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Novel optical selective chromone Schiff base chemosensor for Al^{3+} ion

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ABSTRACT

A novel Schiff-base fluorescent sensor 7-methoxychromone-3-carbaldehyde-((2′-Benzothiazolylthio)-acetyl) hydrazone (**MCAH**) was synthesized. The new chemosensor possesses dual **PET** processes simultaneously introducing by both nitrogen and sulfur donors. Upon binding Al^{3+}, a significant fluorescence enhancement with a turn-on ratio over 500-fold was triggered. The detection limit of **MCAH** for Al^{3+} was 3.19×10^{-8} M.

1. Introduction

Aluminum is an indispensible element due to its abundance and use in every sphere of life from utensils to medicine. Natural abundance of aluminum in the biosphere is around 8% of the total mineral components. A trivalent cation of aluminum is found in most animal and plant tissues as well as in natural waters everywhere. As a non-essential element for biological life, aluminum toxicity is a great concern for human health causing bone and joint diseases, neuronal disorder, dementia, myopathy [1–4]. In recent years, fluorescent chemosensors have attracted significant interest because of their potential application in medicinal and environmental research [5–8]. Amongst several methods for the detection of Al^{3+} in the literature, spectrofluorimetry is widely used for its high sensitivity, selectivity, rapidity and easy operational procedure [9–14]. The poor coordination ability of Al^{3+} compared to the transition metal ions makes the development of an Al^{3+} fluorosensor difficult [15–18]. For this purpose several fluorescent probes such as Schiff bases, triazoles, triazole-pyridyl, calixarene, and secondary/tertiary amines have been developed for detecting Al^{3+}. All the fluorescent receptors reported for Al^{3+} till now have a few serious lacunae like interferences by Fe^{3+} and Cu^{2+} most commonly. At the same time their synthetic protocols are a bit tedious one [19–24]. Here, we reported a new **PET** type Schiff base probe named as 7-methoxychromone-3-carbaldehyde-((2-Benzothiazolylthio) acetyl) hydrazone (**MCAH**). The probe has been chosen because of its easy availability by classical organic syntheses and low detection limit [25–28]. Relatively low interference was observed for the detection of Al^{3+} in the presence of Fe^{3+} and Cu^{2+} and it features visible light excitation (410 nm) and emission (480 nm) profiles. It consists of two parts: one is a signaling moiety which is a chromone entity and the other is the binding site having imine groups and an S atom. In the absence of metal ions, the fluorescence intensity of the fluorophore is greatly reduced due to photoinduced electron transfer (**PET**). But in the presence of metal ions, **PET** is restricted and the fluorescence intensity is greatly enhanced due to rigid chelated complex formation.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were measured on the Bruker 300 MHz instruments using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV–vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. Elemental analyses were carried out on an Elemental Vario EL analyzer.

2.2. Synthesis

7-methoxychromone-3-carbaldehyde was obtained according to the literature procedures [29]. Synthesis of **MCAH** was based on the following method (Scheme 1): a methanol solution (10 mL) of (2-Benzothiazolylthio)acetic acid hydrazide (0.253 g, 1 mmol) was

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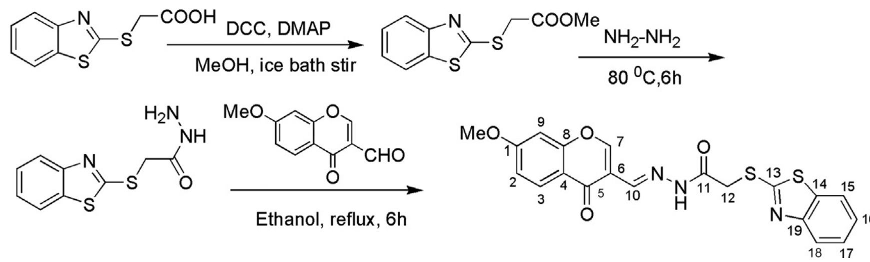

Scheme 1. Synthesis of 7-methoxychromone-3-carbaldehyde-((2′-Benzothiazolylthio) acetyl) hydrazone (**MCAH**)..

added dropwise to a solution (20 mL) of 7-methoxychromone-3-carbaldehyde (0.204 g, 1 mmol) in ethanol. Then the solution was reflux for 6 h under stirring and some white precipitant appeared. The mixture was filtered and dried under vacuum. Recrystallization from DMF/methanol (V:V=1:1) gave 7-methoxychromone-3-carbaldehyde-((2-Benzothiazolylthio) acetyl) hydrazone (**MCAH**), which was dried under vacuum. Yield, 48.3%, m.p: 177–179 °C. Anal. Found (Calcd for $C_{20}H_{15}N_3O_4S_2$, 425.05): C, 56.39 (56.46); H, 3.42 (3.55); N, 9.76 (9.88). ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ 9.25 (s, 1H, 10-H), 8.58 (s, 1H, 15-H), 8.45 (m, 2H, 16-H, 17-H), 8.27 (d, 1H, 3-H), 7.87 (s, 1H, 18-H), 7.77 (s, 1H, 7-H), 7.63 (s, 1H, 9-H), 7.52 (d, 1H, 2-H), 5.10 (s, 1H, –NH), 4.34 (s, 2H, –CH$_2$), 3.73 (s, 3H, –CH$_3$O). ^{13}C NMR (DMSO-d$_6$, 300 MHz): δ 174.15 (5-C), 168.16 (11-C), 166.52 (1-C), 164.11 (8-C), 157.63 (7-C), 154.16 (13-C), 152.53 (10-C), 139.98 (9-C), 136.50 (14-C), 134.75 (3-C), 126.45 (16-C), 124.50 (17-C), 121.87 (15-C), 121.11 (18-C), 118.06 (4-C), 117.02 (6-C), 105.31 (2-C), 101.05 (9-C), 56.22 (–OCH$_3$), 35.13 (12-C). MS (ESI) m/z 426.2 $(M+H)^+$ (Figure S8).

2.3. Analysis

Stock solutions (5 mM) of the nitrate salts of Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^+, Cd^{2+}, In^{3+}, and Pb^{2+} in ethanol were prepared. Stock solutions of **MCAH** (5 mM) were prepared in ethanol. Test solutions were prepared by placing 20 μL of the probe stock solution into cuvettes, adding an appropriate aliquot of each ions stock, and diluting the solution to 2 mL with ethanol solutions. Both the excitation and emission slit widths were 3.0 nm.

3. Results and discussion

MCAH forms colorless and nonfluorescent solutions in either aqueous media or organic solvents, including **DMF** (dimethyl formamide), **THF** (tetrahydrofuran), **DMSO** (dimethylsulfoxide), ethanol, methanol, or **CH_3CN** (acetonitrile). Addition of aluminum ions to **MCAH** in ethanol leads to the development of a yellowgreen color and yellowgreen fluorescence (Figure S1). The fluorescence intensity at 480 nm in the presence of 1 equiv. mole ratio of Al^{3+} was 500 times stronger than that of the free ligand at same wavelength.

The photophysical properties of **MCAH** were investigated by monitoring the fluorescence behavior upon the addition of several metal ions in ethanol. At 410 nm excitation, **MCAH** alone did not show any significant fluorescence. The addition of Na^+, Mg^{2+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^+, Cd^{2+}, In^{3+}, and Pb^{2+}responds with very little enhancement in the fluorescent intensity. In contrast, the addition of Al^{3+} results in a great enhancement of the emission intensity positioned around 480 nm as shown in Fig. 1. The probe exhibited high selectivity for Al^{3+} over other metal ions.

The observed changes in UV–vis absorption spectra are shown in Figure S2. Upon addition of Al^{3+}, the absorbance bands at 385 nm and 410 nm enhanced and decreased at the 290 nm region

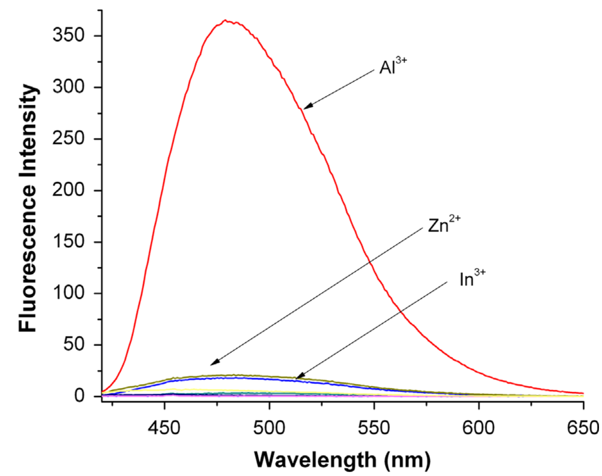

Fig. 1. Fluorescence responses of **MCAH** (50.0 μM) in ethanol with 500.0 μM of Na^+, Mg^{2+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^+, Cd^{2+}, In^{3+}, and Pb^{2+} and 50.0 μM of Al^{3+}. Excitation wavelength was at 410 nm.

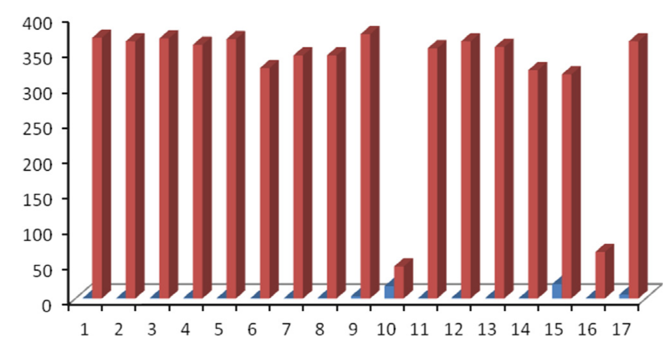

Fig. 2. Relative fluorescence of **MCAH** and its complexation with Al^{3+} in the presence of various metal ions. Blue bar: **MCAH** (50.0 μM) and **MCAH** with 10 equiv. of Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, and In^{3+} stated. Red bar: 50.0 μM of **MCAH** and 1 equiv. of Al^{3+} with 20 equiv. of metal ions stated (λ_{ex}=410 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the UV–vis spectra. A clear isosbestic point was observed at 325 nm when spectra were recorded with varying concentrations of Al^{3+}, this indicated the formation of the **MCAH**–Al^{3+} complex.

To explore the possibility of using **MCAH** as a practical ion selective fluorescent chemosensor for Al^{3+}, competition experiments were carried out. For this purpose, **MCAH** was treated with 1 equiv. of Al^{3+} in the presence of 10 equiv. of other metal ions. Relatively low interference was observed for the detection of Al^{3+} in the presence of other metal ions (Fig. 2). **MCAH** responding for Al^{3+} in the presence of In^{3+}, Fe^{3+} is relatively low but clearly detectable. Therefore, **MCAH** was shown to be a promising selective fluorescent sensor for Al^{3+} in the presence of most competing metal ions.