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Fluorescent BINOL-based sensor for thorium recognition and a density functional theory investigation

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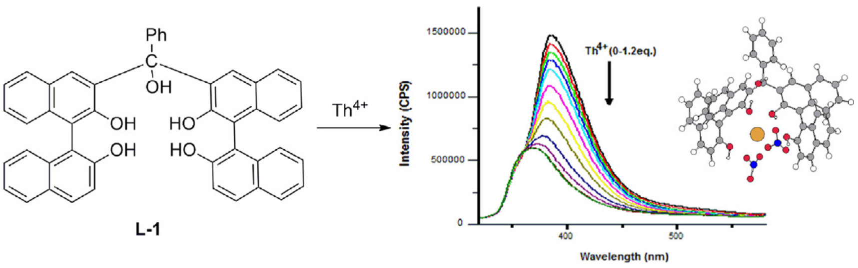
HIGHLIGHTS

- The first case of one-to-one stoichiometric responding fluorescent sensor for thorium.
- An easy preparation and novel BINOL-based chemical sensor.
- This sensor for thorium ion recognition by fluorescence spectrophotometry with high selectivity and sensitivity.
- This sensor shows good accuracy for analysis of thorium ions in river water.
- DFT calculations indicate that a strong binding interaction exists between the **L-1** and Th^{4+}.

GRAPHICAL ABSTRACT

A novel BINOL fluorescence sensor **L-1** for the recognition of thorium ion with high selectivity and sensitivity.



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ABSTRACT

A novel 1,1′-bi-2-naphthol (BINOL) derivative fluorescence sensor **L-1** for the recognition of thorium ion with a fluorescence quench response. This ligand showed high selectivity and sensitivity for thorium ion recognition. Coordination effects were investigated by DFT calculations, and the coordination modes and sites were confirmed. Moreover, the coordination abilities of the **L-1** ligand with Th^{4+} and UO_2^{2+} were evaluated.

1. Introduction

Thorium is a naturally occurring radioactive element widely distributed over the earth's crust. The scientific importance and commercial value of thorium is illustrated by its presence in a vast array of industrial and medical applications, as well as its use as a fertile material for producing nuclear fuel [1]. However, thorium mining processes generate a substantial amount of waste products that, without proper disposal, are detrimental to the environment. Studies have shown that continuous exposure to thorium may increase the risk of developing cancer of the lung, pancreas, or bone, and causes changes in genetic material [2–4]. Because of the

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widespread use of thorium and its toxic properties, the development and improvement in analysis methods for the determination of thorium would be useful.

Many techniques have been used for the determination of thorium, including nuclear techniques [5–7], inductively coupled plasma/mass spectrometry [8–10], electrochemistry [11,12], ion chromatography [13], and X-ray fluorescence [14,15]. Although these methods have good sensitivity, they involve the use of expensive equipment with high operating costs, complex sample preparation, and strict control of experimental conditions.

Among the wide variety of analytical methods, spectrophotometry offers multiple advantages such as simplicity, rapidity, low cost, high selectivity, and sensitivity for trace analysis [16]. Although spectrophotometric methods have been developed for many metal ion determinations [17], only a few reports have been concerned with thorium ion analysis, mostly employing UV–vis detection [16]. Moreover, the chemical probes for Th^{4+} suffer from (1) interference from $UO_2{}^{2+}$ and (2) poor sensitivity, requiring large quantities of metals for signal acquisition.

Fluorescence spectrophotometers operate with better sensitivity and anti-interference abilities than UV–vis spectrophotometers [18]. However, reports on the determination of thorium by fluorescence spectrophotometry are very rare. Optically active 1,1′-bi-2-naphthol (BINOL) and its derivatives have attracted particular attention for their fluorescence and molecular recognition properties [19–22]. Previous research has also indicated that polyhydroxy compounds complex with thorium very efficiently [16]. Herein, we present a strategy for designing a novel BINOL-based chemical sensor for thorium ion recognition by fluorescence spectrophotometry.

2. Experimental and theoretical

2.1. Measurements

The ^1H NMR, ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer (400 MHz or 100 MHz, respectively). ESI-MS spectral data were recorded on a Finnigan LCQDECA mass spectrometer. Absorption spectra were recorded on Hitachi U1900 spectrophotometer. Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon).

2.2. Reagents and solutions

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies. $Th(NO_3)_4$, $UO_2(NO_3)_2$, Ho_2O_3, PrO_2, Er_2O_3, Sm_2O_3, CeO_2, TbO_2, Yb_2O_3, Gd_2O_3, La_2O_3, Tm_2O_3, Y_2O_3, Lu_2O_3, Nd_2O_3, $FeCl_3$, $CrCl_3$, $CoCl_2$, $ZnCl_2$, $NiCl_2$, $PbCl_2$, $CuCl_2$, $AgNO_3$, $CdCl_2$, $AlCl_3$, $MnCl_2$, LiCl, KCl, $MgCl_2$, and $CaCl_2$ were used after drying.

2.3. Preparation of *L-1*

Under nitrogen, (***R***)-**2** (5.0 mmol, 1.87 g) was dissolved in ether (100 mL) in a flask equipped with a side arm and a magnetic stirring bar. The solution was cooled to 0 °C, and n-BuLi (25.0 mmol, 2.5 M in hexane, 10 mL) was added dropwise. The reaction mixture was stirred for 3 h at 0 °C, and then benzoyl chloride (2.5 mmol, 0.35 g) was added slowly. The reaction was allowed to warm to room temperature overnight to afford a cream-like mixture, and quenched with saturated aqueous NH_4Cl solution. The organic layer was separated and the aqueous solution was extracted with ethyl acetate. The organic phase was dried with $MgSO_4$ and evaporated to dryness. The crude product directly used in the next step reaction. This crude solid (2.0 g) was dissolved in DCM:EtOH = 1:1 (50 mL) to which 3 N HCl (10 mL) was added. After the mixture was heated at reflux (80 °C) for 6 h, 10% $NaHCO_3$ (30 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate, and the organic phase was washed with water and dried with Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography (hexane/EA = 3:1) to obtain **L-1** as a white solid.

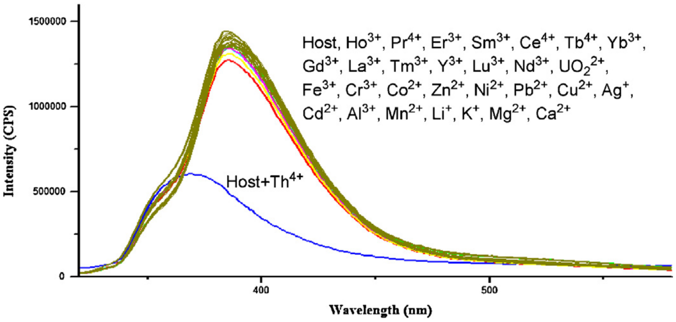

Fig. 1. Fluorescence responses of **L-1** (20 μM, $\lambda_{ex} = 300$ nm) upon the addition of metal ions (1 equiv.) in 1:1 $MeOH:H_2O$ (v/v).

2.4. Preparation of *L-2*

Under air, **L-1** (2.0 mmol, 1.35 g) and K_2CO_3 (10 equiv.) was dissolved in acetone (50 mL) in a flask equipped with a magnetic stirring bar. CH_3I (5 equiv.) was added dropwise. The reaction vessel was placed in a 60 °C oil bath, and then stirred at this temperature for 10 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 20 mL of ethyl acetate, and washed with brine (15 mL) and water (15 mL). The organic layer was dried over anhydrous Na_2SO_4. After concentrated in vacuo, the crude product was purified by column chromatography (DCM:hexane = 3:1) to obtain **L-2** as a white solid.

2.5. Computational details

All calculations were performed at the density functional theory (DFT) level, by means of the hybrid Becke-3-Lee–Yang–Parr (B3LYP) functional method [23,24], as implemented in Gaussian 03 program [25]. Th and U atoms were described using an effective core potential (SDD) [26] for the inner electrons, and its associated double-ζ basis set for the outer ones. The 6-31G(d, p) basis set [27,28] was used for the C, H, O, N atoms. To obtain a further insight into the electronic properties of the complexes, natural bond orbital (NBO) [29,30] analysis at the B3LYP/[6-31G(d, p), SDD] level was also performed.

3. Results and discussion

3.1. Sensitivity of *L-1*

We first investigated the fluorescence responses of **L-1** (20 μM) toward Th^{4+} and other metal cations in 1:1 H_2O:MeOH. Fluorescence spectra were obtained by excitation of the fluorophore at 300 nm and observation of the strong emission peak of **L-1** at 385 nm. Fig. 1 displays the spectra for the interactions of **L-1** with equimolar amounts of various metal cations. The addition of Ho^{3+}, Pr^{4+}, Er^{3+}, Sm^{3+}, Ce^{4+}, Tb^{4+}, Yb^{3+}, Gd^{3+}, La^{3+}, Tm^{3+}, Y^{3+}, Lu^{3+}, Nd^{3+}, $UO_2{}^{2+}$, Fe^{3+}, Cr^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Ag^+, Cd^{2+}, Al^{3+}, Mn^{2+}, Li^+, K^+, Mg^{2+}, and Ca^{2+} had no obvious effect on the fluorescence emission. When an equivalent of Th^{4+} was added to the solution of **L-1**, dramatic fluorescence quenching (quenching efficiency $(I_0 - I)/I_0 = 64\%$, $\lambda = 385$ nm) was observed, suggesting that compound **L-1** showed a specific response with Th^{4+} ions due to the chelation-enhanced fluorescence quenching (CHEQ) effect [31].