

An Encapsulation of the Rare Earth Complex in Modified Mesoporous Molecular Sieve MCM-41

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Abstract: The encapsulation of a rare earth (RE) complex $\text{Eu}(\text{DBM})_3\text{phen}$ in modified Si-MCM-41 with 3-aminopropyltriethoxysilane is reported for the first time. The luminescence intensity of the RE complex in the modified Si-MCM-41 is about 9 times as strong as in unmodified Si-MCM-41 and the luminescence of the RE complex in the modified Si-MCM-41 has good color purity.

Keywords: Modify, rare earth complex, luminescence, color purity.

Rare earth (RE) organic complexes usually exhibit intense narrow band emission *via* an energy transfer from the ligands to the central rare earth ions under UV excitation. Although RE complexes especially for the complex with β -diketone, have strong luminescence, their photostability and thermal stability are not very good enough for the phosphor. Therefore, the key problem related to rare earth complex is to try to find a suitable matrix material to load them. Inorganic solid matrixes are promising host materials due to their good optical, thermal and chemical stability. In fact, many RE complexes have already been encapsulated in or adsorbed on host materials including silica¹, sol-gels² and Y zeolite³. Mesoporous material MCM-41 contains a hexagonal array of mesopores with a pore diameter of 20–100 Å and good photo and thermal stability. A vast range of its applications^{4–6} is focused on catalysis, sorption and photochemistry, but there are no reports on RE complexes in the mesoporous material. NMR studies⁷ reveal that MCM-41 contains many silanol groups both before and after the template molecules have been removed. Since the high energy vibration of the OH groups will heavily quench the luminescence of RE ions⁸. In this paper, we have modified MCM-41 using 3-aminopropyltriethoxysilane (APTS) and compared the luminescence properties of the RE complex in the modified and unmodified MCM-41⁹.

The synthesis of Si-MCM-41 is accord to the reference¹⁰. The synthesis of modified Si-MCM-41 is accord to the reference¹¹. The assemblies containing RE complex $\text{Eu}(\text{DBM})_3\text{phen}$ (DBM:dibenzoylmethane, phen:1,10-phenanthroline) were accomplished by mixing a $\text{Eu}(\text{DBM})_3\text{phen}$ solution in dimethyl formamide (DMF) and the modified

and unmodified Si-MCM-41 materials in chloroform. The mixtures were stirred at room temperature for 48h, filtered, washed with chloroform until the filter liquors give no luminescence under UV radiation, and then dried at ambient temperature and stored in desiccator for measurements.

Figure 1. XRD PATTERNS. (a) MODIFIED Si-MCM-41, (B) assembly of modified Si-MCM-41 with $\text{Eu}(\text{DBM})_3\text{phen}$

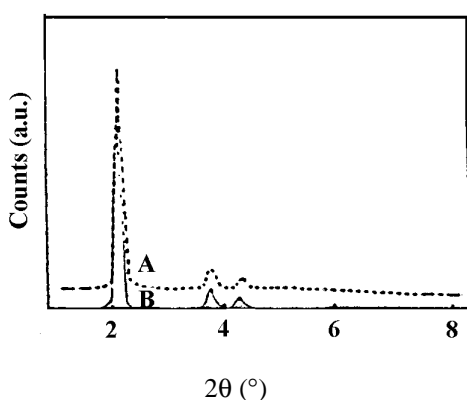
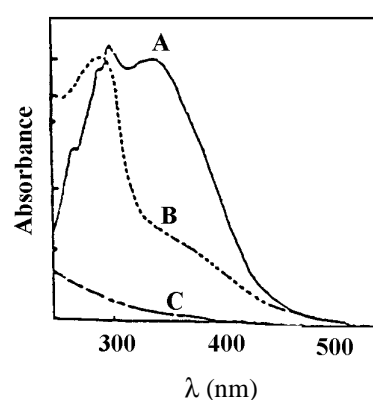


Figure 2. UV-visible spectra. (A) RE complex, (B) assembly of modified Si-MCM-41 WITH $\text{Eu}(\text{DBM})_3\text{PHEN}$ (C) modified Si-MCM-41.



X-ray powder diffraction (XRD) patterns of the Si-MCM-41 modified with APTS and the assembly of the RE complex are shown in **Figure 1**. Comparison of **Figure 1A** and **Figure 1B** shows that the structure of Si-MCM-41 still retained after assembled.

Figure 2 shows the UV spectra of the modified Si-MCM-41, the RE complex and the corresponding assembly, respectively. The spectrum of the RE complex (**Figure 2A**) has two absorption peaks located at 348 nm and 385 nm, while the absorption of the assembly (**Figure 2B**) at $\lambda=342$ nm. The modified Si-MCM-41 has almost no absorption (**Figure 2C**) in the region from 300 nm to 600 nm. Especially, the spectrum profiles of the RE complex $\text{Eu}(\text{DBM})_3\text{phen}$ and the corresponding assembly are very similar. This indicates that $\text{Eu}(\text{DBM})_3\text{phen}$ is encapsulated in the channels of the modified Si-MCM-41¹².

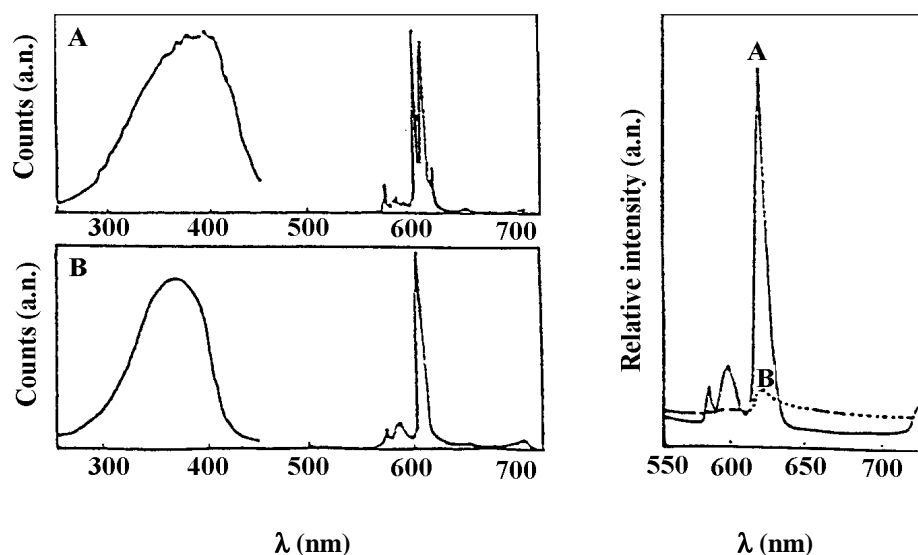
Figure 3 shows excitation and emission spectra of the assembly and the corresponding pure RE complex. Both of the emission spectra exhibit the characteristic emission of arising from the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J=0, 1, 2, 3, 4$) with a ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ red emission as the dominate group. This strongly suggests that an efficient energy transfer from the ligands to Eu^{3+} can take place not only in the pure RE complex (**Figure 3A**) but also in the complex encapsulated in Si-MCM-41 (**Figure 3B**). Compared to the intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, the intensities of other level transitions are much weaker, indicating that the RE complex in the assembly has good monochromaticity.

For comparison, emission spectra of the RE complex in the modified and unmodified Si-MCM-41 are presented in **Figure 4**. Both of the spectra show the characteristic emission bands of Eu^{3+} . The luminescence intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of the RE complex in the modified Si-MCM-41 (**Figure 4A**) is about 9 times as strong as in unmodified

Si-MCM-41 **Figure 4B**), showing that the OH groups in the channels have been displaced by the modified agent after modification. Due to the decreasing of the nonradiative transition ration, the luminescence intensity increases.

Figure 3. Excitation and emission spectra. (A) RE complex. (B) assembly of modified Si-MCM-41 with Eu(DBM)₃ phen

Figure 4. Emission spectra. (A) Eu(DBM)₃phen in the modified Si-MCM-41. (B) in the unmodified Si-MCM-41.



The fluorescence decay curves of Eu³⁺ related to the transition ⁵D₀→⁷F₂ emission for the pure RE complex and the corresponding assembly are measured. The fluorescence times are 608 μ s in the former and 823 μ s in the latter, respectively. The relatively rigid matrix structure of the assembly inhibits the vibration of the ligands around, and leads to longer luminescence lifetime of Eu³⁺ in the assembly than that of the corresponding pure RE complex.

The content of Eu³⁺ in the assembly was measured by ICP-AES to be 3.8%. On the other hand the relative luminescence intensity of the assembly is appropriately 27.1% that of the corresponding pure RE complex, suggesting that the unit molecule of the RE complex in the assembly can give stronger luminescence than the corresponding pure RE complex powder.

Acknowledgments

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