the evidence mentioned above for in-situ forming of Eu complexes in inorganic/organic mesophase thin films, the  $\text{Eu}^{3+}$  ions are combined with the ligands. It means that the  $\text{Eu}^{3+}$  ions are located inside the pores of the silica framework. In addition, the monoexponential decay profiles suggest that only one luminescence center is contained in the both two inorganic/organic mesophase thin films, the facts demonstrate that all the in-situ formed ternary Eu–DBM–phen complex and binary Eu–phen complex ultimately reside within the micelles and the mesopore silica framework separates the complexes to prevent the aggregation.

Compared with the pure  $\text{Eu}(\text{DBM})_3\text{phen}$  complex and the mesophase thin film doped with binary Eu–phen complex, the mesophase thin film doped with ternary Eu–DBM–phen complex has the longest lifetime. It may be related to less important nonradiative relaxation pathways in the mesophase thin film doped with ternary Eu–DBM–phen complex. Combined with the quantum efficiency of  $\text{Eu}^{3+}$  ions  $^5\text{D}_0$  level, we can study the luminescence properties of this material deeply.

### 3.4. Emission quantum efficiency

On the basis of the corrected emission spectrum and the observed luminescence lifetime of the  $^5\text{D}_0$  emitting level, the quantum efficiency ( $\Phi_{\text{Ln}}$ ) of  $\text{Eu}^{3+}$  ion in the samples can be calculated according to the method described in

detail by Werts et al. [27]. The corrected emission spectra can present a relatively spectral photon flow vs. the wavelength. The emission intensity  $I$  taken as the integrated intensity  $S$  of the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  emission spectrum can be defined as

$$I_{ij} = \hbar\omega_{ij}A_{ij}N_i \approx S_{ij}, \quad (1)$$

where  $i$  and  $j$  are the initial ( $^5\text{D}_0$ ) and final levels ( $^7\text{F}_j$ ), respectively,  $\hbar\omega_{ij}$  is the transition energy,  $A_{ij}$  is Einstein's coefficient of spontaneous emission, and  $N_i$  is the population of the  $^5\text{D}_0$  emitting level. As most transitions exhibit a fine structure for the samples used in this study, the entire transition is integrated and the fine structure ignored. As mentioned above, the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition in the  $\text{Eu}^{3+}$  ions is practically independent of the ions' surroundings due to its magnetic dipole nature. The energy of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition as well as its dipole strength can be assumed as constant. The radiative lifetime of the  $\text{Eu}^{3+}$  ions can then be related to the corrected emission spectrum, as in

$$\frac{1}{\tau_{\text{R}}} = A_{\text{MD},0}n^3 \left( \frac{I_{\text{tot}}}{I_{01}} \right), \quad (2)$$

where  $\tau_{\text{R}}$  is the radiative lifetime,  $A_{\text{MD},0}$  is the spontaneous emission probability for the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition in vacuo (which can be obtained from the theoretically calculated dipole strength), and  $A_{\text{MD},0}$  has a value of  $14.65 \text{ s}^{-1}$ .  $n$  is the refractive index of the medium (mesophase thin film). In the experiments, the refractive index of the mesophase thin film ( $n = 1.47$ ) was obtained using an ellipsometer. The refractive index of the pure Eu complex is approximately 1.5.  $I_{\text{tot}}/I_{01}$  is the ratio of the total area of the corrected  $\text{Eu}^{3+}$  emission spectrum to the area of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  band. The radiative lifetimes  $\tau_{\text{R}}$  of the three samples are listed in Table 1.

Table 1

Luminescence lifetimes ( $\tau_{\text{obs}}$ ) of the Eu(DBM)<sub>3</sub>phen complex, the mesophase silica thin film doped with in-situ formed Eu(DBM)<sub>3</sub>phen complex, and the mesophase silica thin film doped with in-situ formed Eu(phen)<sub>3</sub> complex

	$\tau_{\text{obs}}$ ( $\mu\text{s}$ )	$\tau_{\text{R}}$ ( $\mu\text{s}$ )	$\Phi_{\text{Ln}}$
Eu(DBM) <sub>3</sub> phen	318 ± 4	1774	0.179
Eu(DBM) <sub>3</sub> phen-mesophase	815 ± 1.5	2519	0.325
Eu(phen) <sub>3</sub> -mesophase	330 ± 0.75	2002	0.164

Radiative lifetimes ( $\tau_{\text{R}}$ ) calculated on the basis of the corrected emission spectra. The luminescence quantum efficiency ( $\Phi_{\text{Ln}}$ ) is found using Eq. (5).

The quantum efficiency of the luminescence step  $\Phi_{\text{Ln}}$  expresses how well the radiative processes compete with nonradiative processes.

$$\Phi_{\text{Ln}} = \frac{k_{\text{r}}}{k_{\text{r}} + k_{\text{nr}}}, \quad (3)$$

where  $k_{\text{r}}$  and  $k_{\text{nr}}$  denote the radiative and nonradiative transition rates, respectively. Nonradiative processes influence the observed luminescence lifetime ( $\tau_{\text{obs}}$ ); however, the radiative lifetime ( $\tau_{\text{R}}$ ) is not affected by these processes:

$$\tau_{\text{obs}} = \frac{1}{k_{\text{r}} + k_{\text{nr}}}, \quad \tau_{\text{R}} = \frac{1}{k_{\text{r}}}. \quad (4)$$

The quantum efficiency  $\Phi_{\text{Ln}}$  can then be expressed as

$$\Phi_{\text{Ln}} = \frac{\tau_{\text{obs}}}{\tau_{\text{R}}}. \quad (5)$$

Using the observed luminescence lifetime  $\tau_{\text{obs}}$  from the decay curve and the radiative lifetime  $\tau_{\text{R}}$  from the corrected emission spectrum, the quantum efficiency  $\Phi_{\text{Ln}}$  is calculated. The results are listed in Table 1. In these experiments, the quantum efficiency of the mesophase thin film doped with in-situ formed ternary Eu–DBM–phen complex is higher than these in both the pure Eu complex and the mesophase thin film doped with in-situ formed binary Eu–phen complex. The higher quantum efficiency indicates that the radiative process that competes with the nonradiative depopulation of the  $\text{Eu}^{3+}$  excited state in the mesophase thin film doped with in-situ formed ternary Eu–DBM–phen complex is more operative. Using the in-situ synthesis method, the ternary Eu–DBM–phen complex can be combined in the hydrophobic regions in the pores and separated by the silica framework. Compared with the pure Eu(DBM)<sub>3</sub>phen complex, the higher quantum efficiency of the mesophase thin film doped with in-situ formed ternary Eu–DBM–phen complex may be related to the separation of the complex in the mesopores preventing the aggregation. It indicates that the radiative process well compete with the nonradiative process. For the quantum efficiency of the mesophase thin film doped with ternary Eu–DBM–phen complex being higher than that in the mesophase thin film doped with binary Eu–phen complex, it may be resulted from the fact that the energy transfer from DBM ligand to  $\text{Eu}^{3+}$  ions is more efficient than that

from the phen ligand. Since the triplet state of the DBM ( $20\,400\text{ cm}^{-1}$ ) [35] is closer to the  $^5\text{D}_0$  energy level of  $\text{Eu}^{3+}$  ion ( $17\,250\text{ cm}^{-1}$ ) [26] than that of the phen ( $22\,100\text{ cm}^{-1}$ ) [36], in case of the mesophase thin film doped with ternary Eu–DBM–phen complex, the DBM is the dominative ligand to transfer energy to  $\text{Eu}^{3+}$  ion. The higher quantum efficiency means that adding DBM ligand to in-situ form the ternary Eu–DBM–phen complex improves the luminescence properties of the mesophase thin film doped with Eu complex.

#### 4. Conclusions

Luminescent mesophase silica thin film doped with in-situ formed ternary Eu–DBM–phen was prepared by a one-step synthesis method. XRD and TEM analyses confirm that the homogenous thin film has a typical 2d-hexagonal mesostructure. Under a 325 nm laser excitation, the mesophase thin film exhibits the strong characteristic emissions of  $\text{Eu}^{3+}$  ions. The corrected emission spectrum for the mesophase thin film suggests that the ternary Eu–DBM–phen complex is in-situ formed during the synthesis of the composite films. The decay process indicates that only one luminescence center is contained in the mesophase thin film, and that the mesophase silica thin film is homogeneous. To compare with the pure Eu(DBM)<sub>3</sub>phen complex and the mesophase silica thin film doped with in-situ formed binary Eu–phen complex, the quantum efficiencies of the three samples were calculated. The results show that the mesophase thin film doped with ternary Eu–DBM–phen complex possesses highest quantum efficiency. The method of incorporating the in-situ ternary Eu–DBM–phen complex into the mesophase thin film offers considerable potential to reduce the contribution of nonradiative processes and optimize the luminescence quantum efficiency of lanthanide complexes.

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