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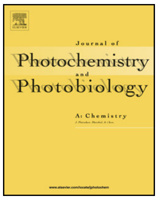

A turn-on fluorescent sensor for highly selective recognition of Mg^{2+} based on new Schiff's base derivative

Guan-qun Wang, Jin-can Qin, Long Fan, Chao-Rui Li, Zheng-yin Yang*

College of Chemistry and Chemical Engineering, State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, PR China

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ABSTRACT

A new senser Isatin-3-(7′-Methoxychromone-3′-methylidene) hydrazone based on chromone Schiff base was synthesized to detect Mg^{2+}. The complexation behavior of chemosensor with different metal ions in ethanolic solution was studied on UV–vis absorption spectra and fluorescent spectra. Results showed that the chemosensor **HL** displayed a 70-fold fluorescence enhancement upon the addition of Mg^{2+} due to the photo-induced electron transfer (**PET**) effect. On the other hand, metal ions except Mg^{2+} did not cause significant change in either the absorption or the fluorescence spectrum of **HL**. In addition, **HL** showed a good selectivity to Mg^{2+} over other metal cations, especially Ca^{2+}, which often responds together with Mg^{2+}. Therefore, **HL** can act as an efficient sensor for magnesium ion.

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1. Introduction

The magnesium ion (Mg^{2+}) is the fourth most abundant cation in the human body, the second plentiful intracellular cation and has been recognized as an essential biological ion for all living things over the past century [1–3]. It plays important physiological roles in numerous cellular processes, such as enzyme-driven biochemical reactions, activities of membrane proteins including ion channels, and the regulation of Ca^{2+} signaling [4–6]. Moreover, Mg^{2+} is also critical for bone remodelling and skeletal development [7,8]. Recently, some research confirmed that Mg(II) is a crucial modulator of cell function and magnesium deficiency leads to cell death [9,10]. Its estimated total concentrations in mammalian cells varies between 14 and 20 mM [11,12]. For an adult human, the daily intake of magnesium should reach 300 mg which could come from green vegetables, seafood, whole-grains and dairy products [13]. Deficiencies or excess intake of the ion can result in multifarious diseases [14,15]. A decrease in Mg^{2+} concentration has been implicated in the development of cardiac, hypokalaemia, hypocalcaemia and neurological manifestations. Migraines, diabetes, osteoporosis, and coronary heart disease have been associated with chronic low magnesium [16,17]. In contrast, high levels of Mg^{2+} are contributed to a number of age-related and neuronal diseases ranging from hypertension to Alzheimer's disease [18–20]. Thus, Mg^{2+} represents an interesting paradox in the human body. Although Mg^{2+} has been shown to regulate many phenomena in cells, developing Mg^{2+} probes is often overlooked. The underlying molecular mechanisms have not been illuminated in detail due to the scarcity of efficient chemical tools for the study of this ion [21]. In this regard, the development of reliable and sensitive analytical methods for Mg^{2+} has attracted increasing interest in the areas of chemical and biological sciences.

Many analytical methods like atomic absorption, ion-selective electrodes (ISEs), and NMR are available for the detection of Mg^{2+} [22–25]. Among the various types of detection methods, fluorescence analytical methods are very important and effective ways to detect metal ions due to their high sensitivity, good selectivity, high response speed and simple operation [26–28]. Till now, various families of fluorescent probes for Mg^{2+} have been developed. Crown ether derivatives, polymer based ligands and nanoparticles, have also been successfully employed for selective detection of Mg^{2+} ions [29–32]. However, these synthetic fluorescent sensors require intricate synthetic.

Methodologies, long preparation time and high cost of synthesis. In addition, most of the reported Mg^{2+} sensors are limited in distinguishing Mg^{2+} from Ca^{2+} owing to the similar chemical properties and are useful only where the Mg^{2+} ion concentrations are much higher than those of Ca^{2+} ion.

In the present work, we have developed a fluorescence chemosensor based on isatin-3-hydrazone and 7-Methoxychromone-3-carbaldehyde. The free receptor **HL** almost did not show fluorescence emission at 547 nm when it was excited at 491 nm. Upon the addition of Mg^{2+}, the probe displays a highly sensitive and selective response with remarkably enhanced fluorescence intensity in ethanol. This restricts the photoinduced electron transfer (**PET**) process and enhances the fluorescence output of **HL**

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* Corresponding author. Fax: +86 931 8912582.
E-mail address: yangzy@lzu.edu.cn (Z.-y. Yang).

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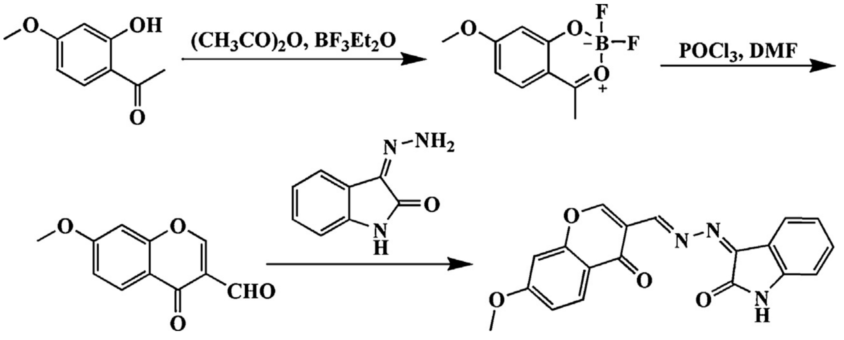

Scheme 1. Synthetic route of **HL**.

via chelation enhanced fluorescence (**CHEF**) effect. So far, very few Mg^{2+} sensors have been synthesized and can distinguish Mg^{2+} from Ca^{2+}. Hence, **HL** is suitable for selective detection of Mg^{2+} as fluorescence "turn-on" sensor.

2. Experimental

2.1. Materials and instrumentation

All chemicals were of reagent grade quality, obtained from commercial sources, and were used as received without further purification. Melting points were determined using a Beijing XT4-100× microscopic melting point apparatus. ^1H NMR spectra were recorded on JNM-ECS 400 MHz instruments spectrometers with TMS (tetramethylsilane) as internal standard and DMSO-d_6 as solvent. Mass spectra were recorded in ethanol solvent on a Bruker Esquire 6000 spectrometer. UV–vis absorption spectra were obtained with a Shimadzu UV-240 spectrophotometer and recorded in quartz cells with 1 cm optical path length. Emission spectra were measured using a Hitachi RF-5301 fluorimeter.

2.2. Synthesis of intermediates and probes

7-Methoxychromone-3-carbaldehyde was prepared as the previously reported procedure [33]. Isatin-3-hydrazone was obtained according to the literature method reported earlier [34]. It was synthesized by reaction of isatin with hydrazine hydrate in ethanol. The synthetic route of Chemosensor Isatin-3-(7′-Methoxychromone-3′-methylidene) hydrazone is outlined in Scheme 1.

7-Methoxychromone-3-carbaldehyde (0.204 g, 1 mmol) and Isatin-3-hydrazone (0.161 g, 1 mmol) were added in a 50 mL flask with 20 mL of methanol as solvent, then the solution was kept

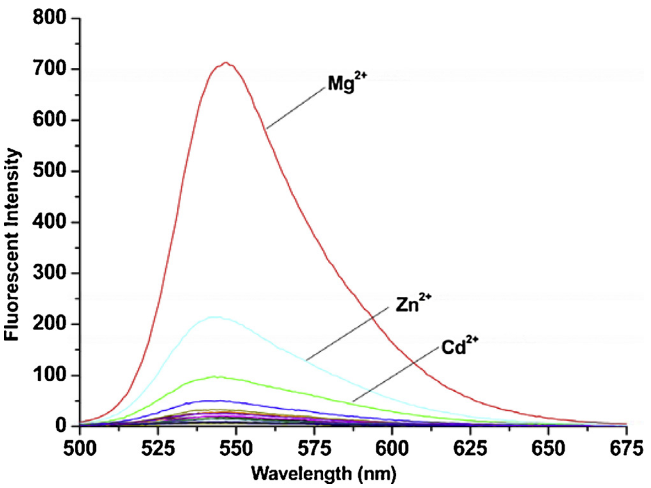

Fig. 2. Emission spectra of **HL** (10 μM) upon addition of different anions (1 equiv. K^+, Na^+, Li^+, Zn^{2+}, Cd^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+}, Co^{2+}, Ca^{2+}, Cr^{3+}, Al^{3+} and Mg^{2+}) in ethanol.

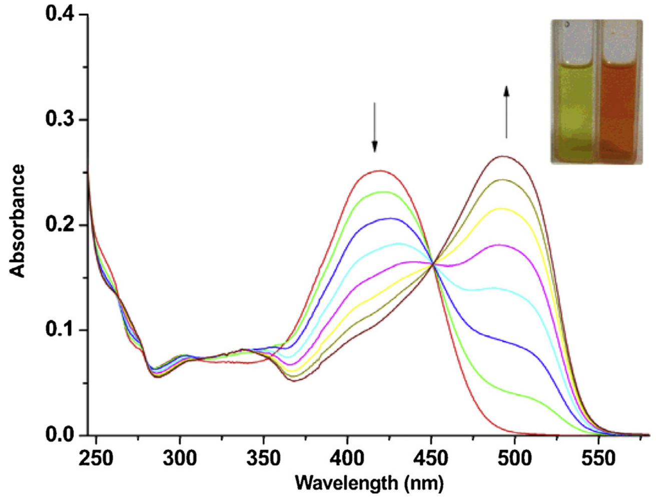

Fig. 1. Changes in the absorption spectra of **HL** (10 μM) in ethanol after addition of Mg^{2+} (0–7 equiv). Inset: color of **HL** (left) and **L** + Al^{3+} (right).

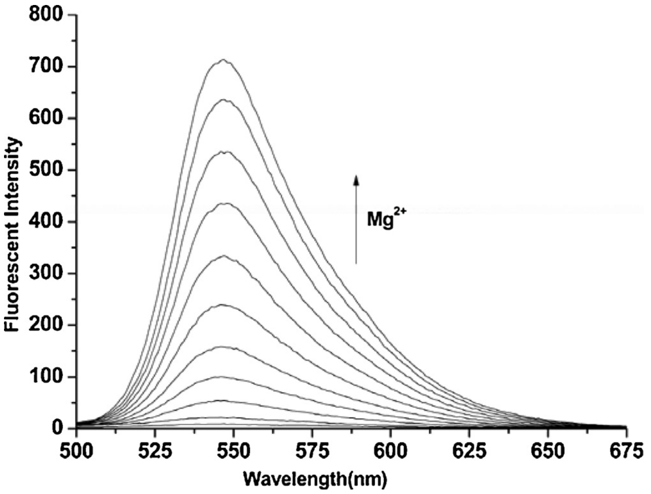

Fig. 3. Fluorescence spectra of **HL** (10 μM) with addition of increasing amount of Mg^{2+} (0–10 μM) in ethanol. Excitation wavelength was 491 nm, and emission was at 547 nm.

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