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A fluorescent chemosensor for sequential recognition of gallium and hydrogen sulfate ions based on a new phenylthiazole derivative

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ABSTRACT

A new highly selective turn-on fluorescent chemosensor based on 2′-hydroxyphenylthiazole for the detection of gallium and hydrogen sulfate ions in acetonitrile was synthesized and characterized. The mechanism of fluorescence was based on the inhibition of excited state intramolecular proton transfer (ESIPT). The sensor demonstrated high selectivity for gallium as compared to aluminum and other cations and allowed sequential detection of hydrogen sulfate.

1. Introduction

Gallium does not occur in free form in nature but gallium(III) salts exist in trace amounts in diaspore, sphalerite, germanite, bauxite, coal, and zinc ores [1]. Gallium is a rare element, which is found in very small amounts in soil, but has been shown to regulate the growth of plants, which is especially important for Chinese traditional and herbal medicine. In most compounds, gallium has an oxidation state of +3. Gallium(III) arsenide and gallium(III) nitride are mainly used as semiconductor materials in the electronics industry to produce optoelectronic devices such as laser diodes and light emitting diodes (LEDs) [2]. Gallium(III) can also be used as a dopant in semiconductors for the production of transistors [3]. The remarkable ability of liquid gallium to wet surfaces, including human teeth, has stimulated interest in gallium alloys as possible filling materials in dentistry [4]. In clinical practice, radioactive gallium and stable gallium nitrate are used as diagnostic and therapeutic agents in cancer and disorders of calcium and bone metabolism. In addition, more recent studies have revealed that gallium compounds may be utilized as antimicrobial agents against certain pathogens [5]. Consequently, the levels of this potentially hazardous element in the environment are gradually increasing. Therefore, there is a need for profound and reliable methods for determination of the trace concentrations of gallium(III) in various media, especially in water because of its vital importance.

Although gallium has no known physiological function in the human body, gallium(III) is known to be highly toxic and carcinogenic for animals and humans. A single dose of 100 mg kg^{-1} of GaAs results in acute pulmonary inflammation and pneumocyte hyperplasia after 14 days of ingestion [6]. Chronic exposure to GaAs with concentration lower than 1 mg L^{-1} (2-year observation period) produced systemic toxicity and definite pulmonary lesions. In addition, testicular toxicity was observed and tumor occurrence increased significantly in mice when GaAs was injected intraperitoneally. Therefore, the detection of gallium is crucial for health and economic purposes.

Among the entire range of oxo anions, the detection of HSO_4^- is important as it is found in many agricultural fertilizers, industrial raw materials, nuclear fuel waste and can have deleterious effects as a pollutant when it gets into the environment [7]. At high pH values, amphiphilic HSO_4^- dissociates to produce toxic SO_4^2, causing irritation of skin, eyes, and respiratory paralysis [8]. The detection of the HSO_4^- ion is of current interest due to its Janus-faced properties in various fields [9].

Several analytical techniques such as spectrophotometry, membrane, co-precipitation, extraction and chromatography, ICP-AES, ICP-MS, X-ray diffraction, fluorescence spectrometry, calorimetry, AAS, fluorimetry, polarography, and ion-selective electrodes (ISEs),

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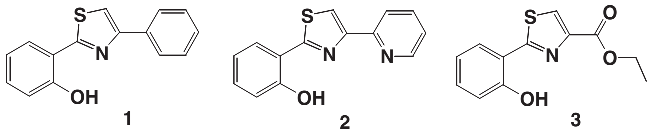

Fig. 1. Structures of chemosensors **1**, **2**, and **3**.

have been reported for the determination of gallium [10–12]. Compared to other methods, fluorimetry has the advantages of higher sensitivity, better selectivity, smaller sample amounts, and simpler and faster determination, so it has received more attention. Many reagents for gallium detection have been used in fluorimetry, e.g., 8-hydroxyquinoline [13], butylrhodamine B [14] and lumogallion [15], but the interference of elements from the same group, such as Al^{3+} and In^{3+}, could not be avoided. Several fluorescent chemosensors for Ga^{3+} detection have been reported but only a few of them had good selectivity for Ga^{3+} over Al^{3+} [16].

Despite its crucial roles in biological processes, only a few sensors for HSO_4^- have been reported to date [17]. Given the fact that the hydrogen sulfate anion has a large standard Gibbs energy of hydration (−1080 kJ mol^{-1}), the recognition and separation of HSO_4^- from an aqueous media is a challenging task [18]. However, only a few examples of HSO_4^- anion recognition have been reported in recent years. In nature, the HSO_4^- anion is recognized and transported by the HSO_4^--binding protein, which binds HSO_4^- through hydrogen bonds [19]. Accordingly, hydrogen-bonded complexes were widely used in the design of anion sensors because a stable object hydrogen-bonded complexes could be formed to use the amides [20], thioureas [21], ureas [22], and imidazole [23] which regarded as the hydrogen donor to form R—H···X— anion hydrogen bonds and the tautomeric azophenol containing receptors.

In our previous work [24], we reported the synthesis of thiazole derivatives with different substituents at position 4 and their application as anions, Zn^{2+}, Cu^{2+}, and Al^{3+} sensors. We have also developed a thiazole-based chemosensor where the copper complex was used as a highly selective and sensitive "*On-Off*" type cyanide chemosensor that works via displacement of Cu^{2+} by CN^- [25].

Schiff base fluorescent sensors are versatile organic blockers possessing comparable accessibilities and structure variations. Thus, taking into account the properties of a Schiff base and the electron donating property of nitrogen in the thiazole ring, we prepared compounds **2** and **3** as a Zn^{2+} and an Al^{3+} sensor, respectively (Fig. 1). We have previously used **1** as a fluoride ion [24] sensor where due to the inhibition of the ESIPT only on fluoride ion binding a red shift is produced in absorbance and an enhancement of fluorescence (Figs. S1 and S2). But due to the presence of a nitrogen and oxygen-rich coordination environment, which provides a hard-base environment for the hard-acid Ga^{3+}, we found that it could also be used as a gallium chemosensor. Anion recognition with metal complexes has an advantage as they furnish electrostatic interactions, and not hydrogen bonding, that can authenticate anion binding even in semi-aqueous medium. Most of the hydrogen sulfate anion sensors are based on hydrogen bonding [20–23] and only few are reported with Cr^{3+} and Al^{3+} complexes [26]. Moreover due to the affinity of gallium for the hydrogen sulfate anion, the complex of **1-Ga^{3+}** has a high sensitivity and good selectivity to the latter.

2. Results and discussion

Sensor **1** was prepared following the procedures described in the literature [24], and its structure was confirmed by spectroscopic methods. Initial studies of the UV–vis absorption and fluorescent emission of **1** were carried out in CH_3CN. The binding of **1** toward Ga^{3+} in the form of perchlorate salt was examined by UV–vis spectroscopy. In the absence of gallium, **1** displays an absorption band with the maximum at 332 nm ($\log \varepsilon = 4.07$), whereas the addition of Ga^{3+} to **1** results in a red shift of the absorption band maximum to 350 nm ($\log \varepsilon = 4.20$) (Fig S3). This can be attributed to the π–π* transition, which is favored by the planar orientation of the complex enforced by the intramolecular hydrogen bonding [27].

Sensor **1** showed weak fluorescence with a low quantum yield ($\Phi = 0.0059$) at 375 and 504 nm which corresponds, respectively, to the enol and keto peaks resulting from excited state intramolecular proton transfer (ESIPT). In the presence of Ga^{3+}, sensor **1** demonstrates an emission band at 430 nm with a higher quantum yield ($\Phi = 0.0653$), due to the inhibition of ESIPT by the metal binding (Fig. 2a).

The UV–vis titration of **1** was carried out in CH_3CN. The absorption bands of **1** linearly increased and decreased up to 1 equiv of Ga^{3+} (Fig. 2b), indicating the formation of a 1:1 complex with high binding affinity.

This finding is characteristic for the 2′-hydroxyphenylthiazole derivatives when the complexation process is accompanied by the deprotonation of the hydroxyl group [24,25]. Moreover, there are four clearly defined isobestic points in the titration spectra of **1,** which also implies the conversion of the free sensor **1** to the only Ga^{3+} complex [28]. The binding constant of the complex between the sensor **1** and Ga^{3+} was determined by non-linear fitting of the corresponding UV–vis titration data and yielded a value

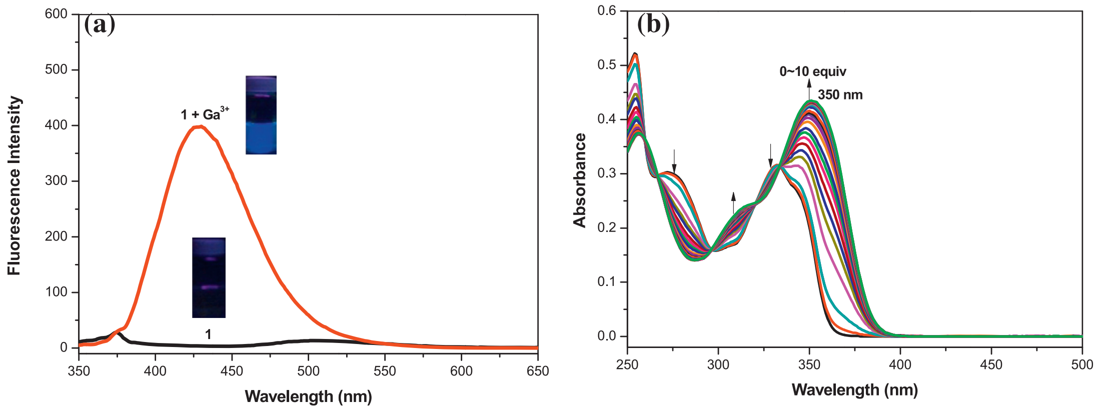

Fig. 2. (a) Fluorescence spectra of **1** (2 μM) with 10 equiv of $Ga(ClO_4)_3$ in CH_3CN ($\lambda_{ex} = 333$ nm). (b) UV–vis spectra of **1** (30 μM) titrated by $Ga(ClO_4)_3$ from 0 to 10 equiv in CH_3CN.