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Highly sensitive bifunctional sensor of a dinuclear terbium complex

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ABSTRACT

A new dinuclear terbium complex (Tb-complex) is designed and synthesized based on 2,4,5-Trifluoro-3-methoxybenzoic acid (HTFMBA). The exact structure of the Tb-complex is determined to be $[Tb_2(TFMBA)_6(phen)_2]$ (phen = phenanthroline). It crystallizes in the triclinic space group *P*-1, and it is further characterized by FT-IR, PXRD, EA, TGA and luminescence. Tb-complex shows very high luminescence quantum yield (QY) of 61.5%. Detailed investigation reveals that the Tb-complex is a highly sensitive and selective bifunctional sensor for detecting SO_4^{2-} and CH_3Hg^+. Responsive behavior shows the detection has excellent linear relationship between luminescence and the concentration of SO_4^{2-} and CH_3Hg^+. The limit of detection (LOD) for detecting SO_4^{2-} and CH_3Hg^+ are as low as 5×10^{-7} M and 2.8×10^{-9} M, respectively. This is the first bifunctional sensor that could probe the highly toxic CH_3Hg^+, and it is the most sensitive chemosensor for detecting CH_3Hg^+. Further investigation also reveal that the Tb-complex is applicable in sensing SO_4^{2-} and highly toxic CH_3Hg^+ in real water samples.

1. Introduction

The development of sensors for the rapid, facile, highly sensitive and selective detection of various analytes has attracted increasing attention [1,2]. Organic compounds have been widely investigated as fluorescent sensors [3], but they suffer from some limitations such as poor photostability, narrow excitation spectra, and broad absorption bands with red tailing. In the last decade, new kind of fluorescent probes, such as metal nanoclusters (NCs) [4], quantum dots (QDs) [2], and semiconductor nanocrystals have been suggested to overcome these limitation. Nevertheless, the main drawbacks of NCs and QDs lie in their expensive and complicated synthetic routes, and toxic compositions are commonly present in these sensors [5].

Lanthanide complexes have shown great potential applications in the area of luminescence sensing [6–9], due to their low biotoxicity, unique photophysical properties, such as long lifetimes, broad excitation spectra, large Stokes shifts, as well as characteristic and line like lanthanide-centered luminescence bands [10]. However, lanthanide ions generally display high and variable coordination numbers (4–12), and with very small energy differences between different coordination numbers. This results in increased difficulties in controlling synthesis of lanthanide complexes/clusters, in comparison to the situation of the transition metals [11].

Mercury is a well-known highly toxic environmental pollutant [12], nevertheless, its main organic form of CH_3Hg^+ is more toxic to animals than Hg^+ [13], due to its lipid solubility and ability to pass through cell membranes [14]. CH_3Hg^+ is a well-known potent neurotoxin that causes damage to nervous system, especially in infants and pregnant women. CH_3Hg^+ is able to bio-accumulate and bio-amplify in the human body through the food chain. SO_4^{2-} is usually a pollutant that coexists with the metal ion pollutants, and it also exists in acid rain. Herein, the sensing of highly toxic CH_3Hg^+ and SO_4^{2-} in water is of emergency and valuable. Usually, complicated hyphenated techniques based on separation techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), or capillary electrophoresis (CE) coupled with sophisticated detection such as atomic fluorescence spectrometry (AFS) [15], mass spectrometry (MS) [16], or inductively coupled plasma mass spectrometry (ICPMS) [17], are used for detecting CH_3Hg^+ and SO_4^{2-}. In addition, tedious extraction and pre-concentration procedures are usually needed [18,19]. Nowadays, facile and quick response sensors that can be used for on-site detection are urgently needed, focused on the sensitive and selective sensing of toxic species such as CH_3Hg^+ and SO_4^{2-}. To date, no work regarding the bifunctional detection of CH_3Hg^+ and/or SO_4^{2-} has been reported. Zeng et al. had developed several sensitive lanthanide complexes sensor for CH_3Hg^+, Co^{2+}, Zn^{2+} and also some other species [20–22]. These work

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and some other studies reported by other groups have promoted the development of lanthanide complexes sensors [23–26].

In this study, a prodrug 2,4,5-Trifluoro-3-methoxybenzoic acid (HTFMBA), which is usually used as a key intermediate in manufacturing third generation fluoroquinolonic antibiotics [27], was selected to synthesize the Tb-complex. The complex is characterized by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), elemental analysis (EA), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA) and luminescence. It is found that the highly luminescent Tb-complex is a highly sensitive and selective bifunctional sensor applicable in real water samples for the sensing of SO_4^{2-} and CH_3Hg^+. The sensing mechanism in this work is also discussed in detail.

2. Experimental section

2.1. Materials and methods

$Tb(NO_3)_3{\cdot}6H_2O$ and HTFMBA (98.0%) was purchased from TCI (Shanghai, China), and used without further purification. NaOH was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Methylmercury chloride (CH_3HgCl) was purchased from Alfa Aesar (95%). Other chemicals (A.R.) are commercially available and used without further purification.

Single crystal X-ray diffraction data was measured on a Bruker SMART 1000 CCD, with Mo-Kα radiation (0.71073 Å). The structure was refined by full-matrix least-squares methods with SHELXL-97 module [28]. Phase purity of as synthesized sample was determined by PXRD, using a DMAX2200VPC diffractometer at room temperature. EA (C and H) was performed on an EA3000 elemental analyzer. FT-IR was tested in KBr pellets and recorded on a Nicolet 330 FT-Irspectrometer. Thermogravimetric analysis (TGA) was tested under atmosphere, on a Netzsch-Bruker TG-209 unit with heating rate of $10\,^{\circ}C\,min^{-1}$. Luminescence spectra and luminescence lifetimes were recorded on an Edinburgh FLS920 at the room temperature, with the dwell time of 0.20 s. Luminescence QY was also collected by the same Edinburgh FLS920 which equipped with an integrating sphere.

3. Results and discussion

3.1. Crystal structure analysis

Crystallographic data and structure refinement parameters for Tb-complex are listed in Table S1. It crystallizes in the triclinic space group *P*-1, with cell parameters $a = 12.3478(8)$ Å, $b = 14.8065(9)$ Å, $c = 21.0163(13)$ Å, $\alpha = 91.8650(10)^{\circ}$, $\beta = 104.2520(10)^{\circ}$, $\gamma = 105.9830(10)^{\circ}$, $V = 3559.3(4)$ Å^3 and $Z = 2$. Tb-complex has the formula $[Tb_2(TFMBA)_6(phen)_2]$. Each asymmetric di-nuclear cluster contains two Tb^{3+}, two phen and six TFMBA (Fig. 1a). There is no coordination and crystalline H_2O in the structure which is convenient for constructing highly luminescent lanthanide clusters, since the oscillation effect of O—H, N—H and C—H around the lanthanide ions would decrease or quench the metal centered luminescence.

Two phen molecules chelate to Tb^{3+} and arrange at the two ends of the Tb-complex. Two of the six ligands chelate to Tb^{3+} (Fig. 1a), and other four ligands bridge the adjacent two Tb^{3+} to form dinuclear cluster (Fig. 1b). Each Tb^{3+} is coordinated by one phen and six O (from four bridged and one chelated TFMBA) to form a TbO_6N_2 cluster, the six O and two N in Tb1 and Tb2 are arranged in a distorted bi-capped triangular prism mode (Fig. 1c–d). The invasion of phen decreases the space around Tb^{3+} to accommodate H_2O, which is also good news for obtaining highly luminescent lanthanide complexes, since there is no oscillation effect of O—H, N—H and C—H from the solvents to decrease/quench the Tb^{3+} centered luminescence [29]. Dinuclear Tb-complex is further connected by weak interactions of Van der waals (VDW) force and hydrogen bonds to form a 3D networks of complex molecules (Fig. 1e) [30]. In this structure, the six F atoms (F2, F3, F5, F6, F8 and F14) and some $-O-CH_3$ are disordered, and with very large atomic displacement parameters (ADP) according to program PLATON [31], such disorder could be attributed to lack of weak interactions keeping the molecules together in the crystal.

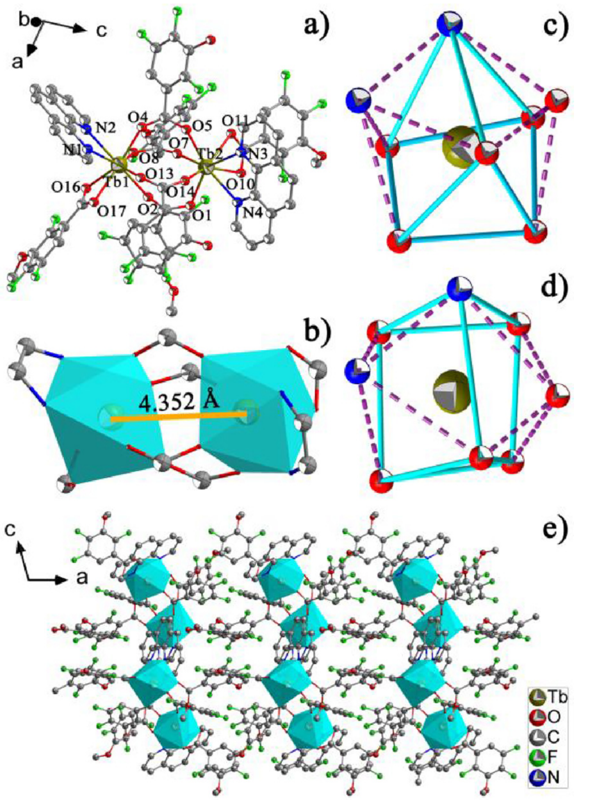

Fig. 1. a) The dinuclear structure of Tb-complex; b) Tb-complex is bridged by four carboxyls; c) the atoms around Tb1 arranged in distorted bi-capped triangular prism mode; d) the atoms around Tb2 arranged in distorted bi-capped triangular prism mode; e) 3D structure of the Tb-complex (view along *b* axis) that connected by weak interaction. All the hydrogen atoms in the structure are omitted for clarity.

Luminescence of Tb-complex stock solution was measured at room temperature. When fixing at the strongest emission of $^5D_4 \rightarrow {}^7F_5$ transition (544 nm), the excitation spectrum displays a broad band covering from 241 to 325 nm (Fig. 2a), indicating the Tb-complex is a broad wavelength excitation material. The emission was recorded at the best excitation of 302 nm. Characteristic line emissions at 544, 582 and 621 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_3$ transitions of Tb^{3+} [32], respectively, were observed (Fig. 2a). The Tb-complex has a high luminescence QY of 61.5% (Ex = 302 nm), since the luminescence QY of lanthanide cluster/complexes larger than 60% of are rarely reported. The high luminescence QY of the Tb-complex ascribed to two reasons: Firstly, no coordination or crystalline H_2O in the Tb-complex would increase the luminescence emission, since less oscillation effect of O—H will decrease the energy consumption of metal centre; and secondly, the H on the ligand of TFMBA is replaced by the fluorine, resulting in less C—H oscillation in the Tb-complex. The observed transient decay curve of Tb-complex is well-fitted with mono-exponential decay at 298 K and has a relatively long value of 1.012 ms while monitoring at 544 nm (Fig. 2b).

3.2. SO_4^{2-} and CH_3Hg^+ sensing

Luminescent lanthanide complexes have been applied to detect many species, such as CO2-3, OH^-, HSO-4, H^+, amino acids, acetone, highly explosives, halide ions, proteins, Ag^+, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+},