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A new bifunctional Schiff base as a colorimetric and fluorescence sensor for Al^{3+} and CN^-

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ABSTRACT

A bifunctional Schiff base fluorescent sensor **2** (receptor **2**) was prepared and its metal ions and anions sensing properties were investigated. Receptor **2** exhibited an excellent selective fluorescence response toward Al^{3+} and colorimetric response (from yellow to colorless) toward CN^-, respectively among a series of ions. Moreover, the detection limits of receptor **2** for Al^{3+} and CN^- were determined to be 14 nM and 73 nM, respectively. The two detection limit values were sufficiently low to detect nano-molar concentration of Al^{3+} and CN^-.

1. Introduction

Development of new receptors for the detection of different analytes simultaneously is emerging as an area of great interest [1,2], since such system would lead to faster analytical processing and potential cost reductions. However most of the reported sensors are effective only in selective recognition of a particular analyte. Since the recognition units of the sensors are distinctive in sensing cations or anions behavior, thus, developing such sensors with multiple analyst recognition capability is a challenging task.

Among metals, aluminum is the third most prevalent metallic element in the Earth. Its toxicity not only hampers plant growth but also damages the human nervous system to induce Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc [3–9]. Detection of Al^{3+} is crucial in controlling its concentration level in the biosphere [10] and its direct impact on human health. However, compared to other transition metal ions, the detection of Al^{3+} has always been problematic due to the lack of spectroscopic characteristics and poor coordination ability [11]. In addition, most of the reported Al^{3+} sensors suffer from interference caused by Fe^{3+} and Cu^{2+} [12–14], poor water solubility [15] and tedious synthetic methods of preparation [16].

On the other hand, among anions, CN^- is one of the most toxic anions and harmful to environment or human health. However, CN^- is still widely used in gold mining, plastics production and other industrial activities [17]. Widespread use of CN^- leads to the deterioration in the environment. Thus, great efforts have been devoted to the development of sensors for the recognition of CN^- [18–26]. Furthermore, many of the reported CN^- sensors suffer from disturbance by anions such as F^- and AcO^-. Therefore, reliable and efficient ways of detecting the presence of CN^- are desirable.

Development of a bifunctional sensor, which could recognize a metal ion and an anion simultaneously, is a significant and challenging task. Up to know, only few reported sensors could select detection of Al^{3+} and CN^- simultaneously [27].

Herein, we have synthesized two dansyl based compounds incorporating imine (receptor **2**) and amine (receptor **3**) units as the recognition site (Scheme 1) and further elucidated their ion recognizing ability. Receptor **2** exhibits high sensitivity and selectivity toward Al^{3+} and CN^- simultaneously among a series of ions.

Receptor **2** could be readily prepared by reaction of 2-aminophenol with 2-hydroxynaphthalene-1-carbaldehyde, followed by coupling with 5-(dimethylamino)naphthalene-1-sulfonyl chloride. Further, reduction of receptor **2** could afford receptor **3**, as shown in Scheme 1. The structure of receptor **2** and receptor **3** were confirmed by NMR spectra (Figs. S1–S5), Mass data and X-ray crystallography. The crystal of receptor **2** was obtained by slow evaporation in methanol and its structure is shown in Fig. 1.

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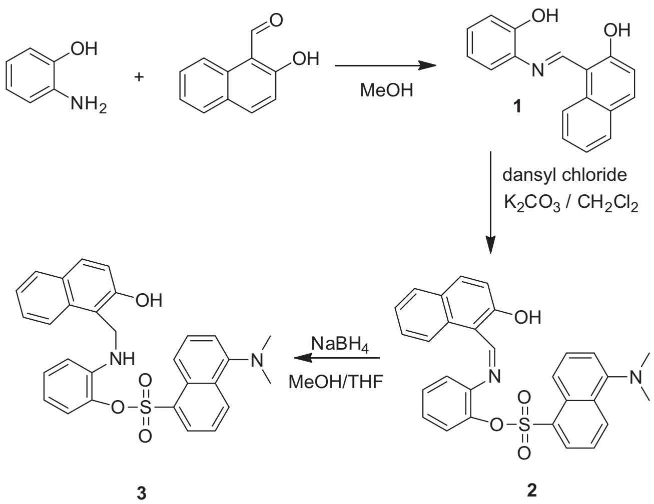

Scheme 1. Synthesis of receptor **2** and **3**.

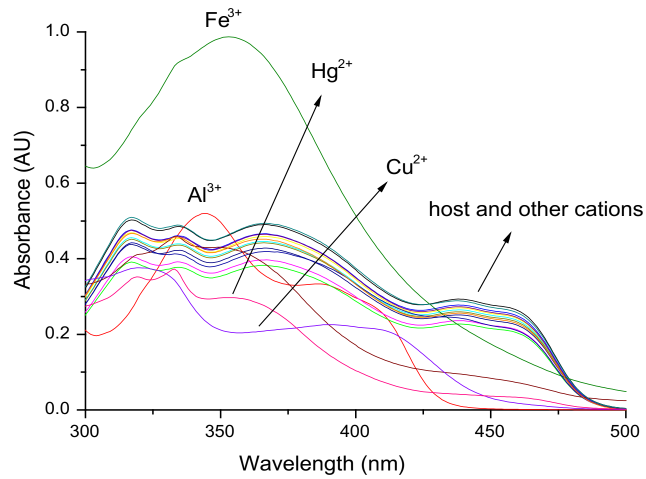

Fig. 2. UV/vis spectra of **2** (40 μM) recorded in MeOH after addition of 10.0 equiv of various metal ions.

2. Results and discussion

*2.1. Fluorescence and absorption studies of receptor **2** toward various metal ions*

The UV–vis and fluorescence spectra of receptor **2** were investigated in MeOH by the presence of various metal ions (as perchlorate salts): Li^{+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+}, Hg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Al^{3+}. Fig. 2 showed no significant variations in the absorption spectrum of receptor **2** from 300 nm to 500 nm among most of the added cations except for Fe^{3+}, Al^{3+}, Hg^{2+} and Cu^{2+}. Upon addition of Al^{3+}, the solution of receptor **2** showed a dramatic color change from yellow to colorless which could easily be detected by the naked eye (Fig. 3).

From the fluorescence spectra of receptor **2** (Fig. 4), receptor **2** alone and other cations all displayed very weak single fluorescence

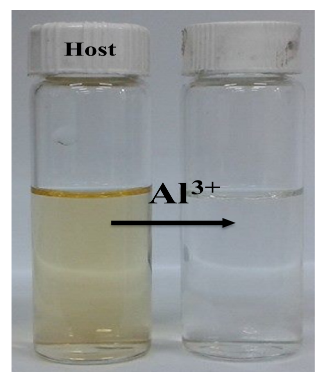

Fig. 3. The color changes observed by naked eye of receptor **2** (40 μM) upon addition of 10.0 equiv of Al^{3+} in MeOH.

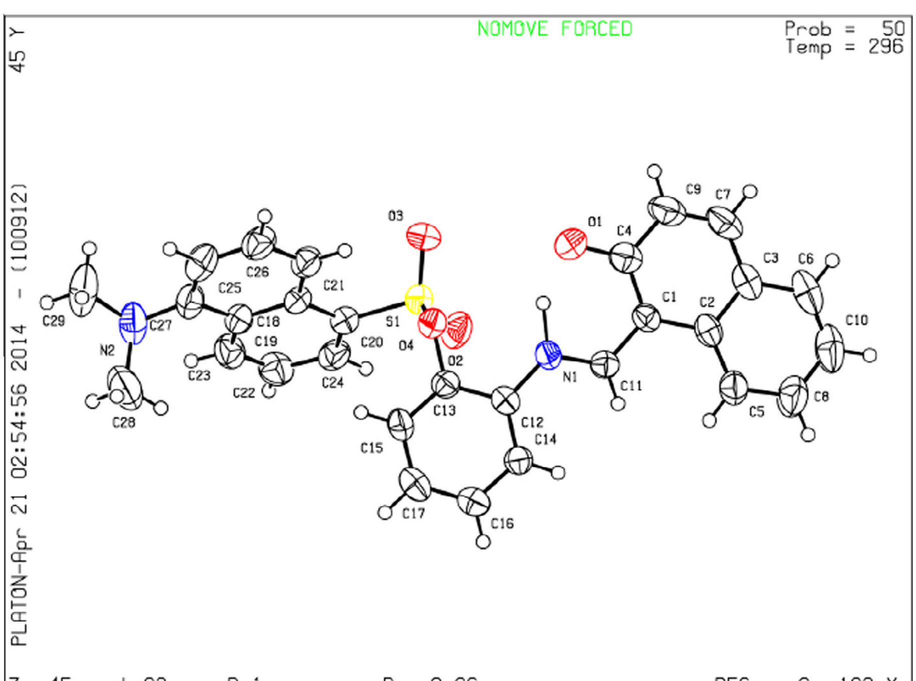

Fig. 1. Crystal structure of **2**.