

Research paper

A multi-ion fluorescent probe for Mg^{2+}/Zn^{2+} based on a novel chromone-dendron Schiff base

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ABSTRACT

A multi-ion fluorescent probe for Mg^{2+}/Zn^{2+} , 7-methoxychromone-3-carbaldehyde-(3',4',5'-tris(benzoyloxy) benzoyl) hydrazone (**L**), based on a novel chromone-dendron Schiff base was designed and synthesized. The simultaneous detection of Mg^{2+} and Zn^{2+} was realized by regulating solvent: **L** showed excellent selectivity and high sensitivity toward Mg^{2+} in ethanol and Zn^{2+} in aqueous solution. The clear binding mode and corresponding turn-on mechanism (PET) were elucidated in this paper.

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1. Introduction

Magnesium, as the most prevalent divalent cation in cells, is involved in practically all metabolic pathways: it is a required cofactor for the normal function of adenosine triphosphate (ATP) and Mg^{2+} -dependent enzymes, and is essential in stabilizing membranes and DNA structure, regulating ion channels, cell cycle and apoptosis. Magnesium deficiency is linked with cardiovascular disorders such as acute myocardial infarction, arrhythmia and hypertension [1–6]. Zinc is the second most abundant transition metal ion in the human body, and plays a critical role in enzyme activation, gene expression, signal transduction, and modulation of brain excitability. Zinc deficiency causes growth retardation and delayed sexual maturation in children, while zinc dysregulation is implicated in Alzheimer's disease [7–11].

Due to the vital importance of Mg^{2+} and Zn^{2+} in biochemical and physiological processes, a number of methods have been developed for their determination, for example AAS, ICP-MS, ICP-OES, and ion-selective electrodes [12–14]. Amongst all these methods, fluorescent probes have aroused particular interest for their high sensitivity, operational simplicity, as well as real-time detection. Moreover, they do not require expensive facilities and have potential applications in biological system [15–19]. However, the

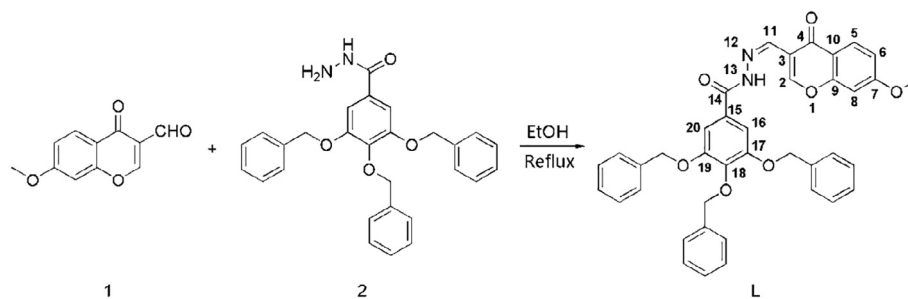
properties of fluorescent probes for Mg^{2+} or Zn^{2+} still need to be improved. For instance, some probes have suffered from poor selectivity due to the similar chemical properties of Mg^{2+} and Ca^{2+} , Zn^{2+} and Cd^{2+} [20,21]. On the other hand, some probes have low water solubility and require toxic organic solvents, restricting their practical applications in biological and environmental systems [22,23]. Therefore, the design of a highly selective practical probe for Mg^{2+} and Zn^{2+} remains an urgent task.

To solve these problems, Schiff base may be a good choice. Schiff-base compounds are widely used in fluorescent probes owing to their favorable coordination environment for metal ions [24–26]. Beyond this, chromone and its derivatives are excellent fluorophores that usually serve as signal reporter in probes [27,28], dendrimer and dendron are characterized by repetitive three-dimensional structures that allow multiple intermolecular interactions and contribute to efficient sensing [29,30]. Thus, a Schiff base combining chromone and dendron is a desirable candidate for fluorescent probes.

Here, we present a fluorescent probe (**L**) based on a novel chromone-dendron Schiff base, which connects chromone derivative with poly(aryl ether) dendron. **L** can be utilized as a multi-ion fluorescent probe by regulating solvent: it shows high selectivity toward Mg^{2+} in ethanol and Zn^{2+} in aqueous solution. The excellent fluorescence turn-on performance based on PET effect makes **L** a highly sensitive probe.

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Scheme 1. Synthesis of 7-methoxychromone-3-carbaldehyde-(3',4',5'-tris(benzyloxy) benzoyl) hydrazone (L).

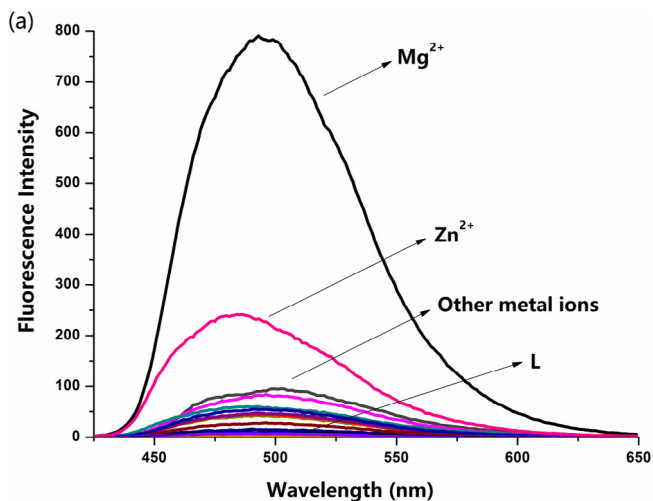


Fig. 1a. Fluorescent spectra of L (50 μM) in response to 1.0 equiv. Ag^+ , Al^{3+} , Ba^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , Ni^{2+} , Pb^{2+} , Zn^{2+} . $\lambda_{\text{ex}} = 414 \text{ nm}$, slit width (ex/em): 5/1.5 nm, in EtOH.

2. Experimental

2.1. Apparatus and reagents

All chemicals were obtained from commercial suppliers and used without further purification. ^1H NMR spectra were measured

on the JNM-ECS 400 MHz instruments using TMS as an internal standard. ESI-MS spectra were determined on a Bruker esquire 6000 spectrometer. HR-MS spectrum was obtained on high resolution mass spectrometer (LTQ-Orbitrap-ETD). 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. The melting point was determined on a Beijing-XT4-100 \times melting point microscopic apparatus. The pH measurement was conducted with a FE28 pH meter and a LE438 pH electrode.

2.2. Synthesis of 7-methoxychromone-3-carbaldehyde-(3',4',5'-tris(benzyloxy) benzoyl) hydrazone (L)

7-methoxychromone-3-carbaldehyde (Compound 1) and 3,4,5-tris(benzyloxy) benzohydrazide (Compound 2) were synthesized according to literature methods [30–33]. The synthetic route of L was shown in Scheme 1. An ethanol solution (14 mL) of Compound 1 (0.102 g, 0.5 mmol), then the mixture was stirred for 6 h under reflux, yielding a white precipitate. The crude product was filtered, dried under reduced pressure to give white solid L. Yield: 74.4%, mp: 181–182 $^{\circ}\text{C}$. ^1H NMR (400 MHz, DMSO-d_6) (Fig. S1): δ 11.66 (s, 1H, $-\text{NH}-$), 8.71 (s, 1H, H^{11}), 8.62 (s, 1H, H^2), 8.03 (d, 1H, $J = 8.8 \text{ Hz}$, H^5), 7.49–7.26 (m, 17H, 3Ar-H, H^{16} , H^{20}), 7.20 (d, 1H, $J = 2.4 \text{ Hz}$, H^8), 7.12 (dd, 1H, $J_1 = 8.8 \text{ Hz}$, $J_2 = 2.4 \text{ Hz}$, H^6), 5.21 (s, 4H, $\text{C}^{17}-\text{O}-\text{CH}_2-$, $\text{C}^{19}-\text{O}-\text{CH}_2-$), 5.04 (s, 2H, $\text{C}^{18}-\text{O}-\text{CH}_2-$), 3.93 (s, 3H, $-\text{CH}_3$). HQ-MS (Fig. S2): m/z 663.21 $[\text{M} + \text{Na}]^+$.

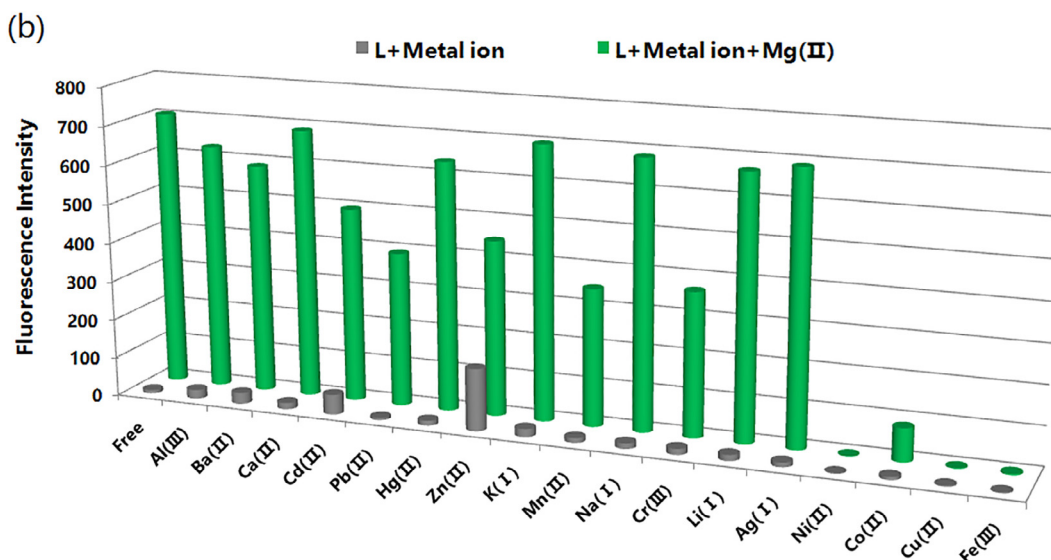


Fig. 1b. Fluorescence intensity of L (50 μM) at 493 nm after the addition of 1.0 equiv. various cations (gray bars) and after further addition of 1.0 equiv. Mg^{2+} (green bars). $\lambda_{\text{ex}} = 414 \text{ nm}$, slit width (ex/em): 5/1.5 nm, in EtOH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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