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Controlled Placement of Luminescent Molecules and Polymers in Mesostructured Sol−Gel Thin Films

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Functionalization of ordered mesoporous silica materials by organic molecules has recently received considerable interest.[1−4] In these new systems, control of the location and the orientation of the guest species within the host architecture is critical to achieve desired properties. Postdoping techniques have previously been widely used for the production of organically modified MCM-41 type materials,[5−12] but by using these methods the loading and localization of the organic groups are governed mainly by diffusion, and the dopants can only be localized in the empty pores. To overcome this limitation, an alternative route that directly incorporates the organic moieties into the mesoporous structure during a one-pot synthesis is preferred.[13−24]

In this paper we demonstrate three one-step methods to design hybrid mesoporous silica thin films in which the desired molecule is deliberately placed in a specified region of the mesostructure. We use our recently developed method of making continuous mesostructured surfactant-templated thin films with long-range order by a rapid dip-coating process.[21,25−27] The mesostructured thin films made with ionic surfactants contain three distinct regions (Figure 1): the silica framework, the ionic interface that is formed by the charged surfactant heads, and the organic region that is formed by the hydrophobic interior of the micelle.

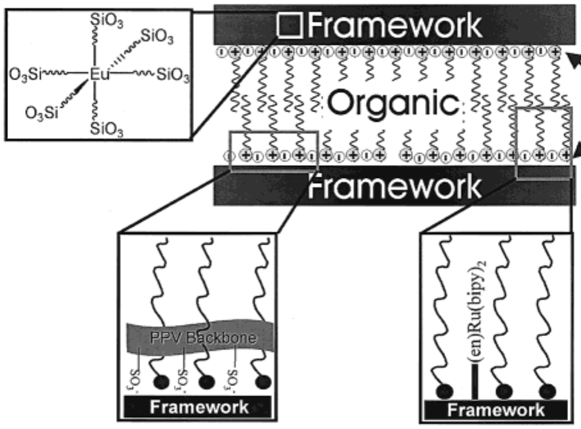

Figure 1. Sketch of the three regions of mesostructured sol−gel films. The framework consists of silica or modified silica, the organic region contains the hydrocarbon tails of the surfactant templates, and the ionic region contains the surfactant headgroups, the counterions, and residual solvent. The surrounding frames show sketches of the localization of luminescent molecules in the structure.

The first route, designed to place the desired molecule in the framework, involves hydrolysis and condensation of the desired molecule that is derivatized with multiple trialkoxysilane functionalities. When a hexa-silylated precursor is used, the molecules themselves form the framework. This approach is demonstrated with an Eu^{3+} complex in which each of the three ligands is first derivatized by two $Si(OEt)_3$ groups. The second approach utilizes an organic conducting polymer containing sulfonate groups. The polymer is dissolved in the initial sol, and, as the film is formed, the organic backbone is incorporated in the organic region of the film while the sulfonate groups reside in the ionic interface region. In the third route, we utilize an ionic metal complex that is functionalized with one alkoxysilane group at the end of a hydrocarbon chain. The alkoxysilane end becomes bonded to the framework in the final mesostructure, but the ionic end resides in the ionic interface region. In these studies we choose luminescent molecules and use spectroscopy to demonstrate that these molecules are located in the desired region of the mesostructures.

In our first example, the luminescent functionality consists of an Eu^{3+} complex that acts as a building block of the silicate framework.[28,29] The films are characterized by X-ray diffraction (XRD). The Eu^{3+}-activated hybrid films have peaks that are identical to those in films without Eu^{3+}. Luminescence measurements were performed on Eu^{3+}-activated amorphous and mesoporous thin films at 77 K and room temperature by using 308

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[28] Eu^{3+}-activated organic−inorganic mesoporous materials are prepared by co-condensation of tetraethoxysilane (TEOS) and *N*,*N*-bis(triethoxysilanepropyl)-2,6-pyridine dicarboxamide ligand (SL) in the presence of cetyltrimethylammonium bromide (CTAB) as a template. TEOS, ethanol, water, and HCl (mol ratios: 1:3.8:1:5 × 10^{-5}) are first refluxed at 60 °C for 90 min to form the stock solution. The SL ligand is then dissolved in this solution using a 1:9 SL-to-TEOS mol ratio. Distilled water and HCl are added, increasing the concentration of HCl to 7.34 mM. This sol is stirred for 15 min, aged at room temperature for additional 15 min, and diluted with ethanol.[19] The final molar composition is 1 Si/22.4 EtOH/5.1 H_2O/0.004 HCl. Europium chloride (Eu/SL = 1/3) is added prior to the addition of CTAB (4 wt %). Transparent films are obtained by dip-coating on freshly cleaned glass slides with a pulling rate of 10 cm/min. Amorphous films are also prepared by the dip-coating method using the same sol composition but excluding the templating surfactant.

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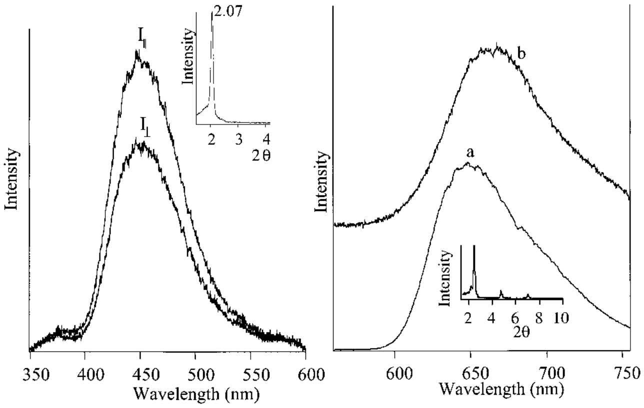

Figure 2. Left: Polarized fluorescence spectra of MPS-PPV in a mesostructured thin film excited at 366 nm. Right: Emission spectra of (a) mesostructured and (b) amorphous silica thin films containing a ruthenium complex tethered to the silica. The inset show the XRD patterns of the films.

nm excitation from an excimer laser. Emission spectra recorded for these two types of luminescent films show the typical ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) radiative transitions from the Eu^{3+} ions. There are no significant spectral differences between amorphous and mesoporous films. In particular, no variation in the fluorescence intensity ratio between the electric dipolar ${}^5D_0 \rightarrow {}^7F_2$ and the magnetic dipolar ${}^5D_0 \rightarrow {}^7F_1$ transitions is detected, and the line widths relative to the ${}^5D_0 \rightarrow {}^7F_2$ multiplet remain identical. The Eu^{3+} (${}^5D_0$) luminescence decays were investigated under UV excitation by monitoring the ${}^5D_0 \rightarrow {}^7F_2$ transition at 616.6 nm. For mesoporous hybrid films, a single-exponential decay is observed both at room temperature ($t = 0.95$ ms) and 77 K ($t = 1.05$ ms). Amorphous films show similar behavior with lifetimes of 0.88 ms and 1.03 ms at 298 and 77 K respectively. These similarities indicate that the Eu^{3+} ions lie in the silica framework.

Our second method of deliberate placement of a luminophore in the mesostructured film uses a water-soluble polymer, poly(2,5-methoxy-propyloxysulfonate)phenylene vinylene (MPS-PPV)[30] that has a chain length of 1900 units. The negative sulfonates are expected to reside in the ionic layer together with the positive alkylammonium headgroups of the surfactant. The sol is prepared in a manner similar to that used for the Eu-containing materials.[31] XRD data (Figure 2) confirm that the mesostructure is the same as that of the undoped film (2-d hexagonal).[32]

The orientation of the polymers within the matrix is investigated by fluorescence polarization.[11,12] If the polymers reside in the ionic layer, they will be oriented preferentially along the rods in the hexagonal structure. The luminescence transition dipole is aligned parallel to the polymer chain axis.[33] Because most of the polymer strands are longer than the width of a cylindrical micelle, on average the strands are forced to run parallel to the rods within which they are confined. Thus, their luminescence will be polarized parallel to the rods. Films that are excited by unpolarized 366 nm UV light exhibit polarized emission with the polarization direction parallel to pull direction, showing that the polymers are preferentially oriented (Figure 2 left). Emissions from lamellar SDS-templated films and from unstructured amorphous silica films are unpolarized. (The luminescence is wavelength dependent; the bond maximum is centered about 580 nm when films or solutions of comparable concentrations are excited at 514 nm.)

The third method for functionalizing the mesoporous film is to chemically attach molecules containing an ionic luminophore to the framework.[34] In this case the luminophore is a ruthenium(II) complex with one substituted ethylenediamine and two bipyridine ligands. The ethylenediamine is substituted with a propyl chain containing a trimethoxysilane group that undergoes hydrolysis and condensation to bond to the silicate framework. The ionic metal resides in the ionic region at the interface between the organic and inorganic regions. The mesostructure of the films is confirmed by XRD. The presence of the three peaks (identical to those in films without the Ru) show the long-range order is not disrupted by the ruthenium complex.

Emission spectra of the films are taken to determine the location of the chelated metal complex. Figure 2a (right) shows the spectrum of a film containing $Ru(bpy)_2ATT^{2+}$ taken at 77 K. A broad peak centered at 650 nm is observed which is very similar to the emission peak reported for $[Ru(bpy)_2en]^{2+}$ in methanol.[35] The band maximum of $Ru(bpy)_2\ ATT^{2+}$ in an amorphous silicate film (Figure 2b) is at 665 nm. The similarities between the solution and mesostructured film spectra and the shift in the pure silica film indicate that the ruthenium is not in the silica framework but rather in the ionic region that contains some residual alcohol and water.

The methods of deliberately placing a molecule in a desired region of a mesostructured film that are described here are general and can be used for a variety of organic, inorganic, and biomolecules. The desired molecules are uniformly distributed throughout the chosen region of the films because they are uniformly distributed in the inital sol. The synthesis conditions must be carefully chosen because the mesostructure formation involves a delicate interplay between micelle formation, framework formation, and film formation. The methods demonstrated here open the possibility of making new types of photoactive materials.

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