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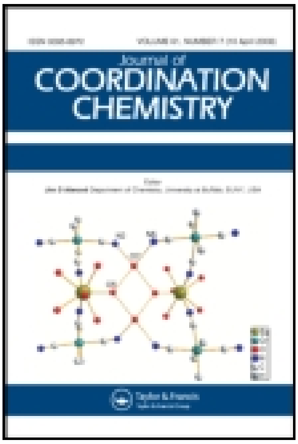

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Preparation and luminescent properties of a terbium complex incorporated into the pores of mesoporous silica MCM-41 by a sol–gel method

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A complex of terbium and a new podand-type polyaromatic carboxylic acid [3,6-*bis*[(4′-carboxyphenoxy)methyl]-1,2,4,5-tetramethylbenzene(H_2BCM)] have been synthesized, introduced into the pores of mesoporous silica by the sol–gel method, and characterized by IR, UV-Vis, X-ray diffraction, and inductively coupled plasma atomic emission spectrometry. The Tb complex encapsulated in the pores of mesoporous silica MCM (Mobil composition of matter)-41 (MCM-41-$Tb_2(BCM)_3$) displayed characteristic luminescence emission of the pure Tb complex ($Tb_2(BCM)_3$); compared with the complex itself, the unit-mass luminescence intensity of the mesoporous silica hybrid material is enhanced four times. The luminescence lifetime of Tb^{3+} in the hybrid material is also longer than that in pure complex.

Keywords: Terbium complex; Synthesis; Luminescence properties; MCM-41; Hybrid material

1. Introduction

Mesoporous siliceous materials have been widely studied since scientists at Mobil Corp. reported pioneering work on a family of ordered silica-based molecular sieves [1–5]. Mesoporous materials include the thermally stable MCM (Mobil composition of matter)-41 and MCM-48 phases. The structure of MCM-41 can be described as a hexagonal arrangement of parallel cylindrical pores embedded in a matrix of amorphous silica. The main properties of these mesoporous materials are their high pore volume (about $1\,cm^3\,g^{-1}$), large surface area (about $1000\,m^2\,g^{-1}$), and very narrow distribution of pore sizes (2–10 nm). A number of important applications have been implemented in these materials, such as adsorption and separation, ion exchange, catalysis, and molecular hosts [6–12].

Mesoporous materials have started to attract attention as hosts for optical and magnetic functionalities, which may have applications in microelectronics, optoelectronics, and magnetic recording [13–16]. Some lanthanide ions, especially Eu^{3+} and Tb^{3+}, possess good luminescence characteristics (high color purity) based on the 4f-electronic transitions, and a variety of rare earth compounds activated by Eu^{3+} and

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Tb^{3+} have been studied for practical applications as phosphors. Many rare earth complexes with β-diketone, aromatic carbocylic acid, and phenanthroline ligands have been prepared [17–20]. In order to make these materials applicable for technological uses, the complexes must be incorporated into a stable rigid matrix such as a polymer or silica matrix. In general, there are two methods to introduce a rare earth complex to a silica matrix. First, it can be introduced into a silica matrix by melt mixing or sol–gel method, a simple, widely reported method [21, 22], but the content of the rare earth is limited due to concentration luminescence quenching. Second, it can be bonded to silica chains by copolymerization. This method can overcome concentration luminescence quenching [23–25], but the preparation is complicated.

Mesoporous SiO_2 contains a hexagonal array of mesopores with a diameter of 20–100 Å and high specific surface areas, so the pores of these mesoporous materials are large enough to encapsulate lanthanide complexes without the need for the "ship-in-bottle" approach that is necessary for introduction of these complexes in conventional zeolites. The introduction of the rare earth complex to the pores of silica may reduce concentration luminescence quenching and the complication of copolymerization.

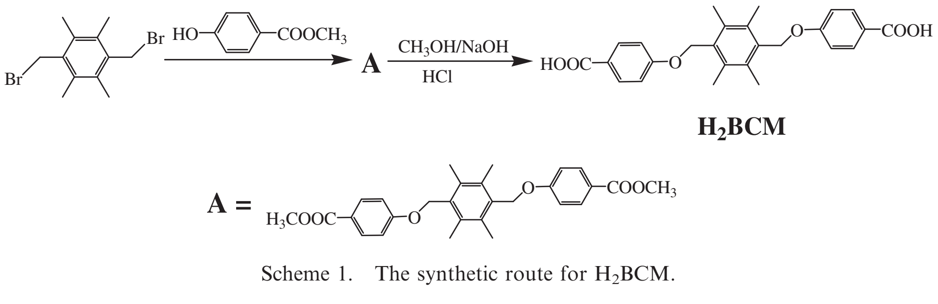
Mesoporous solids loaded with nanoparticles within their pores have received considerable attention recently for their unique properties [26–32]. Because the pores in porous solids are interconnected and open to the ambient environment, the nanoparticles within the pores are also in contact with the ambient environment, and hence, easily affected by it.

In this study, a mesoporous silica hybrid material containing terbium(III) complex with a podand-type polyaromatic acid ligand with long and flexible arms, [3,6-*bis*[(4′-carboxyphenoxy)methyl]-1,2,4,5-tetramethylbenzene(H_2BCM)] (scheme 1) was prepared by the sol–gel method. Luminescence properties of the mesoporous silica hybrid material and the corresponding pure complex were systematically investigated; the unit-mass luminescence intensity of the complex in the pores of mesoporous silica is greatly increased.

2. Experimental

2.1. *Materials and physical measurements*

Tetraethoxysilane (TEOS 95%, Aldrich) and cetyltrimethylammonium bromide (CTAB, AR) were used without purification. N,N-dimethylformamide (DMF) and



Scheme 1. The synthetic route for H_2BCM.

ethanol (EtOH) were used to dissolve the Tb complex at room temperature. HCl was used for adjusting the pH in the MCM-41 preparation. Other chemicals were obtained from commercial sources and used without purification. The Ln(III) was determined by EDTA titration using xylenol orange as an indicator. Carbon, nitrogen, and hydrogen were determined using an Elementar Vario EL. The IR spectra were recorded from 4000–400 cm^{-1} using KBr pellets and a Nicolet Nexus 670 FTIR spectrometer. UV-Visible spectra were measured using a Lambda 35 spectrometer. X-ray diffraction (XRD) patterns were recorded on a Japan Rigaku D/max–RD XRD spectrometer with a copper target at an operating voltage of 40 KV and an electric current of 100 mA. Differential thermal analysis/thermogravimetry (DTA/TG) of the complex was made on a TG-DTA analyzer (DSC-200 F_3 MAIA, Netzsch, Germany) using about 10 mg powder and working at a heating rate of 5°C min^{-1} in static air. Inductively coupled plasma atomic emission spectrometry was recorded on an IRIS Advantage ER/S. Luminescence spectra were obtained at room temperature on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. (The excitation and emission slit widths were 1 nm. All the samples were measured under the same conditions.). Luminescence lifetime measurements were performed on an Edinburgh FLS920 time-resolved fluorescence spectrophotometer.

2.2. *Synthesis of MCM-41*

CTAB, 0.24 g, was added to 8.46 g of distilled water and heated with stirring until complete dissolution, followed by addition of 2.19 g of HCl (37%). To this solution, 1.04 g of TEOS was added dropwise under vigorous stirring. The molar composition of the gel TEOS : CTAB : NH_3 : H_2O is 1 : 0.13 : 12 : 94. The precipitate was filtered, washed with copious amounts of water, and MCM-41 with template was obtained. The template was removed by calcination of as-synthesized MCM-41 at 823 K for 6 h.

2.3. *Synthesis of L*

The synthetic route for L is shown in scheme 1. Ethylparaben, 1.52 g (10.0 mmol) and 1.65 g potassium carbonate (12 mmol) were refluxed in acetone (50 cm^3) for 30 min. Then, 0.946 g of 2,3,5,6-tetramethyl-1,4-dibromomethylbenzene (3 mmol) was added to the solution. The reaction mixture was refluxed for 10 h and the hot solution was filtered off. The collected organic phase was concentrated in vacuum. A mass of white compound **A** was prepared, yield 80%.

This white compound, **A**, was added to methanol (35 mL) and 3 M sodium hydroxide (12 mL), then was refluxed for 8 h (in the course of refluxing, deionized water was continuously added in the reactor). After cooling, the solution was filtered and HCl was added to adjust the pH (1–2) of the stirring solution. The resulting solid was filtered and dried *in vacuo* over P_4O_{10} for 48 h, yield 75%; m.p. 236–238°C; Anal. Calcd for $C_{26}H_{26}O_6$: C, 71.87; H, 6.03%. Found: C, 71.58; H, 6.18%. ^{1}H-NMR (d–DMSO, 300 MHz): 2.32 (s, 12 H), 5.21 (s, 4 H), 6.96–7.78 (m, 8 H); 11.65(s, 2 H). IR (KBr pellet, cm^{-1}): 3420(m), 2966(m), 1683(s), 1604(m), 1511(m), 1473(s), 1425(s), 1307(s), 1293(s), 1249(s), 982(s), 774(s), and 692(m).

2.4. *Synthesis of the Tb complex*

H_2BCM (0.10 mmol) was dissolved in 5 cm^3 of ethanol and water (V : V = 5 : 1), and triethylicamine was added to adjust the pH = 6. Then, a solution of 0.1 mmol terbium nitrate in 5 cm^3 of ethanol was added dropwise to the solution. The mixture was stirred at room temperature for 4 h. The precipitated white complex was filtered, washed with ethanol/water, dried *in vacuo* over P_4O_{10} for 48 h and submitted for elemental analysis, yield 75%. The data of the elemental analysis indicated that the complex has the composition $Tb_2(BCM)_3{\cdot}4H_2O$ (Anal. Calc: C, 55.52; H, 4.78. Found: C, 55.74; H, 5.16; and N, 0.57%). The TG and DTA curves for the complex show that the complex has no melting point and the water molecules in the complex are all coordination water with endothermic peak at *ca* 152°C, corresponding to loss of water consistent with the theoretical value.

2.5. *Synthesis of MCM-41-Tb₂(BCM)₃*

The $Tb_2(BCM)_3$ was mixed with mesoporous silica in DMF (the weight ratio of mesoporous silica to the Tb complex was 2 : 1) and stirred for 2 days at room temperature. The resultant suspension was then filtered to give a white powder, which was washed repeatedly with DMF until the filtrate remained colorless, and was then dried *in vacuo* over P_4O_{10} for 48 h.

3. Results and discussion

3.1. *The XRD analysis*

The XRD patterns of MCM-41 and MCM-41-$Tb_2(BCM)_3$ are shown in figure 1. MCM-41-$Tb_2(BCM)_3$ exhibited characteristic peaks of MCM-41, but no peaks due to $Tb_2(BCM)_3$, indicating that the MCM-41 structure was retained after the encapsulation process and $Tb_2(BCM)_3$ is dispersed in channels of MCM-41.

The Tb^{3+} content in MCM-41-$Tb_2(BCM)_3$ measured by an inductively coupled plasma spectrometer was 0.42%.

3.2. *IR spectra*

The IR spectra of MCM-41-$Tb_2(BCM)_3$ (a), $Tb_2(BCM)_3$ (b), and MCM-41 (c) are shown in figure 2. In figure 2(a), the broad band around 3447 cm^{-1} is assigned to stretching vibrations of O–H and 1647 cm^{-1}, corresponding to their bending vibration. The strong peaks at 1084 and 796 cm^{-1} are attributed to Si–O–Si symmetric stretching and bending vibrations, respectively. The band at 463 cm^{-1} corresponds to the bending of Si–O–Si. The shoulder at 966 cm^{-1} is related to the vibration of silanol groups. The IR spectrum of MCM-41-$Tb_2(BCM)_3$ contained absorption bands from $Tb_2(BCM)_3$ at 1552 and 1425 cm^{-1} ($\nu_s COO^-$), indicating that the $Tb_2(BCM)_3$ complex has been encapsulated in the pores of mesoporous silica MCM-41 without decomposition or serious modification.

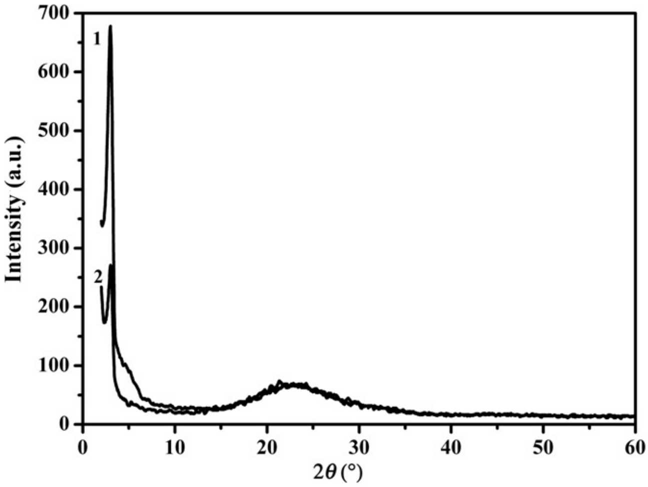


Figure 1. XRD patterns of MCM-41(a) and MCM-41-$Tb_2(BCM)_3$ (b).

3.3. *UV-Visible absorption spectra*

The UV-Visible absorption spectra of the hybrid material doped with Tb complexes and the pure terbium complex powders are shown in figure 3. The Tb complex has two main absorptions at 272 and 330 nm, while the hybrid material doped with Tb complex has two main absorption peaks at 238 and 312 nm. The UV-Visible spectra show that the Tb complex is doped in the hybrid material. The microenvironments in the hybrid material result in blue shifts of the terbium complex absorptions.

3.4. *Luminescence study*

Emission spectra of MCM-41-$Tb_2(BCM)_3$ and $Tb_2(BCM)_3$ are shown in figure 4. Both emission spectra exhibit the characteristic emission of Tb^{3+} arising from the $^5D_4/^7F_J$ ($J = 6, 5$) transition, with the transition $^5D_4/^7F_5$ green emission dominant. As expected, the terminal groups of this ligand have the conjugate chromogen to activate Tb^{3+} to emit characteristic wavelengths. For MCM-41-$Tb_2(BCM)_3$, the energy transfer from the ligand to Tb ions took place smoothly, as for the original complex, and consequently strong green emission based on Tb^{3+} was observed.

The content of the complex in the pores of mesoporous silica MCM-41 and its relative luminescent intensity of the $^5D_4/^7F_5$ transition and the relative intensity of the transition $^5D_4/^7F_6$ compared with the complex are listed in table 1. The complex of a unit-mass in pores of mesoporous silica MCM-41 gives stronger luminescence than the corresponding pure complex. Compared with the complex, the luminescence intensity (the relative intensity divided by the mass) of the hybrid material increases a factor of 4. Organized media can profoundly influence the photophysical and photochemical processes on guest molecules. This host provides an interesting microchemical environment for the guest molecule. When the complex is encapsulated in the pores of mesoporous silica MCM-41, the molecules were confined in micropores and nonradiative transitions were decreased, resulting in high luminescence efficiency.

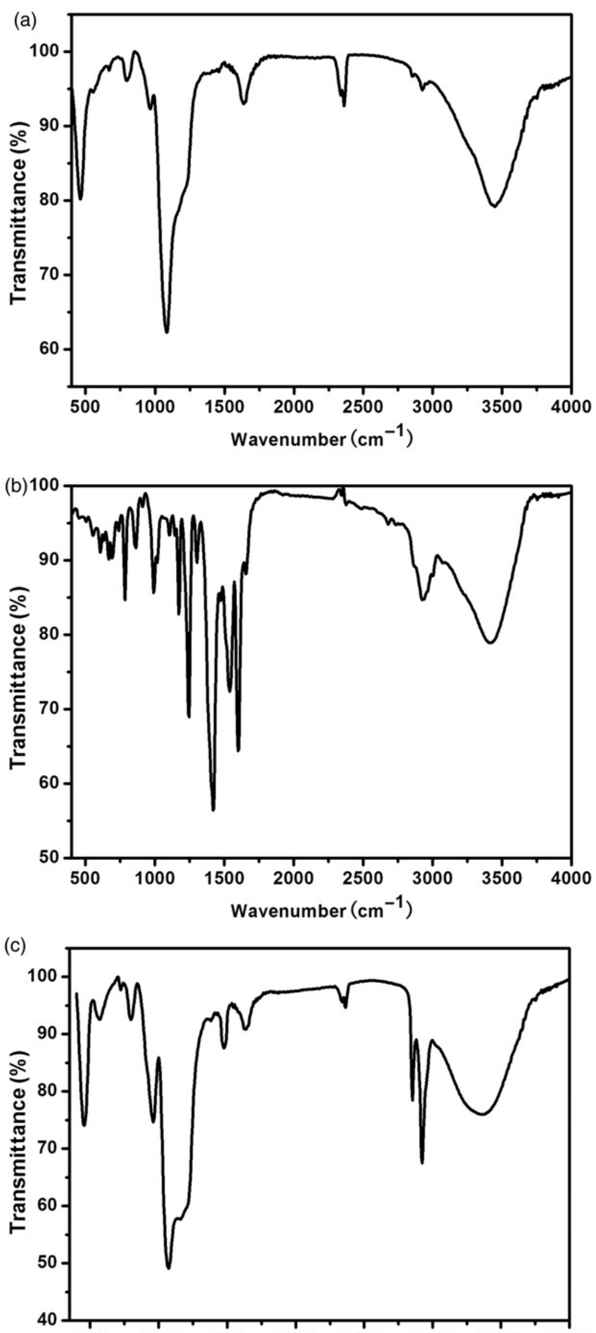


Figure 2. Infrared spectra of MCM-41-$Tb_2(BCM)_3$ (a), $Tb_2(BCM)_3$ complex powder (b), and MCM-41 (c).

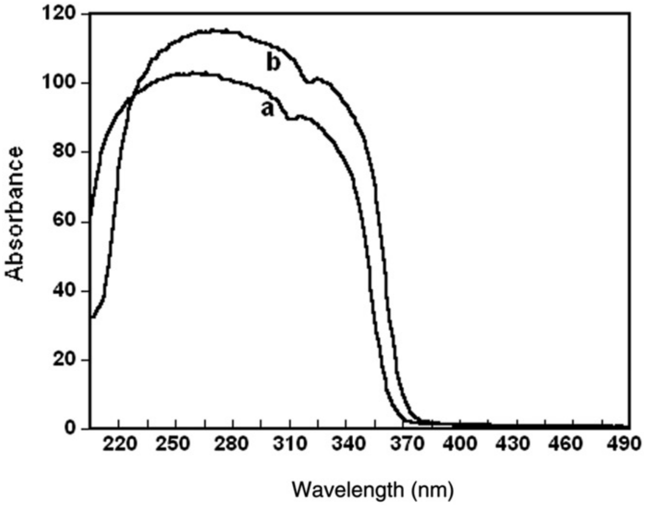


Figure 3. UV-Visible absorption spectra for MCM-41-$Tb_2(BCM)_3$ (a) and $Tb_2(BCM)_3$ complex powder (b).

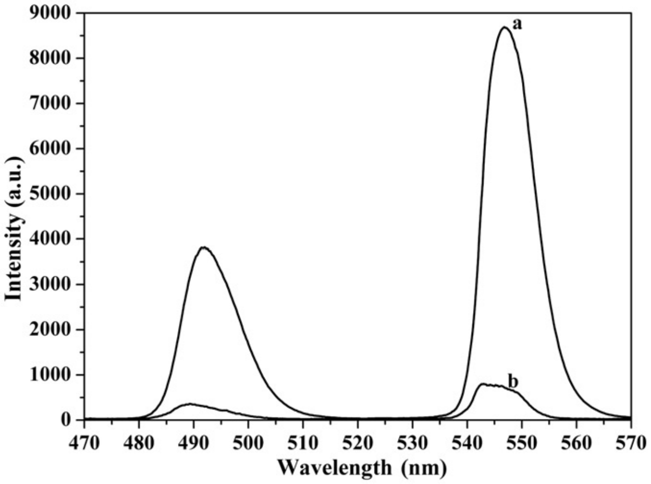


Figure 4. Luminescence spectra of $Tb_2(BCM)_3$ complex powder (a) and MCM-41-$Tb_2(BCM)_3$ (b).

The lifetimes summarized in table 2 show that the MCM-41-$Tb_2(BCM)_3$ hybrid material has longer lifetime than the corresponding pure complex. It is well known that luminescence lifetime of Tb^{3+} is related to vibrations of nearby ligands. The excitation energy of Tb^{3+} can be absorbed by the vibration of the ligands, thus decreasing the lifetime of Tb^{3+}. The isolation of the complex molecules and the relatively rigid matrix structure inhibits the vibration of the ligands around Tb^{3+}, leading to a longer luminescence lifetime of Tb^{3+} in SiO_2 matrix than those of pure complex. This result is also supported by the IR spectra.

Table 1. Relationship between the content of the Tb complex and luminescent intensities.

Materials	$Tb_2(BCM)_3$	MCM-41-$Tb_2(BCM)_3$
The content of Tb in the RE complex (wt.%)	18.84	0.42
Relative intensities of $^5D_4 \rightarrow {}^7F_5$	8691	802
Relative intensities of $^5D_4 \rightarrow {}^7F_6$	3819	359

Table 2. The luminescent lifetimes of Tb ions in the hybrid material and pure complex.

Materials	Lifetime (μs)
$Tb_2(BCM)_3$	719
MCM-41-$Tb_2(BCM)_3$	1291

4. Conclusions

Novel hybrid luminescence material encapsulating the terbium complex of a new podand-type polyaromatic acid ligand, 3,6-*bis*[(4′-carboxyphenoxy)methyl]-1,2,4,5-tetramethylbenzene(H_2BCM), MCM-41-$Tb_2(BCM)_3$, in the pores of mesoporous silica MCM-41 has been prepared. The pores of mesoporous silica MCM-41 provide a good microenvironment for improving the unit-mass luminescence intensity of the complex. When the complex is encapsulated in the pores, the molecules were confined in micropores and nonradiative transitions were decreased. Therefore, energy is effectively absorbed by the ligands and transferred to Tb^{3+}. Emission intensities of the hybrid materials encapsulated with the terbium complex are stronger. Compared with the complex, the luminescence intensity (the relative intensity divided by the mass) of the hybrid material increases four times. Luminescence lifetime of Tb^{3+} in the hybrid material is longer than in pure complex. Thus, the hybrid material becomes an interesting medium for potential usage in optoelectronic fields.

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