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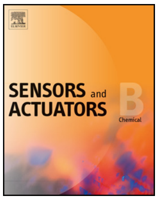

Highly selective fluorescent sensing for fluoride based on a covalently bonded europium mesoporous hybrid material

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ABSTRACT

A novel silylated ligand (L–Si) derived from a derivative of phenanthroline (2-(2-hydroxyphenyl)-imidazo[4,5-f]-1,10-phenanthroline, denoted as L) was designed, and it played key roles in the assembly of new organic-inorganic mesoporous hybrid functional material. Firstly, the two N atoms of pyridine rings can coordinate to europium ions and sensitize its luminescence. Secondly, the NH of imidzole ring could form hydrogen bonds with fluoride anions. Thirdly, the silylated group can covalently bonded to the frame of SBA-15 mesoporous silica via in-situ synthesis approach. In addition, 2-thenoyltrifluoroacetonate (TTA) was selected as the second ligand for the purpose of better luminescence. Finally, the europium luminescent mesoporous hybrid material Eu(L–S15)$_2$TTA was obtained through the coordination reaction between europium ion and L–S15 as well as the second ligand TTA. Eu(L–S15)$_2$TTA not only exhibits excellent luminescent properties and high thermal stability, but also retains the ordered mesoporous structures. More importantly, it displays a high-sensitivity sensing function with respect to fluoride ion. The limit of detection for the fluoride ion is as low as 1.6×10^{-9} M for the fluoride ion.

1. Introduction

In the past few decades, the design and preparation of fluorescent sensor for detecting targeted anions have attracted considerable attention since they play fundamental roles in many biological and environmental systems [1–6]. Among various anions, fluoride is of particular importance because of the significant applications of this anion in nerve gas, drinking water analysis, food additive and nuclear warfare agents [7–11]. Therefore, many researchers have been devoted to the design of fluoride selective sensor.

Recently, lanthanide complexes have been extensively studied as promising sensory materials owing to their excellent optical properties such as narrow emission bands, high color purity, long lifetime and high quantum efficiency [12–17]. However, their practical applications have been limited to a large extent because of their poor photo-/thermo- stability and low mechanical strength. These problems could be solved by immobilizing lanthanide complexes in inorganic solid matrices, such as polymer [18–21], liquid crystal [22–25], or silica-based materials [26–28]. Compared with conventional bulk materials, order mesoporous silica with large surface area, adjustable pore size, high thermal stability and easy recyclability allow them to be favorably used as fluorescent sensors for highly sensitive detection of specific ions. Wang et al. reported the synthesis of lanthanide complexes covalently bonded to mesoporous siclia MCM-41 via post-grafted method, which can efficiently detected fluoride [29,30]. However, the hybrid materials obtained by this method can't preserve regular mesoscopically ordered structures because the organic component is relatively high in the whole molecular system, while in-situ synthesis approach can effectively solve this problem. Therefore, in this work, the in-situ synthesis approach was selected to synthesize the mesoporous hybrid material.

In addition, it needs to be referred that the key procedure to construct such materials is to design a functional ligand, which can not only be modified with silane coupling agent and further covalently bonded to mesoporous silica, but also can coordinate and sensitize lanthanide ions. It is well known that 1,10-phenanthroline and its derivatives are the efficient sensitizers for the luminescence of lanthanide ions. Based on the above considerations, here we synthesize a kind of phenanthroline derivation (2-(2-hydroxyphenyl)-imidazo[4,5-f]-1,10-phenanthroline, denoted as L), which could be grafted to 3-(triethoxysilyl)propyl isocyanate (TESPIC) to obtain a molecular precursor (L–Si) through a hydrogen-

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transfer nucleophilic addition reaction between the hydroxyl group of phenanthroline derivation and the isocyanate group of silane coupling agent TESPIC. And then the precursor L–Si was covalently bonded to the frame of SBA-15 to form mesoporous hybrid material (L–S15) through co-condensation of the precursor L–Si and tetraethoxysilane (TEOS) by using the Pluronic P123 surfactant as template. In addition, in order to enhance the photoluminescent properties of active europium ions, we introduced 2-thenoyltrifluoroacetonate (TTA) as s second ligand to coordinate with the europium ions. Finally, the europium mesoporous hybrid material (denoted as Eu(L–S15)$_2$TTA) was obtained through the coordination reaction between europium ion and L–S15 as well as the second ligand TTA. Eu(L–S15)$_2$TTA not only exhibits excellent luminescent properties, but also retains the ordered mesoporous structures. More importantly, it displays a high-sensitivity sensing function with respect to fluoride. To the best of our knowledge, this is the first example of a covalently bonded europium mesoporous hybrid with mesoscopically ordered structures bearing anion recognition functions.

2. Experimental section

2.1. Materials

Europium nitrate ($Eu(NO_3)_3{\cdot}6H_2O$) was obtained by dissolving Eu_2O_3 (99.99%, J&K Scientific Ltd.) in concentrated nitric acid (HNO_3), and the resultant product was dissolved in ethanol (EtOH) to get its solution. Triblock copolymer poly(ethylene glyco)-block-poly(propylene glycol)-block-poly-(ethylene glycol) (Pluronic P123, $EO_{20}PO_{70}EO_{20}$), 3-(3-(triethoxysilyl)propyl isocyanate (TESPIC, 96%), tetraethoxysilane (TEOS, A.R.), 2-thenoyltrifluoroacetone (TTA, 99%), 1,10-Phenanthroline monohydrate (phen) were obtained from J&K Scientific Ltd. All anions (F^-, Cl^-, Br^-, I^-, $NO_3{}^-$, $HSO_4{}^-$, $H_2PO_4{}^-$, CH_3COO^-) as tetrabutylammonium (TBA) salts were purchased from Aladdin. All the other reagents were purchased from Sinopharm Chemical Reagent Corporation (China) and used without further purification. 2-(2-hydroxyphenyl)-imidazo[4,5-f]-1,10- phenanthroline was synthesized according to the literature [31].

2.2. Synthesis procedures

2.2.1. Synthesis of precursor L–Si.

2-(2-hydroxyphenyl)-imidazo[4,5-f]-1,10-phenanthroline (denoted as L, 2 mmol, 0.626 g) was firstly dissolved in 20 mL of dehydrated tetrahydrofuran (THF), and then 3-(triethoxysilyl)propyl isocyanate (TESPIC, 2 mmol, 0.497 g) was added dropwise into the solution with magnetic stirring. The mixture was refluxed in a covered flask for approximately 12 h under a nitrogen atmosphere, and the termination of the reaction was monitored by thin layer chromatography. The solvent THF was removed quickly using a rotary vacuum evaporator to give the crude product. Further purification was performed by flash column chromatography with CH_2Cl_2/MeOH = 50/1 as eluted solvents. Finally the purified product was obtained as the main band (0.822 g, yield 76%). which was denoted as L. IR (KBr): —CONH— 1654 cm^{-1}, C—Si 1173 cm^{-1}, Si—O 1080 cm^{-1}. ^1H NMR (DMSO-*d*6): 1.14–1.16 (t, 9H), 0.98–1.10 (t, 2H), 1.38–1.42 (m, 2H), 1.57–1.63 (t, 2H), 3.73–3.78 (m, 6H), 7.08–7.11 (t, 2H), 7.40–7.42 (t, 1H), 7.81–7.83 (t, 1H), 7.85–7.87 (m, 2H), 8.94–8.95 (d, 2H), 9.04–9.07 (d, 2H). Anal. Calcd for $C_{29}H_{33}N_5O_5Si$: C, 62.25; N, 12.52; H, 5.90; Found: C, 64.56; N, 13.10; H, 6.02.

2.2.2. Synthesis of L covalently bonded SBA-15 mesoporous material (L–S15)

P123 (2.0 g) was firstly dissolved in the deionized water (15 g) with magnetic stirring, and 2 M HCl solution (60 g) was added at room temperature. Then a mixture of L–Si and TEOS was added into the above solution at 35 °C with stirring for 24 h. The molar ratio composition of P123: TEOS: L–Si: HCl: H_2O is 0.0172: 0.96: 0.04: 6: 208.33. The mixture solution was transferred into a Teflon bottle sealed in an autoclave, which was heated at 100 °C for 48 h. Finally, the autoclave was naturally cooled in the oven. Then, the solid product was filtrated, washed thoroughly with deionized water, and air-dried for 15 h at 65 °C. Removal of the copolymer surfactant P123 was conducted by Soxhlet extraction with ethanol under reflux for 48 h to obtain the sample denoted as L–S15.

2.2.3. Synthesis of europium-containing mesoporous hybrid material (Eu(L–S15) 2TTA)

While being stirred, L–S15 was introduced into an appropriate amount of an $Eu(NO_3)_3$ ethanol solution, then 2-thenoyltrifluoroacetone (TTA) ethanol solution was added into the solution (the molar ratio of $Eu(NO_3)_3$: L-15: TTA = 1: 3: 1). The mixture was refluxed for 8 h, followed by filtration and extensive washing with EtOH. The detailed synthetic process and the predicted structure of Eu(L–S15)$_2$TTA are outlined in Scheme 1.

2.3. Characterizations

^{1}HNMR spectra were recorded in DMSO-*d*6 on a Bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as an internal reference. Fourier Transform Infrared (FTIR) spectra were measured within the 4000–400 cm^{-1} wavenumber range on an Nicolet 6700 spectrophotometer with the KBr pellet technique. Small angle X-ray powder diffraction pattern (SAXRD) were measured using a Rigaku D/max2500VB+/PC diffractometer equipped with a Cu anode in a 2θ range from 0.6 ° to 6 °. Nitrogen (N_2) adsorption–desorption isotherms were recorded on a Nova 2000 analyzer at the liquid nitrogen temperature. Before the measurements, the sample was outgassed for 4 h at 423 K. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and pore size distributions were evaluated from the desorption branches of the nitrogen isotherms using the Barrett–Joyner–Halenda (BJH) model. Transmission electron microscope (TEM) observation was carried out by using a JEOL JEM2011 transmission electron microscope operated at 200 kV. SEM images were obtained by using a TS 5136 MM instrument. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris Diamond thermal analyzer up to 800 °C at a heating rate of 10 °C/min under N_2. The fluorescence excitation and emission spectra were obtained on a Hitachi F-4600 spectrophotometer. The luminescence lifetime measurements was measured with an Edinburgh FLS920 phosphorimeter using a 450 W xenon lamp as the excitation source.

3. Results and discussion

3.1. Characterization of mesoporous hybrid material Eu(L–S15)$_2$TTA

The reaction process was monitored by FTIR spectra. The FTIR spectra of the precursor L–Si (a), mesoprous hybrid matertial L–S15 (b), and europium-containing mesoporous hybrid material Eu(L–S15)$_2$TTA (c) are presented in Fig. 1. As shown in Fig. 1a, the broad band located at 3356 cm^{-1} was attributed to the stretching vibration of —NH group. Three adjacent peaks at 2975, 2928, and 2887 cm^{-1} corresponded to C—H stretching vibrations of —CH_2— groups in grafted TESPIC. The sharp band located at 1654 cm^{-1}