Preparation, characterization, and luminescence properties of novel hybrid material containing europium(III) complex covalently bonded to MCM-41

Dan Wang a, Bin Li a,b,*, Liming Zhang b, Jun Ying a, Xiudong Wu a

Abstract

In this paper, a novel luminescent organic–inorganic hybrid material containing covalently bonded ternary europium complex in mesoporous silica MCM-41 has been successfully prepared by co-condensation of tetraethoxysilane (TEOS) and the modified ligand 2-phenyl-1H-imidazo[4,5-f][1,10]phen-3-(triethoxysilyl)propyl isocyanate (PIP-Si) in the presence of cetyltrimethylammonium bromide (CTAB) surfactant as template. PIP-Si containing 1,10-phenanthroline covalently grafted to 3-(triethoxysilyl)propyl isocyanate is used not only as a precursor but also as the second ligand for Eu(TTA)_3·2H_2O (TTA: 2-thienyltrifluoroacetate) complex to prepare a novel functionalized mesoporous material. The resulted mesoporous composite materials, which demonstrate strong characteristic emission lines of Eu³⁺ ⁵D₀→⁷F_j (j=0, 1, 2, 3, 4), were characterized by Fourier transform infrared (FT-IR), small-angle X-ray diffraction, excited-state decay analysis. Emission intensity of the Eu(III) complex covalently linked to MCM-41 (Eu-MCM-41) increases with the increasing irradiation time, demonstrating better photostability compared with both pure Eu(III) complex and physically incorporated sample.

1. Introduction

Historically, rare-earth complexes have been well known to give sharp, intense emission lines upon ultraviolet light irradiation because the effective intramolecular energy transfer from coordinated ligands to luminescent central lanthanide ion, which in turn undergoes corresponding radiative emitting process (the so-called “antenna effect”) [1–3]. However, the poor photostability of rare-earth complexes limits their practical applications. Recently, it is reported that their photophysical properties could be modified by interaction of a host structure. Consequently, luminescence properties of rare-earth complexes supported on solid matrices are studied extensively. For instance, rare-earth complexes were covalently linked to or physically incorporated on host materials, including sol–gel matrix [4] and silica matrix [5]. Among them, mesoporous molecular sieve used as a support for rare-earth complexes has attracted particular attention [6–9]. Xu et al. [10,11] and Zhang and co-workers [12–15] encapsulated different rare-earth complexes into mesoporous channels of MCM-41 and SBA-15 via wet impregnation. In the past few years, many studies focus on covalently grafting of ligands of rare-earth complexes to backbone of networks via Si–C bonds [16,17]. However, there is no report of study on photostability of Eu(III) complex covalently grafted to mesoporous materials.

In this paper, we report a novel Eu(III) complex, which is covalently bonded to the framework of MCM-41 by co-condensation of modified phenanthroline (PIP-Si) and tetraethoxysilane (TEOS) using cetyltrimethylammonium bromide (CTAB) surfactant as template. Highly luminescent complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction.

2. Experimental

2.1. Materials and reagents

Analytical grade solvents and compounds were used for preparations. TEOS (Tianjin Chemicals Co.), 3-(triethoxysilyl)-propyl isocyanate (ICPTES, Aldrich), CTAB (Aldrich). All reagents were of analytical grade. Water used in our work was deionized. Europium chloride was obtained by dissolving Eu₂O₃ (99.99%, Shanghai yuelong) in hydrochloric acid.

Keywords: Europium complex MCM-41 Photostability Covalently bond

1. Introduction

Historically, rare-earth complexes have been well known to give sharp, intense emission lines upon ultraviolet light irradiation because the effective intramolecular energy transfer from coordinated ligands to luminescent central lanthanide ion, which in turn undergoes corresponding radiative emitting process (the so-called “antenna effect”) [1–3]. However, the poor photostability of rare-earth complexes limits their practical applications. Recently, it is reported that their photophysical properties could be modified by interaction of a host structure. Consequently, luminescence properties of rare-earth complexes supported on solid matrices are studied extensively. For instance, rare-earth complexes were covalently linked to or physically incorporated on host materials, including sol–gel matrix [4] and silica matrix [5]. Among them, mesoporous molecular sieve used as a support for rare-earth complexes has attracted particular attention [6–9]. Xu et al. [10,11] and Zhang and co-workers [12–15] encapsulated different rare-earth complexes into mesoporous channels of MCM-41 and SBA-15 via wet impregnation. In the past few years, many studies focus on covalently grafting of ligands of rare-earth complexes to backbone of networks via Si–C bonds [16,17]. However, there is no report of study on photostability of Eu(III) complex covalently grafted to mesoporous materials.

In this paper, we report a novel Eu(III) complex, which is covalently bonded to the framework of MCM-41 by co-condensation of modified phenanthroline (PIP-Si) and tetraethoxysilane (TEOS) using cetyltrimethylammonium bromide (CTAB) surfactant as template. Highly luminescent complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction. Thus, the ternary europium complex Eu(TTA)_3·2H_2O into the PIP-MCM-41 hybrid materials with a ligand exchange reaction.
2.2. Synthesis of hydrolyzable 1,10-phenanthroline functionalized PIP-Si ligand

The PIP-Si was prepared using 2-phenyl-1H-imidazo [4,5-f] [1,10]phenanthroline (PIP-OH) and ICPTES as staring materials. The synthesis of PIP-OH was performed by oxidation of 1,10-phenanthroline in a mixture of concentrated sulfuric acid and nitric acid, followed by condensation of 1,10-phenanthroline-5,6-dione and 4-hydroxy-benzaldehyde, according to a slightly modified imidazole ring preparation method [18–20]. The detailed synthetic procedure of PIP-Si has been described elsewhere [21] and can be summarized as follows: PIP-OH (0.25 g) was mixed with an excess of ICPTES (1 mL) in a round-bottom flask, then the mixture was kept under nitrogen in an ultrasonic bath for about 15 min. After having stirred under nitrogen at 80 °C for 72 h, the residual was added dropwise into about 30 mL of cold hexane to precipitate a white-yellow solid from the mixture. The final filtered-off precipitate was washed with several portions of cold hexane and then dissolved in absolute ethanol. The solution was filtered, and ethanol was eliminated by evaporation to obtain a solid compound. The compound can be dissolved in a small portion of dichloromethane, suggesting that the reaction between PIP-OH and ICPTES occurred since the starting PIP-OH was not soluble in dichloromethane. The solution was added dropwise into about 30 mL of cold hexane to reprecipitate the compound and dried in vacuo. The product obtained by the method described above is pure enough for use as a starting product for the preparation of hybrid materials.

2.3. Synthesis of phen-functionalized MCM-41 mesoporous material (PIP-MCM-41)

The synthetic procedure of intermediate mesoporous silica PIP-MCM-41 was similar to the previous publication with some minor modifications [15]. The synthetic procedure was as follows: concentrated NH\textsubscript{3}·H\textsubscript{2}O (4.5 mL) was mixed with deionized water (10 mL) and CTAB (0.41 g) at 35 °C. To this homogeneous solution TEOS (1.9 mL) and PIP-Si (0.11 g) were added under vigorous stirring. The molar ratio of the synthetic mixture was PIP-Si/TEOS/CTAB/NH\textsubscript{3}H\textsubscript{2}O/H\textsubscript{2}O=0.02:1.0:0.139:3.76:66.57. The mixture was stirred for 10 h at room temperature and then transferred into a Teflon bottle sealed in an autoclave, which was then heated at 100 °C for 48 h. The solid product was filtered, washed with H\textsubscript{2}O, and dried for 12 h at 60 °C. The surfactant was removed by acid/solvent extraction, using a solution of 1 M HCl in ethanol. This mixture was refluxed for 72 h, then filtered and washed with EtOH to remove the residual HCl. The product was dried at 60 °C for 12 h in vacuo to obtain the synthesized PIP-MCM-41.
2.4. Synthesis of MCM-41 mesoporous material covalently bonded with Eu(TTA)₃PIP ternary complex (Eu-MCM-41)

The PIP-MCM-41 was added to an Eu(TTA)₃·2H₂O ethanol solution under stirring. Eu(TTA)₃·2H₂O was prepared by the method described in Ref. [2]. The mixture was heated under reflux for 12 h and was recovered by filtration. Then the sample was soaked in an appropriate amount of acetone and heated under reflux for half an hour, followed by filtration and extensive washing with acetone to remove the excess of Eu(TTA)₃·2H₂O. In the obtained material, the PIP-Si acts as a bidentate ligand and expels two water molecules from the first coordination sphere of Eu(TTA)₃·2H₂O complex. In this way, Eu(TTA)₃PIP was formed and the Eu(III) complex was attached to the MCM-41 mesoporous material. The resulting sample was dried at 60 °C under vacuum for 12 h and the hybrid mesoporous product Eu-MCM-41 was obtained as outlined in Scheme 1.

2.5. Synthesis of MCM-41 mesoporous silica with the physically incorporated Eu(TTA)₃Phen complex (MCM-41/Eu)

The Eu(TTA)₃Phen complex was synthesized following the literature procedure [22]. The MCM-41/Eu composite system was prepared similar to that of the Eu-MCM-41 except that PIP-MCM-41 and Eu(TTA)₃·2H₂O were replaced by pure MCM-41 and the Eu(TTA)₃Phen complex, respectively.

2.6. Instrumentation and measurements

The FT-IR spectra were recorded within a 400–4000 cm⁻¹ region by an FT-IR spectrophotometer (Model Bruker Vertex 70 FTIR) with a resolution of ± 4 cm⁻¹ using the KBr pellet technique. Small-angle X-ray diffraction (SAXRD) patterns were recorded on a Rigaku-Dmax 2500 diffractometer using Cu Kα₁ (λ=0.15405 nm) radiation at a 0.02° (2θ) canning step. Excitation and emission spectra were recorded at room temperature using a Hitachi F-4500 spectrophotometer equipped with a continuous 150 W Xe-arc lamp. In the experiments of spectral change induced by UV light irradiation, monochromic light separated from the same Xe-arc lamp was used as the irradiation source, with a slit of 10 nm. The fluorescence lifetime of Eu(III) in Eu-MCM-41 was obtained with a 355 nm light generated from the Fourth-Harmonic-Generator pump, using pulsed Nd:YAG laser as the excitation source. All measurements were performed at room temperature.

3. Results and discussion

3.1. FT-IR spectra results

Fig. 1 shows the FT-IR spectra of PIP-Si (A), surfactant-extracted PIP-MCM-41 (B), and Eu-MCM-41 (C), which proves the successful covalent grafting between Eu(TTA)₃PIP and functionalized MCM-41 type mesoporous material. In Fig. 1A, the spectrum of PIP-Si is dominated by νas(C–Si, 1193 cm⁻¹) and νas(Si–O, 1078 cm⁻¹) absorption bands, characteristic of trialkoxysilyl functions. While, in Fig. 1B and C, the occurrence of the grafting reaction is evidenced by the bands located at 1653 and 1645 cm⁻¹, originating from the –CONH– amide group of PIP-Si. The formation of the Si–O–Si framework is evidenced by the bands located at 1080 cm⁻¹ (νas(Si–O–Si), 799 cm⁻¹ (νs(Si–O–Si)), and 458 cm⁻¹ (δ, Si–O–Si) (ν represents stretching, δ in-plane bending, s symmetric, and as asymmetric vibrations). The appearance of absorption peaks of these groups in the final Eu-MCM-41 sample is consistent with the fact that the organic groups have been successfully grafted to the Si–O–Si networks of the inorganic matrix through the hydrolysis–condensation reaction. And from Fig. 1B, the surfactant-extracted PIP-MCM-41 exhibits very weak ν(C–H) vibrations in the region of 2700–3000 cm⁻¹, which confirms that most of the surfactant has been removed.

3.2. SAXRD analysis

The powder X-ray diffraction analyses performed on surfactant-extracted PIP-MCM-41 (A) and Eu-MCM-41 (B) are compared in Fig. 2. These patterns feature distinct Bragg peaks in the 2θ range of 0.8–2.5°, which can be indexed as (1 0 0), (1 1 0), and (2 1 0) reflections of a two-dimensional hexagonal structure of MCM-41 material [23]. The presence of these three diffraction peaks indicates that all of the samples have a MCM-41 type architecture with long range order. Compared with the d₁₀₀ spacing value of PIP-MCM-41, that of Eu-MCM-41 is nearly unchanged, indicating that the framework hexagonal ordering...
has been retained very well upon the introduction of Eu(TTA)$_3$·2H$_2$O.

3.3. Excitation and emission spectra

Fig. 3 shows the excitation and emission spectra for Eu-MCM-41 (A), MCM-41/Eu (B), and Eu(TTA)$_3$ Phen (C) ($\lambda_{ex}=365$ nm, $\lambda_{em}=614$ nm).

3.4. Excited state lifetime

Fig. 4 shows the typical excited-state intensity decay profile for Eu-MCM-41. The excited-state decay curve of Eu-MCM-41 sample can also be well fitted by single exponential equation, confirming that Eu(III) complex covalently grafted to the network of functionalized mesoporous MCM-41 are located on the same microenvironment sites, and the distribution is uniform and homogeneous.

3.5. Photoluminescence stability

Stability of rare-earth complexes under UV irradiation is very important for practical applications. To investigate the photoluminescence stability, ultraviolet light irradiation-induced spectral changes in different samples are also studied. Fig. 5 shows the dependence of Eu-MCM-41 (A), MCM-41/Eu (B), and Eu(TTA)$_3$ Phen (C) normalized emission intensity at 614 nm on irradiation time. As shown in Fig. 5, the emission intensity of $^5D_0 \rightarrow ^7F_2$ in pure complex decreases with increasing exposure time, whereas, that in sample B is nearly constant. It is more interesting to observe that the intensity in sample A even increases with increasing exposure time. Xu’s group also observed the improvement of photostability of Eu complexes encapsulated in MCM-41 pores [10,11]. However, the improvement is not as large as our results, which can be explained as follows. The Eu(III) complex in the present sample is better distributed into the mesoporous molecular sieves and covalently grafted is so effective in stabilizing intensity of the Eu(III) complex. Actually, both the functionalized MCM-41 and pure MCM-41 provide rigid environments to reduce energy consumption on vibration of ligands and collision of intermolecular of complexes. The emission intensity enhancement with exposure time in sample A can be attributed to optical modification of surface defects. During sample preparation, a large number of surface defects are involved in the inner surface of pores, acting as nonradiative relaxation paths. Under UV light exposure, the defects are modified gradually, causing photoluminescence increase [24,25].

4. Conclusion

In this article, we report a covalent grafting strategy using one-pot co-condensation methods about preparation of the materials.
based on Eu(III) complex covalently assembled within functiona-
lized MCM-41 mesoporous materials. Their excitation and
emission spectra, lifetimes and photoluminescence stability
were systemically studied. Eu(III) complex covalently grafted in
MCM-41 emitted bright characteristic emission of Eu(III) ions
and its photoluminescence stability was improved considerably
in comparison to the pure complex and corresponding one that
physically incorporated in MCM-41, which was attributed to the
modification of surface defects under the exposure of ultraviolet
light. Improved photostability of Eu(III) organic complex makes
possible for their applications in areas of optical and electrical
devices.

Acknowledgements

The authors gratefully thank the financial supports of One
Hundred Talents Project from Chinese Academy of Sciences and
the National Natural Science Foundations of China (Grant no.
50872130).

References