



Conversion of Lewis acid-base interaction into readable emission outputs by novel terbium hybrid nanosphere



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ABSTRACT

A novel luminescent organic-inorganic hybrid terbium material containing a boronic acid receptor site has been designed and synthesized. Ultra-violet excitation of the material results in green emission from the terbium core. Homogenous spherical nanoparticles with the average diameter of 60 nm were achieved by embedding the terbium complex onto a silica surface. The boron–fluoride interactions of the new material in an aqueous environment provide for a new on-off luminescence sensor for fluoride ions in the field of lanthanide based multifunctional materials.

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1. Introduction

Fluoride recognition has attracted considerable attention in the past decades due to its important role in biological and environmental system [1–3]. Especially the development of fluorescent probes with selective optical sensing properties is of great interest for their fast responses and easy detections [4,5].

Optical sensors such as organic dyes, semiconductor nanoparticles and transition metal complexes have been developed as potential candidates [6,7]. However, the problems of broad emission bands, short lifetimes, low signal/noise ratio and autofluorescence from influencing species could not be avoided. Accordingly, lanthanide elements and corresponding probes with excellent photophysical features such as long lifetime, sharp emission peaks and large Stokes shifts are presently the subject of a new direction [8–14]. It has been clarified that these ions or complexes are sensitive to vibrations by energy transfer to adjacent water or alcohol molecules [8]. Therefore, their emissions are

susceptible to quenching in aqueous solution and the strategies to address this challenging objective have been developed. From last decade, a few lanthanide containing silica- or siloxane-based hybrid materials have been assembled and they could maintain the luminescence features in an aqueous environment [15,16].

In view of recognition modes, several lanthanide complexes as fluoride responsive luminescent sensors have been prepared and the main driving forces were established on hydrogen bond interactions (such as imidazoles, ureas or thioureas) [17–22]. But it is known that F[−] sensors based on hydrogen bond formation can be only carried out in common organic solvents (aprotic solvents). Meanwhile, the interference from other anions may be difficult to exclude [23,24]. These drawbacks would severely restrict the practical application of such H-bond dependent sensors in the natural environment. In recent years, the electron-deficient Lewis acid coordination by orbital overlap has been considered and boron–fluoride interactions expressed by fluorescence changes are easily recognizable in polar solvents [25–31]. To the best of our knowledge, the utilization of Lewis acid-base effect between boron and fluoride in the field of lanthanide organic-inorganic hybrid sensors has never been reported. In this report, we designed a novel terbium-based fluorescent probe bearing the phenylboronic acid receptor, which exhibited high sensitivity and selectivity toward F[−] over other anions in water. For the sake of improving the stability in

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aqueous media, the corresponding complex was encapsulated into a silica backbone. The homogenous spherical nanoparticles were achieved. The nanoparticles achieved gave a striking change in luminescence during the recognition process. Furthermore, ^{19}F NMR spectroscopy revealed the emission on-off mechanism was attributed to the formation of strong boron–fluoride interactions.

2. Experimental

2.1. Materials

Tb_4O_7 (99.9%) was purchased from Shanghai Yuelong company. Terbium perchlorate was obtained by dissolving Tb_4O_7 in concentrated perchloric acid. 4-boronobenzoic acid, Triton X-100, 3-aminopropyltriethoxysilane (APTES, 99%), tetraethyl orthosilicate (TEOS) and all the tetrabutylammonium salts were purchased from J&K Scientific. All the other reagents were purchased from Guangzhou Chemical Reagent Factory and used without further purification.

2.2. Characterization

^{19}F NMR spectra were recorded at 293 K using a Varian 400 (400 MHz) with tetramethyl silane (TMS) as an internal standard, all chemical shifts were reported in the standard notation of parts per million. Fluorescence emission, excitation spectra were measured using an Edinburgh FLS920 spectrometer (Great Britain), equipped with a 450 W xenon lamp source. FT-IR spectra were measured using a Shimadzu Prestige-21. Ultraviolet–visible absorption spectra were collected using a Shimadzu UV-2550 spectrophotometer. TEM was measured using a JEOL JEM-2100HR transmission electron microscope. SEM was measured using a Zeiss Ultra 55 scanning electron microscope. TGA was carried out on a STA409PC system under air at a rate of 10 °C/min. Elemental analysis was carried out in an Elementar Vario EL elemental analyzer. Dynamic Light Scattering measurements were performed on a Malvern Mastersizer-2000.

2.3. Fabrication of surface-modified silica nanoparticles

The initial silica nanoparticles were synthesized using a reverse micro-emulsion method [32]. Briefly, Triton X-100 (35.4 g), n-hexanol (32 mL), and cyclohexane (150 mL) were mixed in a 500-mL glass flask with vigorous magnetic stirring, and deionized H_2O (8 mL) was added. After the addition of TEOS (2 mL), the solution was stirred for 30 min. To initiate silica polymerization, ammonium hydroxide solution (1.3 mL) was added. The polymerization was allowed to proceed for 18 h. The resulting particles were centrifuged, sonicated, and vortexed three times with anhydrous ethanol, followed by washing twice with deionized water.

For the amine-functionalized silica nanoparticles, the as-prepared silica were dispersed into alcohol (20 mL) in a 50-mL round bottom flask, then tetraethyl orthosilicate (1 mL), aminopropyltriethoxysilane (1 mL) and ammonium hydroxide solution (0.6 mL) were added in the flask. Finally, the particles were centrifuged and washed with ethanol and deionized water for three times.

In order to obtain the carboxyl modified SiO_2 , the above amine-functionalized silica were dispersed again in alcohol with excess amounts of succinic anhydride, the mixture was stirred and refluxed at 90 °C for 48 h. The precipitates were centrifuged, sonicated, and vortexed three times with ethanol, followed by washing twice with deionized water. Finally the powder was dried at 80 °C under vacuum.

2.4. Fabrication of terbium hybrid materials

The obtained carboxyl modified SiO_2 (0.5 g) was added in anhydrous ethanol (20 mL) in a round bottom flask. Then, $\text{Tb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (0.1 g) was dissolved in ethanol (10 mL). An appropriate amount of 4-boronobenzoic acid and ammonium hydroxide (0.5 mL) were added to the flask. The mixture was stirred and refluxed at 90 °C for 5 h. After reaction, the precipitate was centrifuged and re-dispersed in ethanol at least three times to remove the excessive ligand and terbium ions.

2.5. Synthesis of Tb complex

In a 50-mL flask, $\text{Tb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ (1.13 g) was dissolved in anhydrous ethanol (20 mL), and then 4-boronobenzoic acid (1.0 g) dissolved in ethanol (10 mL) was successfully added in the flask followed by the addition of ammonium hydroxide (0.5 mL). The mixture was stirred and refluxed at 90 °C for 2 h. The resulting precipitate was collected and washed with water and ethanol, and then dried at 80 °C under vacuum to give the target complex as white powder. EA found: C, 36.68; H, 3.37. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{B}_3\text{O}_{14}\text{Tb} [\text{Tb}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$: C, 36.57; H, 3.21.

3. Results and discussion

To fabricate the terbium-based luminescent nano-sensor, firstly we assembled a nanoscale silica matrix as the direct template by the hydrolysis of tetraethoxysilane in a microemulsion. Secondly, the host was grafted with an amine and then a carboxylic acid function. Finally, terbium ions were chelated with both the carboxyl group on the surface of silica and the ligand (4-boronobenzoic acid). The covalently bonded organic-inorganic sensing composite can be achieved (Fig. 1).

The obtained functional silica host and the terbium-based hybrid material were characterized by FT-IR spectroscopy. Figure S1 shows the absorption of different groups from surface-modified silica hosts. As can be seen, the broad band at around 1090 cm^{-1} is attributed to the Si–O–Si framework in silica. Besides, the band at 3435 cm^{-1} can be assigned to the –OH in the surface of silica. The amino-functionalization was evidenced by the band at 3401 cm^{-1} (the stretching vibration of –NH) and three adjacent peaks at around 2935 cm^{-1} (the asymmetric and symmetric stretching vibrations of CH_2 groups in the grafted 3-aminopropyltriethoxysilane). In the curve for the carbonyl modified silica, the characteristic peak at 1643 cm^{-1} was attributed to the stretching vibration of the –COOH group.

The IR spectra of the benzenboronic acid (ligand), terbium complex and corresponding hybrid material are illustrated in Fig. S2. In the spectrum for the ligand (a), the characteristic bands corresponding to the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ of –COOH are located at 1692 and 1269 cm^{-1} . The second intense band in the spectrum occurs at 1351 cm^{-1} is assigned to the asymmetric B–O stretching vibration [33]. The broad bands at 3159 and 3363 cm^{-1} could be attributed to the –OH stretching vibration of –COOH and –B(OH)₂ groups respectively. In the case of terbium complex (Figure S2b), the formation of coordinated bonds between the carboxylic group and terbium ion is corroborated by the disappearance of a C=O stretching vibration of the COOH. Meanwhile, two new peaks can be observed at 1532 cm^{-1} and 1474 cm^{-1} , which are derived from the asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of carboxylate. For the terbium-containing hybrid material, the result showed that the initial C=O stretching vibration of –COOH groups (1643 cm^{-1}) on the surface of silica shifted to a lower frequency (1625 cm^{-1}) due to the complexation with terbium ions. In addition, the stretching vibration of Si–O band can be also found at

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