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# Mesostructured thin film with covalently grafted europium complex†

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**A mesostructured transparent thin film containing europium complexes was prepared and investigated. The mesostructure of the film was confirmed by XRD and the luminescence spectra reveal that $Eu^{3+}$ has a similar environment in both amorphous and mesostructured films.**

Recently, mesostructured thin films have been prepared by dip-coating or by spontaneous formation at air–water interfaces, in which hexagonal, cubic, or lamellar phases can be generated by changing the surfactant-to-silica ratio.[1–4] At the heart of these studies is the investigation of dye-doped mesostructured compounds. These films could find applications as sensors[5] as well as in optical applications such as materials exhibiting amplified spontaneous emission and lasing.[5–8] The porous structure is especially important for optical sensoring.[9] The thermal stability of the mesostructured thin films is another important factor from an applications point of view.[10]

Lanthanide complexes have long been known to give bright emission under UV irradiation because of the effective energy transfer from ligands to the central ions, the so-called "antenna effect,"[11] and have been used in nonlinear optics and light-emitting devices. So far, these complexes have been excluded from practical use as tunable solid-state lasers or phosphor devices because of their poor thermal stability and mechanical properties.[12,13] Inclusion of lanthanide complexes into mesostructured materials may overcome these shortcomings.[14] Typically, this can be realized by doping mesostructured materials with lanthanide complexes, which can take up molecules in their empty pores. Because the loading and localization of the active groups are governed mainly by diffusion, this leads to a heterogeneous distribution of the lanthanide complexes in the mesostructured matrices. An alternative route that directly incorporates the organic moieties into the mesoporous structure during a one-pot synthesis can overcome this limitation.[15,16]

In this paper, we provide a new one-step method to design hybrid mesostructured silica thin films in which lanthanide complexes are covalently grafted onto the silica. Mesostructured hybrid thin films with covalently bound europium complexes were prepared *via* direct routes involving co-condensation of tetraethoxysilane (TEOS) and the modified phenanthroline (denoted as phen-Si) in the presence of $Eu^{3+}$ by the dip-coating process.

$^{29}$Si MAS NMR spectroscopy shows distinct resonances for siloxane [$Q^n$=Si(OSi)$_n$(OH)$_{4-n}$, $n = 2$–4] and organosiloxane [$T^m$ = RSi(OSi)$_m$(OH)$_{3-m}$, $m = 2$–3] centers in the mesostructured thin film (see ESI). The predominance of $T^3$ compared with $T^2$ organosiloxane centers indicates that condensation of the organo-functionality in the ordered structure was extensive. The presence of phenanthroline is confirmed by FTIR. Besides the characteristic Si–O–Si framework vibrations (1050, 480, 750 and 900 cm$^{-1}$), an FTIR spectrum of the ordered thin film shows vibration modes centered at 1700, 1651, 1544 and 1510 cm$^{-1}$, originating from the phen-Si group (see ESI).

Fig. 1(a) shows the XRD structure of the as-synthesized mesostructured film. The XRD pattern shows a very intense fundamental peak with a $d$ value of 29 Å, which is accompanied by a weak peak in the low-angle $2\theta$ region. The two peaks can be indexed as (100) and (110) on a hexagonal unit cell with $a_0 = 33$ Å ($a_0 = 2d_{100}/\sqrt{3}$).[17,18] Shown for comparison in Fig. 1(b) is the XRD pattern of a bulk mesostructured sample synthesized using the same sol composition. As shown in Fig. 1(b), three XRD peaks are observed at low angles of $2\theta = 1$–5°,which can be indexed as the (100), (110) and (200) reflections of a highly ordered hexagonal mesostructure.

Fig. 2 shows the excitation spectra (top) and the emission spectra (bottom) of the pure Eu complex [Eu(phen)$_2$Cl$_3$], the amorphous thin film, and the mesostructured thin film. As far as the pure Eu complex is concerned, the excitation spectrum consists of a symmetric and broad band ranging from 250 to 500 nm ($\lambda_{max} = 352$ nm) with some small superimposed peaks. In contrast, the excitation spectra of the mesostructured film and the amorphous thin film show only a broad band centered at 290 nm; moreover, the maximum of the broad band shifts towards the high-energy region. The difference tells that the ligand environment has changed in the films. Furthermore, this means that the siloxo part of the structure affects the energy transfer.

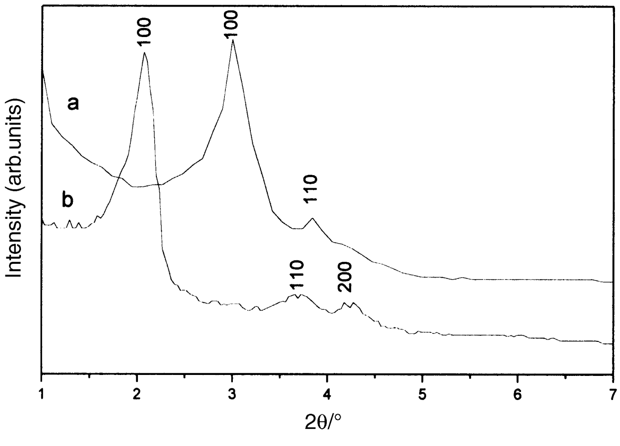

**Fig. 1** XRD patterns of the mesostructured thin film (a) and the bulk mesostructured sample (b).

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† Electronic supplementary information (ESI) available: $^{29}$Si NMR and FTIR spectra of the mesostructured film. See http://www.rsc.org/suppdata/nj/b2/b201436j/

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The corresponding emission spectra were obtained by excitation at 290 nm; only the emission lines of $Eu^{3+}$ $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) were observed with the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ (614 nm) as the most prominent band, and no emission from the ligands is detected. This indicates that effective energy transfer can take place from the ligands (phen-Si) to $Eu^{3+}$ in the thin films. The emission spectra of the films and the pure complex look somewhat similar, which clearly shows Eu is coordinated to nitrogen. Furthermore, minor differences between the emission spectra of the amorphous thin film and that of the mesostructured thin film can be observed (Fig. 2, bottom spectra b and c). In addition, no significant variation in the intensity ratio between the electric dipolar $^5D_0 \rightarrow {}^7F_2$ and the magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transitions is observed. This means that $Eu^{3+}$ has a similar environment in both films.

The $Eu^{3+}$ ($^5D_0$) decays were studied by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm. All of them could be fit to single-exponential law, from which the lifetime can be determined to be 822 μs in the pure complex, 624 μs in the amorphous film, and 608 μs in the mesostructured film. The above mentioned similarities show that $Eu^{3+}$ has a similar environment in both the amorphous and mesoporous films; most probably the complexes are grafted to the silica framework. The combination of mesopority and optical properties should give rise to interesting materials, particularly when host-guest interaction are being examined.

Fig. 3 shows the dependence of the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition on the post-synthesis heat-treatment temperature. The emission intensity rises gradually up to 200 °C and then falls off steeply. The increase in emission intensity with increasing temperature could be due to the elimination of solvated water, which may play a role as an inhibitor for energy transfer from the ligands to the central $Eu^{3+}$. Decomposition of the organic ligands could be responsible for the reduction of the emission intensity above 200 °C.

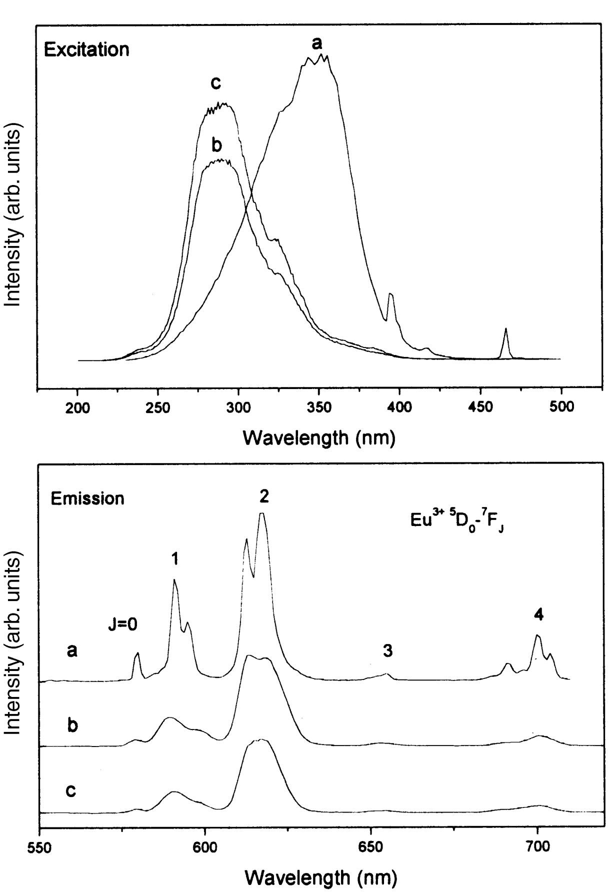


**Fig. 2** Excitation spectra (top) and emission spectra (bottom) of (a) the pure Eu complex $[Eu(phen)_2Cl_3]$, (b) the amorphous thin film, and (c) the mesostructured thin film.

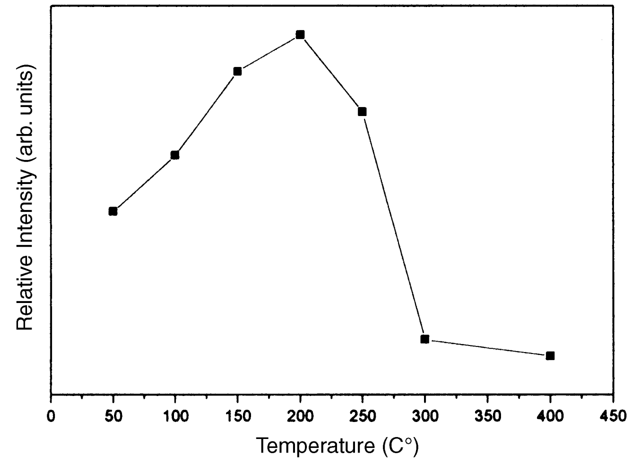
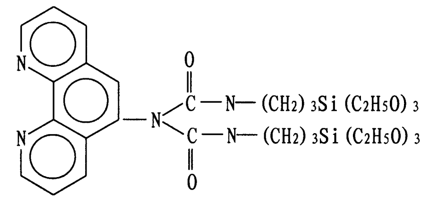


**Fig. 3** Dependence of the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition on the post-synthesis heat-treatment temperature.

In conclusion, we have fabricated a new hybrid organic-inorganic film with ordered structure, which combines the properties of ordered mesostructured silica and that of lanthanide complexes.

## Experimental

Phen-Si was prepared according to literature.[19] Anal. calcd for $C_{32}H_{51}N_5O_8Si_2$: C, 55.5; H, 7.4; N, 10.0%. Found: C, 54.96; H, 7.01; N, 10.82%. $^1H$ NMR: ($CDCl_3$) $\delta$ 0.52 (4H, m); 1.13 (18H, t); 1.60 (4H, m); 3.21 (4H, q); 3.68 (12H, q); 7.26 (2H, br s); 7.69 (2H, m); 7.87 (1H, s); 8.25 (2H, m); 9.23 (2H, m). IR; C=O (1705), –CONH– (1653, 1538 ), C–Si (1194 $cm^{-1}$).



phen-Si

The mesostructured hybrid thin films covalently doped with europium complex were prepared as follows: TEOS, ethanol, water and HCl (mol ratio: 1 : 3.8 : 10 : 0.01) were first reluxed at 50 °C for 90 min to form the stock solution. The coupling agent (phen-Si, 0.72 mmol) and $EuCl_3$ (0.36 mmol) were added, followed by surfactant (3 mmol). Transparent films were obtained by dip coating this solution on freshly cleaned quartz slides. The post-synthesis heat treatment was performed at different temperatures in the 50–400 °C range (heating rate 10 °C $min^{-1}$). For comparison, amorphous films were also prepared using the same sol composition but excluding the templating surfactant.

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