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New highly sensitive and selective fluorescent terbium complex for the detection of aluminium ions

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ABSTRACT

A highly sensitive and selective spectrofluorimetric method has been developed for the rapid determination of aluminium ions. The method is based on the fluorescence enhancement of Tb complex with 3,4-dimetyl-thieno[2,3 b] thiophene-2,5-dicarboxylic acid (LN) after addition trace amount of aluminium ions. The fluorescence of the probe is monitored at the characteristic an emission wavelength of Tb^{3+} at 545 nm with excitation at 300 nm. Optimum detection was obtained in DMSO-H_2O (2:8, v/v) and at pH 6.0 using MOPSO buffer. Under the optimum conditions linear calibration curves were obtained from 0.5 μ mol L^{-1} to 20 μ mol L^{-1} with detection limit of 0.1 μ mol L^{-1}. Effect of interference of other ions was studied.

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1. Introduction

Aluminium is the most abundant metal in the earth's crust. It is extensively used in every sphere of life from utensils to medicine. The increased usage of aluminium containing products may cause their accumulation in the ecosystem leading to detrimental effects. If a significant aluminium load exceeds the body's excretory capacity, the excess is deposited in various tissues, including bone, brain, liver, heart, spleen, and muscle. This accumulation causes morbidity and mortality through various mechanisms [1]. Aluminium in excessive amounts not only hampers plant growth but damages the human nervous system. It has been reported to induce Alzheimer's disease, Parkinson's disease and amyotrophic lateral sclerosis and so on [2,3].

Due to the extensive uses and wide occurrence of aluminium in nature, many methods have been developed for its determination. The most commonly used methods to determine the amount of aluminium are atomic absorption spectroscopy, voltammetry, inductively coupled plasma emission spectrometry or potentiometric and spec-trophotometric sensors [4–8]. Many of these techniques have limitations due to their poor selectivity and sensitivity. Spectrofluorimetry, on the other hand, is more applied because of its high selectivity, excellent sensitivity, ease of automation, cost-effectiveness, rapid response time, and a large linear range of analysis [9].

Herein, we report novel Tb complex with 3,4-dimetyl-thieno [2,3 b] thiophene-2,5-dicarboxylic acid (LN) as a fluorescence chemosensor for the selective and sensitive detection of aluminium in DMSO-H_2O mixture (2:8, v/v), at pH 6 using MOPSO buffer solution. The Tb complex shows weak fluorescence. The presence of trace amount of aluminum ions leads to a significant fluorescence enhancement by 6-fold at 545 nm. In the present work a chemical sensor was applied for fluorimetric determination of the Al(III) in DMSO-H_2O (2:8, v/v) and at pH 6.0 using MOPSO buffer. This work represents a continuation of our work in the field of development of novel luminescent sensors for environmental and biomedical applications [10–14].

2. Experimental

2.1. Measurements and materials

All chemicals were purchased from highly pure analytical grade reagents and used without further purification. Emission and spectral measurements for the interactions of Tb probe with aluminium ion have been investigated using A JASCO-FP6300 spectrofluorometer with 1 cm quartz cell. UV-absorption spectra

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were recorded with A Shimadzu-UV Probe Version 2.33 UV–visible automatic recording spectrophotometer with 1 cm quartz cell. The pH was measured using a Fisher model 825 MP pH meter calibrated daily with fresh buffer solutions at pH 4, 7 and 10. The ^1H NMR spectra were recorded using a 250 MHz Brucker spectrometer. δ values are given relatives to internal $CDCl_3$.

2.2. Synthesis of 3,4-dimetyl-thieno[2,3 b] thiophene-2,5-dicarboxilic acid

This compound was made according to literature procedure [15]. To 150 ml of ethanol was added 6.2 g (19.9 mmol) of diethyl 3,4-dimethylthieno[2,3-*b*]thiophene-2,5-dicarboxylate and 4.8 g of KOH in 60 mL water. The mixture was refluxed for 6 h and then cooled to room temperature. The ethanol was removed under reduced pressure and the product dissolved in the remaining water. The solution was filtered and then acidified (pH 1) resulting in precipitation of the product. The precipitate was filtered of and washed with water. The solid was dried at 50 °C in vacuum, resulting in 4.94 g (19.2 mmol, 96%) of white product.

^1H NMR (300 MHz, DMSO) $\delta = 13.27$ (s, 2H), 2.77 (s, 6H). ^{13}C NMR (75 MHz, DMSO) $\delta = 163.68$, 147.24, 143.70, 139.92, 130.69, 13.87.

2.3. Fluorescence experiments

Stock solutions of $TbCl_3$ and $Al(NO_3)_3$ were prepared (1 mmol L^{-1}) in bi-distilled water, while stock solution of LN was prepared (1 mmol L^{-1}) in DMSO. Test solutions were prepared by placing 0.1 mL of Tb^{3+} and 0.2 mL of LN stock solutions into cuvettes, adding an appropriate aliquot of Al^{3+} ion stock solution, then complete to 10 mL using buffer solution to make the pH work in the range ($pH = 4$ to $pH = 9$) using acetate, TAPS, MOPSO buffer solutions. The fluorescence emission and excitation spectra were recorded after equilibration at room temperature for 5 min. UV–visible spectra of all solutions were recorded in the range of 200–400 nm. Luminescence intensity was measured in a 1 cm quartz cell at an excitation wavelength of 300 nm and an emission wavelength of 545 nm. Repeatability of the proposed method has been carefully investigated and the method proved to be reproducible.

2.4. Determination of complex stoichiometry of LN with terbium (III) ion

In order to determine the best stoichiometry of Tb(III)-LN complex, the Job's method of Continuous Variation has been done. Upon using 10 μ mol L^{-1} of $TbCl_3 \cdot 6H_2O$ and changing the concentration of LN from 1 μ mol L^{-1} to 50 μ mol L^{-1}. By measuring the change in the fluorescence intensity for each reaction mixture at $\lambda_{em} = 545$ nm, and graphing Jop's plot, the maximum change will occur when the mole fraction of the reactants is closest to the actual stoichiometric mole ratio.

2.5. Determination of quantum yield

The quantum yield of Tb(III)-$(LN)_2$ was determined in DMSO-H_2O (2:8, v/v) at concentration of 10 μM using 3-(2-benzothiazolyl)-7-diethylamino-coumarin (Coumarin 6) in ethanol as a reference by the equation [16]:

$$Q_X = Q_R \frac{A_R I_X n_X^2}{A_R I_X n_R^2} \tag{1}$$

Where Q_R is the quantum yield of reference (0.78), A_R and A_X are absorbances of the reference (R) and Tb(III)-$(LN)_2$ (X) at the excitation wavelength, I_R and I_X are the integrated areas under the corrected emission spectra of the reference and Tb(III)-$(LN)_2$, n_R and n_X are the refractive indices of the solutions of the reference and Tb Tb(III)-$(LN)_2$, respectively.

2.6. Determination of the detection limit of Tb probe for aluminum(III)

The detection limit was determined from the fluorescence titration data according to a widely used method [17] in DMSO-H_2O (2:8, v/v) and at pH 6 using MOPSO buffer solution. According to the results of the titration experiment, the fluorescence intensity data at $\lambda_{em} = 545$ nm was recorded with linear range from 0.5 μ mol L^{-1} to 20 μ mol L^{-1}, and the detection limit was 0.1 μ mol L^{-1}.

2.7. The determination of binding constant at different temperatures

The binding constant (K) was determined at different temperatures by the use of Benesi-Hildebrand equation. Where F^o, F are the fluorescence intensities of Tb probe in the absence and presence of Al^{3+} ion, respectively and K the binding constant as the ratio of the intercept to the slope [18].

$$\frac{F^o}{F - F^o} = \alpha + \frac{\alpha}{K\left[Al^{3+}\right]}, \alpha = \frac{1}{F_l - F^o} \tag{2}$$

3. Results and discussion

3.1. Interaction of 3,4-dimetyl-thieno[2,3 b] thiophene-2,5-dicarboxylic acid with Tb(III) ion

3.1.1. Steady-state UV–vis spectroscopy

The absorption spectra of the interaction of LN in ethanol with Tb(III) ion was investigated as shown in Fig. 1. The absorption spectrum of LN in ethanol shows the maximum absorption band at 266 nm and shoulder around 290 nm due to the n- π^* and π–π^* transition [19], respectively with high extinction coefficient ($\varepsilon_{266\ nm} = 3.06 \times 10^4$ L mol^{-1} cm^{-1}). The addition of Tb(III) to the solution containing LN enhances the absorbance with slightly red shift to 269 nm (Fig. 1A), revealing the binding between ligand and Tb(III) ions with high extinction coefficient ($\varepsilon_{269\ nm} = 3.51 \times 10^4$ L mol^{-1} cm^{-1}) and the brightness (ε.Qy) of the probe is 7.01×10^3 L mol^{-1} cm^{-1}. The π-π^* band shifted to lower wavelength as the polarity of solvent increase, following the order: acetonitrile > ethanol > methanol > water at 269 nm, 268.6 nm, 268 nm and 267 nm, respectively. While The molar absorptivity coefficient (ε) for Tb(III)-LN complex in different solvents evaluated show the trend that the molar absorptivity coefficient increased as the polarity of the solvent was lowered as shown in Fig. 1B (water < methanol < ethanol < acetonitrile). The decrease of molar absorptivity (ε) with increasing polarity shows that as the energy gap between two states (ground and excited state) increasing, possibility of transition becomes less, hence decreases molar absorptivity coefficient (ε) [20]. The behavior of Tb(III) complex in ethanol at room temperature was monitored by UV–vis spectroscopy for 24 h. Liberation of the ligand was not observed under these conditions. These suggest that the complexes are stable under the conditions studied.

3.1.2. Steady-state fluorescence spectroscopy in different solvent

The influence of the different solvents on the fluorescence intensities of the Tb(III) complex has been investigated as shown in

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