



Ternary lanthanide (Er^{3+} , Nd^{3+} , Yb^{3+} , Sm^{3+} , Pr^{3+}) complex-functionalized mesoporous SBA-15 materials that emit in the near-infrared range

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ABSTRACT

The ternary lanthanide complexes $[\text{Ln}(\text{hftb})_3\text{phen}]$ ($\text{Ln} = \text{Er}, \text{Nd}, \text{Yb}, \text{Sm}$) and $[\text{Pr}(\text{tfnb})_3\text{phen}]$ have been successfully covalently attached in the ordered SBA-15 mesoporous materials via a functionalized 1,10-phenanthroline group 5-(*N,N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (Phen-Si). The derivative materials [denoted as $\text{Ln}(\text{hftb})_3\text{phen-S15}$ and $\text{Pr}(\text{tfnb})_3\text{phen-S15}$; $\text{Ln} = \text{Er}, \text{Yb}, \text{Nd}, \text{Sm}$; $\text{hftb} = 4,4,5,5,6,6,6$ -heptafluoro-1-(2-thienyl)hexane-1,3-dionate; $\text{tfnb} = 4,4,4$ -trifluoro-1-(2-naphthyl)-1,3-butanedionate] were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and N_2 adsorption/desorption. The fluorescence spectra and luminescence lifetimes of these lanthanide-complex-functionalized materials were also recorded. After ligand-mediated excitation, the emission spectra of the $\text{Ln}(\text{hftb})_3\text{phen-S15}$ and $\text{Pr}(\text{tfnb})_3\text{phen-S15}$ materials all display the characteristic NIR luminescence of the corresponding lanthanide ions through the intramolecular energy transfer from the ligands to the lanthanide ions. With these lanthanide-complex-functionalized materials, the luminescent spectral region from 1300 to 1600 nm, which is of particular interest for telecommunication applications, can be covered completely.

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1. Introduction

Lanthanide complexes, especially $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ complexes, have attracted much attention for their unique luminescent properties in the visible region for application in organic light-emitting diodes (OLED) [1,2]. Recently, the lanthanide ions that are emissive in the near-infrared region (NIR) of the spectrum (800–1700 nm), such as $\text{Er}(\text{III})$, $\text{Nd}(\text{III})$, $\text{Yb}(\text{III})$, $\text{Pr}(\text{III})$, and $\text{Sm}(\text{III})$, have received increasing attention for their potential applications in the optical telecommunication [3,4], laser systems [5], and medical diagnosis [6]. The design of sensitizer-functionalized lanthanide complexes that exhibit efficient luminescence in the NIR region is currently of interest and much effort has been directed toward investigating ligands for efficient sensitization of the NIR-emitting lanthanides [7,8]. It has been reported that the NIR-emitting lanthanide ions are particularly prone to vibrational deactivation [9]. However, ligands and coordinated solvent molecules usually contain C–H and O–H bonds that can cause vibrational quenching of the excited ions, leading to the lower NIR-luminescent intensities. It is well known that deuteration or fluorination of hydrogen-containing ligands,

together with exclusion of coordinated water, can extend the lifetime of NIR luminescence and improve the luminescence intensity from lanthanide complexes [10].

However, due to the low photo- and thermal stability of the NIR-luminescent lanthanide complexes, for practical applications one of the strategies to improve the thermal stability, mechanical and light emission properties could be given by the incorporation of the samples into a rigid matrix [11]. Since the mesoporous silica materials were discovered in the early 1990s [12], the development of ordered mesoporous molecular sieves has been of widespread interest in material science. Mesostructured materials offer the rigidity and photostability, and at the same time have a well-defined hydrophilic/hydrophobic phase separation allowing for more sophisticated tuning of the lanthanide complex microenvironment. In addition, in our previous report, on the basis of certain conditions it was observed that the SBA-15-supported materials show an overall increase in relative lanthanide luminescent intensity and lifetime compared to the MCM-41-supported materials [13].

Herein, the syntheses of NIR-luminescent SBA-15 mesoporous materials attached with ternary lanthanide ($\text{Ln} = \text{Er}, \text{Nd}, \text{Yb}, \text{Sm}, \text{Pr}$) complexes by a functionalized 1,10-phenanthroline group 5-(*N,N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (named as Phen-Si) have been reported. We selected two β -diketone

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ligands with polyfluorinated alkyl group, Hhftb and Htfnb (Hhftb = 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)hexane-1,3-dione, Htfnb = 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione) to match with the 4f excited levels of the title lanthanide ions. Full characterization and detailed studies of NIR-luminescent properties of these mesoporous materials were investigated and discussed.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, Aldrich), 3-(triethoxysilyl)-propyl isocyanate (Aldrich), tri-block copolymer poly(ethylene glyco)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, EO₂₀PO₇₀EO₂₀, Aldrich), ethyl trifluoroacetate (Aldrich), fuming nitric acid, and ethanol were used as received. The solvent chloroform (CHCl₃) was used after desiccation with anhydrous calcium chloride. 1,10-Phenanthroline monohydrate (phen H₂O, 99%, AR) was bought from Beijing Fine Chemical Co. (Beijing, China). Ytterbium oxide (Yb₂O₃, 99.99%), neodymium oxide (Nd₂O₃, 99.99%), erbium oxide (Er₂O₃, 99.99%), samarium oxide (Sm₂O₃, 99.99%), and praseodymium oxide (Pr₆O₁₁, 99.99%) were purchased from Yue Long Chemical Plant (Shanghai, China). Hhftb and 2'-acetonaphthone were from Acros Organics Co. (Geel, Belgium). LnCl₃ (Ln = Er, Nd, Yb, Sm, Pr) were obtained by dissolving Ln₂O₃ (Ln = Er, Nd, Yb, Sm) and Pr₆O₁₁ in concentrated hydrochloric acid (HCl) and removing the surplus HCl by evaporation.

2.2. Synthesis of phen-functionalized SBA-15 mesoporous material (phen-S15)

The starting reagent 5-amino-1,10-phenanthroline (named Phen-NH₂) was synthesized according to Ref. [14]. The modified phen group Phen-Si was prepared by the reaction of 3-(triethoxysilyl)-propyl isocyanate and Phen-NH₂ in CHCl₃ as described in the literature [15,16]. The phen-S15 was synthesized as described in our recent report [13]. The molar composition of the original synthetic mixture was Phen-Si:TEOS:P123:HCl:H₂O = 0.04:1.0:0.0172:6:208.33.

2.3. Synthesis of the [Ln(hfth)₃(H₂O)₂] complex (Ln = Er, Yb, Nd, Sm, Pr)

The synthesis procedure was according to the reported method [16]. The complexes obtained were dried overnight at 80 °C under vacuum.

2.4. Synthesis of the ligand Htfnb

The ligand Htfnb was synthesized by the reaction between 2-acetonaphthone and ethyl trifluoroacetate according to the procedure described in our previous report [17].

2.5. Synthesis of the [Pr(tfnb)₃(H₂O)₂] complex

The synthesis procedure for [Pr(tfnb)₃(H₂O)₂] was similar to that for [Ln(hfth)₃(H₂O)₂] complex except that LnCl₃ and Hhftb were replaced by PrCl₃ and Htfnb, respectively.

2.5.1. Elemental analysis

For [Er(hfth)₃(H₂O)₂], calculated: C, 30.88%; H, 1.38%. Found: C, 30.64%; H, 1.52%. For [Nd(hfth)₃(H₂O)₂], calculated: C, 31.50%; H, 1.41%. Found: C, 31.23%; H, 1.54%. For [Yb(hfth)₃(H₂O)₂], calculated: C, 30.73%; H, 1.38%. Found: C, 30.96%; H, 1.56%. For [Sm(hfth)₃(H₂O)₂], calculated: C, 31.33%; H, 1.40%. Found: C, 31.61%; H, 1.58%. For [Pr(hfth)₃(H₂O)₂], calculated: C, 31.59%; H, 1.41%. Found: C, 31.37%; H, 1.59%. For [Pr(tfnb)₃(H₂O)₂], calculated: C, 52.04%; H, 2.60%. Found: C, 51.89%; H, 2.84% [16].

2.6. Synthesis of SBA-15 mesoporous material covalently bonded with [Ln(hfth)₃phen] ternary complex [denoted as Ln(hfth)₃phen-S15, Ln = Er, Nd, Yb, Sm, Pr]

Phen-S15 was soaked in an excess of [Ln(hfth)₃(H₂O)₂] ethanol solution [12 equiv. of [Ln(hfth)₃(H₂O)₂] per phen moiety] under stirring. The mixture was heated under reflux for 6 h and was recovered by filtration. The excess reactants (such as [Ln(hfth)₃(H₂O)₂] complexes) in the Ln(hfth)₃phen-S15 were removed by Soxhlet extraction with acetone heated under reflux for 10 h. The resulting samples were dried at 80 °C under vacuum for 12 h.

2.7. Synthesis of SBA-15 mesoporous material covalently bonded with [Pr(tfnb)₃phen] ternary complex [denoted as Pr(tfnb)₃phen-S15]

The synthesis method for Pr(tfnb)₃phen-S15 was similar to that for Ln(hfth)₃phen-S15 except that [Ln(hfth)₃(H₂O)₂] was replaced by [Pr(tfnb)₃(H₂O)₂].

2.8. Characterization

The CH elemental analyses were carried out on a VarioEL analyzer. Small-angle X-ray diffraction (XRD) patterns were recorded with a Rigaku-Dmax 2500 diffractometer using Cu K α radiation (40 kV, 200 mA) at a step width of 0.01°. Nitrogen (N₂) adsorption/desorption isotherms were measured by using a Nova 1000 analyzer with nitrogen. The samples were outgassed for 4 h at 120 °C before the measurements. Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and pore sizes by the Barrett-Joyner-Halenda (BJH) methods. The structures of the lanthanide-complex-functionalized mesoporous materials were characterized by transmission electron microscopy (TEM). All of the samples for the TEM characterization were prepared by directly transferring the suspended products to the standard copper grid coated with an amorphous carbon film. TEM was carried out on a JEOL-JEM-2010 at 200 kV. The excitation and emission spectra of

Table 1
Structural parameters of phen-S15, Ln(hfth)₃phen-S15 (Ln = Er, Nd, Yb, Sm) and Pr(tfnb)₃phen-S15 materials

Sample	d_{100} (nm)	a (nm)	S_{BET} (m ² g ⁻¹)	V (cm ³ g ⁻¹)	D (nm)	h_w (nm)
phen-S15	11.04	12.75	938.7	1.43	6.46	6.29
Er(hfth) ₃ phen-S15	11.47	13.24	778.4	1.22	5.74	7.50
Nd(hfth) ₃ phen-S15	11.45	13.22	732.6	1.17	5.75	7.47
Yb(hfth) ₃ phen-S15	11.33	13.08	720.5	1.17	5.70	7.38
Sm(hfth) ₃ phen-S15	11.18	12.91	766.5	1.22	5.74	7.17
Pr(tfnb) ₃ phen-S15	11.18	12.91	784.7	1.24	5.73	7.18

d_{100} is the $d(100)$ spacing, a the cell parameter ($a = 2d_{100}/\sqrt{3}$), S_{BET} the BET surface area, V the total pore volume, D the average pore diameter, and h_w the wall thickness, calculated by $a - D$.

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