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Photofunctional hybrids of lanthanide (Eu^{3+}, Tb^{3+})/beta-diketonate functionalized MCM-41/SBA-15 mesoporous host prepared with 1,4,7,10-tetraazacyclododecane modified siloxane as covalent linkage

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ABSTRACT

Several kinds of novel lanthanide organic–inorganic mesoporous hybrid luminescent materials have been assembled by introducing the ternary lanthanide ions (Eu^{3+}, Tb^{3+}) and beta-diketone (TTA, TAA) into the functionalized mesoporous hosts through the coordination bond and covalent bond by using 3-chloropropyltriethoxysilane modified 1,4,7,10-tetraazacyclododecane (Cyclen-Si) as an organic bridge molecule. These multicomponent hybrids are characterized by FTIR, TEM, XRD, thermogravimetric analysis, diffuse reflectance UV–Vis spectra and nitrogen adsorption–desorption isotherms, especially the photoluminescence properties of them. The luminescent spectra of the hybrids reveal that the MCM-41 based materials show strong emission intensities, high luminescent quantum efficiencies, long luminescent lifetimes and exhibit characteristic red and green luminescence originated from lanthanide ions (Eu^{3+} or Tb^{3+}), which suggesting the Cyclen-Si bridge molecule is favorable for the assembly of lanthanide functionalized luminescent hybrids.

1. Introduction

Luminescent lanthanide complexes have been studied intensively because of their excellent photophysical properties such as high quantum efficiency, line-like emission bands, narrow and intense emission lines, large Stokes shifts and long luminescence lifetimes, which allow them to apply in fields such as lighting and displays, spectroscopic probes in biologically systems, light-conversion molecular devices and optical amplifiers [1–5]. The enhancement of fluorescence properties of lanthanide ions is mainly benefited from the existing of appropriate chelated ligand which would protect the lanthanide ions from vibrational quenching and increase the light absorption rate through the intermolecular energy transfer process–“antenna effect” [6–10]. Recently, there is a growing interest in designing functional ligands which could combine lanthanide complexes to the selected inorganic hosts [11,12]. In the past decades, the inorganic–organic lanthanide hybrid materials have received considerable attention because they integrate the excellent characteristics of organic and inorganic parts, which provide them opportunities in many fields of applications [13–15]. Nowadays, there are many general modified paths for designing bridge molecular as chemical linkages which could be used for the construction of lanthanide hybrid materials with varied host matrix, aim to improve the optical properties of lanthanide complexes [16–22]. Most of the as-derived hybrid materials exhibit improved chemical stability and monophasic appearance even at a high concentration of organic chelates, especially for the silica hosts based materials. Typically, attention has been paid to investigate the luminescent properties of hybrid materials which are constructed by grafted lanthanide complexes onto the silica backbone covalently via the Si–C bonds [23–26].

In the past few years, the use of mesoporous molecular sieves in constructing lanthanide functionalized inorganic–organic hybrid materials has attracted much attentions since it could offer some characteristic properties such as rigidity, regular pore structures, photo-stability and well-defined hydrophilic/hydrophobic phase separation, which allow for sophisticated tuning of the microenvironment around lanthanide complexes. The research efforts in lanthanide functionalized photoluminescent nanopore hybrid materials have involved all types of micropore to mesopore systems, but the most studied host materials are mesoporous silicate systems as well as typical zeolite matrixes [27–34]. Comparison with the other systems, the ordered mesoporous silica can be early prepared via the sol–gel reactions of tetraethyl orthosilicate (TEOS) in the presence of template agent, which provides novel and exciting opportunities for host–guest assembly chemistry of photoactive lanthanide hybrid materials [35–37]. The existing of large

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number of hydroxyl in silicate systems also provides necessary qualification for the modification to its inner face and self-assembly with the other guest molecules. Therefore, our research group has dedicated to the work of preparing lanthanide functionalized mesoporous hybrids through functionalizing the exterior and/or interior surfaces of mesoporous silicate hosts [38–41].

Here, we report the synthesis and characterization of several luminescent mesoporous hybrids, in which the lanthanide complexes are assembled to the silicate hosts through special chemical linkage. We selected 1,4,7,10-tetraazacyclododecane as organic ligand, and modified it with silane coupling reagent to form the precursor Cyclen-Si. Then Cyclen-Si is covalently bonded to the framework of mesoporous MCM-41/SBA-15 in the process of in situ reaction. Subsequently, the luminescent ternary lanthanide complexes functionalized mesoporous hybrids were obtained by introducing Ln^{3+} (Eu^{3+}, Tb^{3+}) and beta-diketone ligands into the mesoporous hosts. Finally, the resulted hybrid materials are characterized in details, especially for its photoluminescent properties.

2. Materials and methods

2.1. Materials

$EuCl_3{\cdot}6H_2O$ and $TbCl_3{\cdot}6H_2O$ were prepared by dissolving the corresponding oxides in concentrated hydrochloric acid, followed by evaporation [42]. Trifluoroacetylacetone (TAA, 98%), thenoyltrifluoroacetone (TTA, 98%), 1,4,7,10-tetraazacyclododecane (Cyclen, 97%), cetyltrimethylammonium bromide (CTAB, 99%), 3-chloropropyltriethoxysilane (CPTEOS, 98%), and tetraethoxysilane (TEOS, 99%) were purchased from Aladdin reagent company. Sodium hydride (60%, dispersion in Paraffin Liquid) was purchased from and used as received. PEG-PPG-PEG Pluronic®P-123 ($EO_{20}PO_{70}EO_{20}$, average Mr ≈ 5800) was purchased from Sigma–Aldrich. Tetrahydrofuran (THF, 99.9%, SuperDry, stabilized with BHT) available by J&K Scientific Ltd. All the other reagents were purchased from China National Medicines Group and used as receive.

2.2. Characterizations

Fourier transform infrared spectra (FTIR) were measured within KBr slices from 4000–400 cm^{-1} using a Nexus 912 AO446 infrared spectrum radiometer. 1H NMR spectra were recorded in $CDCl_3$ on a BRUKER ARX400 spectrometer with tetramethylsilane (TMS) as inter reference. Small angle X-ray powder diffraction patterns (SAXRD) were acquired on Rigaku D/max-Rb diffractometer equipped with Cu anode, whose data were collected within the range of $0.6° \leqslant 2\theta \leqslant 6°$. Nitrogen absorption and desorption isotherms were measured using a Quantachrome Nova 1000 system under the liquid nitrogen temperature; the Brunauer–Emmett–Teller (BET) method was used to calculate the surface area of the mesoporous materials. Transmission electron microscope (TEM) experiments were performed on JEOL2011 microscope system operated at 200 kV. Thermogravimetric analyses (TG) were measured on Netzsch STA 449C system at a heating rate of 5 °C/min under the nitrogen protection. The diffuse reflectance UV–Vis spectra of the powdered samples were recorded by a BWS003 spectrophotometer. Luminescence excitation spectra, luminescence emission spectra and luminescence lifetimes were measured on an Edinburgh Instruments FLS 920 fluorescence spectrometer. The luminescent quantum efficiency is acquired using an integrating sphere (150 mm diameter, $BaSO_4$ coating) with the Edinburgh FLS920 phosphorimeter. The luminescence spectra are corrected for variations in the output of the excitation source and for variations in the detector response.

2.3. Synthesis details

2.3.1. Synthesis of bridge molecule Cyclen-Si precursor

The synthesis of silane coupling agent modified Cyclen precursor was according to the following procedures: Typically, Cyclen (1 mmol) was first dissolved in 40 mL anhydrous THF solvent. Then, a portion of NaH (4 mmol) was added into the solution with stirring. Keep the mixture at room temperature while it is continuously stirred for 2 h. After that, a solution of CPTEOS (4 mmol) in anhydrous THF (20 mL) was added dropwise into the mixture in the ice water condition. After its temperature restored up to room temperature, the mixture was transferred into a two-neck flask and refluxed for 24 h under the protection of Argon atmosphere. Subsequently, the solvent was removed on a rotary evaporator, and viscous oil sample was obtained. The resulted precursor was denoted as Cyclen-Si and used without further purification. ^1H NMR ($CDC1_3$, 400 MHz): δ 0.60 (t, 8H, CH_2Si); 1.22 (t, 36H, $CH_{3\text{-}}CH_2$); δ 3.20 (s, 12H, CH_2N); 3.88 (q, 24H, $SiOCH_2$); 4.16 (m, 5H, CH_2CHCH_2); 6.74–7.54 (m, 8H, ArH) ppm. Elemental Anal. Calc. for $C_{44}H_{100}N_4O_{12}Si_4$ (Mr = 989.63): C, 53.40; H, 10.19; N, 5.66. Found: C, 53.61; H, 10.02; N, 5.52%. FT-IR (KBr): 2975, 2930, 2885 cm^{-1} (–$(CH_2)_3$–), 1200 cm^{-1} (Si–C), 1106 cm^{-1} (Si–O).

2.3.2. Synthesis of Cyclen-functionalized mesoporous MCM-41 material

In a typical procedure, 1.65 g CTAB was dissolved in 39 mL deionized water, and then 18 mL ammonia was added to this solution. To this solution, a mixture of TEOS and Cyclen-Si was added dropwise under vigorous stirring, leading to a composition with a molar ratio of Cyclen-Si:TEOS:CTAB:$NH_3{\cdot}H_2O$:H_2O equals 0.05:0.95:0.139:3.76:66.57. After stirring at room temperature for 24 h, the resulted emulsion was transferred into a Teflon bottle sealed in an autoclave, which was heated at 100 °C for 2 days. Then the solid product was collected with filter and washed thoroughly with deionized water. After dried at 60 °C overnight, the sample was refluxed with ethanol in Soxhlet extraction for 2 days to remove the surfactant CTAB, giving the Cyclen modified mesoporous material MCM-41-Cyclen. Elemental analysis data (wt.%): N 3.02, Si 40.62, suggesting the molar ratio of Cyclen unit in MCM-41-Cyclen is close to 9%.

2.3.3. Synthesis of Cyclen-functionalized mesoporous SBA-15 material

The Cyclen modified mesoporous material SBA-15-Cyclen was synthesized was synthesized according to a modified literature protocol [43]. Typically, 1 g P-123 was dissolved in 7.5 g deionized water, a portion of hydrochloric acid solution (2 mol/L, 30 g) was added to this solution. Keep the mixture at a constant temperature (35 °C), and then a mixture of TEOS and Cyclen-Si was added dropwise under vigorous stirring, leading to a composition with a molar ratio of Cyclen-Si:TEOS:P123:HCl:H_2O equals 0.05:0.95: 0.0172:6:208.33. After stirring at 35 °C for 24 h, the system was transferred into a Teflon bottle sealed in an autoclave and then heated at 100 °C for 2 days. Subsequently, the solid product was collected with filter and washed thoroughly with deionized water. After dried at 60 °C overnight, the sample was refluxed with ethanol in Soxhlet extraction for 2 days to remove the surfactant P123, giving the Cyclen modified mesoporous material SBA-15-Cyclen. Elemental analysis data (wt.%): N 2.81, Si 34.50, suggesting the molar ratio of Cyclen unit in SBA-15-Cyclen is close to 8.5%.

2.3.4. Synthesis of lanthanide complexes functionalized mesoporous materials

The lanthanide functionalized mesoporous hybrid materials with the covalent chemical linkage and beta-diketone sensitizer were prepared as follow: Typically, 0.5 g MCM-41-Cyclen was dispersed into the aqueous solution of $EuCl_3{\cdot}6H_2O$ (0.1 mol/L, 10 mL).