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ORIGINAL ARTICLE

Selective fluorescent probe based on Schiff base derived from hydroxymethyl coumarin and aminated Sudan I dye for Mg^{2+} detection

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Abstract A "turn-on" fluorescent sensor, SU-CM is synthesized for Mg^{2+} detection. The design of SU-CM is based on Schiff base ligand which is derived from the reaction between hydroxymethyl coumarin and aminated Sudan I dye. The low concentration of SU-CM (1×10^{-6} M) exhibits a good sensitivity to Mg^{2+} in isopropyl alcohol solution at room temperature when excited at 372 nm. The titration of Mg^{2+} into SU-CM undergoes a linear enhancement with increasing concentrations of Mg^{2+} up to a final mole ratio of 1:1. In addition, SU-CM also shows an excellent specificity from the results that fluorescent intensity emitted at 474 nm is not influenced by adding other 12 ions. Our research suggests that SU-CM may become a favorable candidate for establishment of an efficient Mg^{2+} response.

1. Introduction

Magnesium ion (Mg^{2+}), the eighth most abundant element on the crust of earth (Hama et al., 2007), is considered to be an essential biological element for all living organisms and plays a vital role in many metabolic processes (Dann et al., 2007; Trapani et al., 2010). As a result, techniques for detecting Mg^{2+} have caused widespread concerns among biologists, environmentalists and chemists. Several methods for detecting Mg^{2+} have been reported such as flow injection analysis (FIA) (Vahl et al., 2010), capillary electrophoresis (Nussbaumer et al., 2010), magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR) (Hifumi et al., 2007), laser-induced spectroscopy (Gornushkin et al., 2002), electrochemical detection

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(Lu et al., 2001) and ion chromatography (Ohta and Tanaka, 1998; Takeuchi et al., 2000; Williams and Barnett, 1992).

In recent years, fluorescent sensors for metal ions have drawn increasing attention and have become globally used primarily owing to their simplicity, high sensitivity and real-time response (Kim and Cho, 2011). Consequently, considerable efforts have been made to develop sensitive and selective fluorescent sensors for Mg^{2+} (Liu et al., 2005). Various fluorescent sensors have been designed and synthesized for detecting Mg^{2+} in the previous research, among which are the KMG series (based on a charged β-diketone) (Komatsu et al., 2004; Suzuki et al., 2002), DCHO series (based on 8-hydroxyquinoline) (Farruggia et al., 2006), 1-naphthaleneacetamide moiety based probes (Hama et al., 2007) and calix arenediamide (Song et al., 2007). However, many fluorescent sensors for Mg^{2+} were designed based on strategies for Ca^{2+} detection, and strong interference of Ca^{2+} may occur during Mg^{2+} recognition (Kim et al., 2007; Komatsu et al., 2005). In addition, Zn^{2+} can also disturb this process (Wang et al., 2011b). Therefore, it is of crucial importance to develop fluorescent sensors for Mg^{2+} detection with high specificity and sensitivity.

Schiff base ligands prepared by the reaction between aldehydes and imines are considered to be "privileged ligands" (Yoon and Jacobsen, 2003) because they can coordinate with diverse metals and stabilize them in various states (Cozzi, 2004; Dong et al., 2011; Hung and Lin, 2009; Roberts and Fritsch, 2010). Schiff base and additional electron donor atoms such as N and O are usually used as the ionophore in fluorescent sensor for determining several cations.

In this study, we reported a novel fluorescence sensor 5 (SU-CM) based on Schiff base ligand and hydroxylmethyl coumarin was selected as fluorophore for Mg^{2+} recognition. The results show that low concentration of SU-CM shows good sensitivity to Mg^{2+} in isopropyl alcohol solution and the response of SU-CM to Mg^{2+} exhibits high selectivity in the presence of other interfering ions, suggesting that it is a promising candidate for establishment of an efficient Mg^{2+} response.

2. Experimental

2.1. Reagents and chemicals

7-Hydroxy-4-methylcoumarin, *p*-phenylenediamine, acetic anhydride, β-naphthol and other solvents and reagents were all commercially available and of analytical-reagent-grade. Tetrahydrofuran (THF) was purified by distillation from sodium in the presence of benzophenone and Et3N was newly distilled before using. The solutions of the magnesium ions and other various metal ions were prepared from their corresponding nitrate salts.

2.2. Apparatus

NMR spectra were obtained by using a 300-Bruker spectrometer 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR and reported as parts per million (ppm) from the internal standard TMS. Solid-state NMR spectra were obtained from the Bruker Avance III 400 MHz NMR spectrometer. Fluorescence spectra were acquired from an RF-5301PC spectrometer (Shimadzu, Japan). Ultraviolet–visible (UV–vis) spectra were obtained from an UV-2550 spectrophotometer (Shimadzu, Japan).

2.3. Synthesis of compounds

2.3.1. 8-formyl-7-hydroxy-4-methylcoumarin (1)

Compound 1 was prepared according to the literature (Kulkarni et al., 2009; Patil et al., 2011). 7-Hydroxy-4-methylcoumarin (10 g, 56.8 mmol) and hexamine (19.9 g, 142 mmol) in 90 ml glacial acetic acid were heated for 6 h. Then 130 ml 20% hydrochloric acid was added and the mixture was further heated for 40 min, after the mixture was cooled and extracted with ether twice (50 ml * 2). The combined organic layer was concentrated under reduced pressure and the crude product was recrystallized from ethanol to afford **1** as light yellow powder. Yield: 10%. ^1H NMR (300 MHz, $CDCl_3$): δ 12.24 (s, 1H), 10.64 (s, 1H), 7.76 (d, 1H), 6.94 (d, $J = 9.0$, 1H), 6.23 (s, 1H), 2.45 (s, 3H).

2.3.2. N-(4-aminophenyl)acetamide (2)

Preparation of 2 is primarily carried out as described elsewhere (Neri et al., 2007) with some modification. A solution of acetic anhydride (4.25 ml, 46.25 mmol) in dry THF (10 ml) was added dropwise over 30 min to the solution of *p*-phenylenediamine (5 g, 46.25 mmol) in dry THF (100 ml). The reaction was stirred overnight at room temperature (RT) and the resulting residue was collected by filtration. Then the solid was recrystallized by methanol and filtered to get **2** as the white solid. Yield: 68%. ^1H NMR (300 MHz, DMSO-d_6): δ 9.45 (s, 1 H), 7.19 (d, $J = 8.7$ Hz, 2H), 6.49 (d, $J = 8.7$ Hz, 2H), 4.80 (s, 2H), 1.94 (s, 2H).

2.3.3. N-(4-((2-hydroxynaphthalen-1-yl)diazenyl)phenyl)acetamide (3)

Sodium nitrite (1.38 g, 20 mmol) dissolved in 4.6 ml distilled water was added slowly to the solution of compound 2 (3 g, 20 mmol) in 50 ml 10% hydrochloric acid. The mixture was stirred at 0 °C for an additional 20 min and then β-naphthol (2.88 g, 20 mmol) in 10 ml 10% sodium hydroxide was mixed and stirred at 0 °C overnight at RT. The precipitate was obtained by filtration and washed with dilute hydrochloric acid for three times to receive **3** as dark red solid. Yield: 73%. ^1H NMR (300 MHz, DMSO-d_6): δ 15.35 (s, 1 H), 10.27 (s, 1 H), 8.70 (d, $J = 8.1$ Hz, 1H), 7.98 (m, $J = 9.0$ Hz, 3H), 7.88 (m, $J = 7.8$ Hz, 3H), 7.67 (t, $J = 7.8$ Hz, 1H), 7.51 (m, $J = 7.2$ Hz, 1H), 7.11 (d, $J = 9.3$ Hz, 1H), 2.01 (d, $J = 4.5$ Hz, 3H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 169.04, 160.98, 143.07, 141.14, 137.73, 132.85, 129.20, 128.98, 128.95, 128.24, 125.51, 122.29, 121.68, 121.64, 120.05, 24.51.

2.3.4. 1-((4-aminophenyl)diazenyl)naphthalen-2-ol (4)

Compound 3 (1.32 g, 5 mmol) dissolved in 30 ml methanol was combined with 20 ml 1 M hydrochloric acid and refluxed overnight. The pH of the mixture was adjusted with sodium hydroxide to 7.4 and concentrated *in vacuo*. The resulting residue was purified by chromatography on silica gel (Petroleum ether: ethyl acetate = 30:1) to give **4** as bright red solid. Yield: 48%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 14.83 (s, 1 H), 8.77 (d, J = 8.4 Hz, 1H), 7.92 (m, J = 6.0 Hz, 2H), 7.80 (d, J = 9.0 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.20 (d, J = 9.0 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 6.22 (s, 2H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 153.03, 152.61, 140.27, 133.48, 132.36, 128.72, 128.59, 128.35, 127.98, 124.60, 124.55, 121.71, 120.34, 114.34.

2.3.5. 7-hydroxy-8-((((4-(2-hydroxynaphthalen-1-yl)diazenyl)phenyl)imino)methyl)-4-methyl-2H-chromen-2-one (5)

Compound 1 (1.32 g, 5 mmol) and compound **4** (1.03 g, 5 mmol) were stirred in 25 ml ethanol for 6 h at RT. The precipitate was obtained by filtration and washed with ethanol (20 ml) for five times to receive **5** as brick red solid. Yield: 57%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.45(s, 1H), 8.61(d, J = 8.1 Hz, 1H), 7.86(d, J = 8.4 Hz, 2H), 7.77(d, J = 9.3 Hz, 1H), 7.69(m, J = 7.8 Hz, 5H), 7.47(t, J = 6.9 Hz, 1H), 7.16(t, J = 6.3 Hz, 1H), 6.90(t, J = 9.6 Hz, 1H), 6.21(s, 1H), 2.46(s, 3H),2.19 (s, 2H). ^{13}C solid-state resolution NMR (400 MHz): δ 171.24, 169.22, 159.40, 153.81, 151.22, 149.22, 143.38, 140.40, 137.99, 133.12, 129.58, 127.39, 125.40, 120.07, 117.50, 115.31, 111.43, 109.99, 105.53, 18.09.

2.4. Analytical procedure

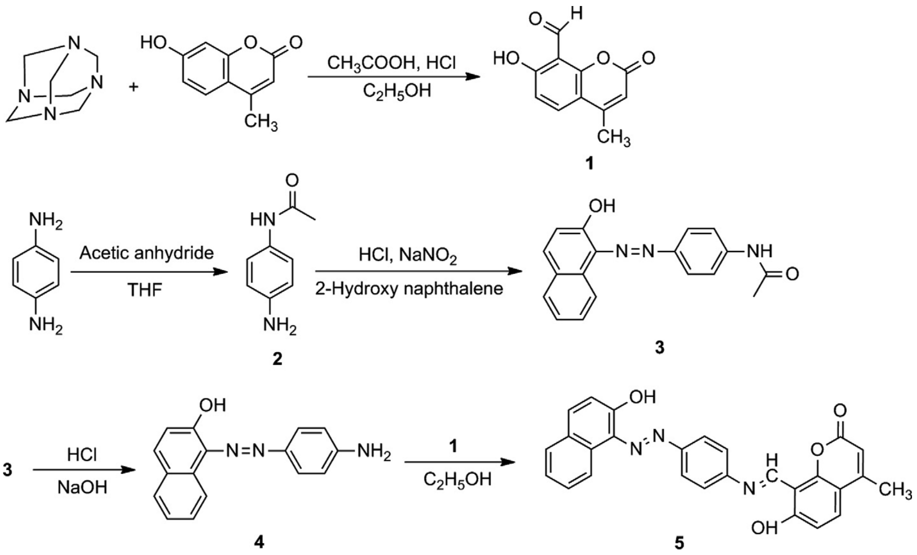
Stock solutions of Mg^{2+} and other kinds of metal ions (nitrate, 1.0×10^{-3} mol/l in H_2O) were added to 3.0 ml ligand in order to achieve the final concentration (1.0×10^{-5} mol/l in isopropyl alcohol). After that, each solution was transferred to a 1 cm quartz cuvette and fluorescence spectra were obtained from an RF-5301PC spectrometer by excitation/emission at 372/**474** nm. Ultraviolet–visible spectra were then acquired from an UV-2550 spectrophotometer by mixing different concentrations of Mg^{2+} (from 0 to $1.0.0 \times 10^{-5}$ mol/l) and a certain concentration of SU-CM (1.0×10^{-5} mol/l in isopropyl alcohol).

3. Results and discussion

The reaction schematics of SU-CM are illustrated in Scheme 1. Noticeably, Schiff base ligand is formed by reaction between hydroxymethyl coumarin and aminated Sudan I dye. The ^{1}H NMR and ^{13}C NMR spectra are displayed in SI 1.

As shown in Fig. 1, the fluorescence responses of SU-CM to various metal ions in isopropyl alcohol were investigated to evaluate the selectivity of SU-CM to various ions. Significant fluorescence enhancement could be observed after Mg^{2+} addition by a molar ratio of 1:1 and the corresponding fluorescence intensity increased by approximately 47-fold (Fig. 1A). Meanwhile, after introducing other metal ions such as Ag^+, Ca^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, K^+, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+}, there was almost no obvious fluorescent response (Fig. 1B). High selectivity of SU-CM suggests that it may be a good candidate for an efficient Mg^{2+}-responsive sensor in radiometric measurements (Carol et al., 2007; Ishida et al., 2010). However, the fluorescence intensity increased up to 6-fold and the maximum wavelength of fluorescent emission had an apparent blue shift (from 474 nm to 433 nm) after adding Cu^{2+}. Meanwhile, with increasing concentrations of Cu^{2+}, the color of the solution changed gradually from light yellow to colorlessness, showing that Cu^{2+}also exhibited comparable chelating affinity to SU-CM (Li et al., 2009; MX Liu et al., 2011; Wang et al., 2011a). Similar results were also obtained from the UV–Vis spectra of SU-CM with various other ions (SI 2).

In many cases, the influence of solvents is significant for the fluorescence spectra of complexes (Azab et al., 2010; Mac et al., 2007; Poteau et al., 2000; Rauf et al., 2012). Considering the application of SU-CM in different systems, the fluorescence emissions of SU-CM-Mg^{2+} complex in different solvents were also explored (SI 3). For some non-polar solvents such as dichloromethane, chloroform, petroleum ether and toluene, the fluorescence emission was very weak and blue shifted by 50 nm or more. The results may be attributed to the difference between the excited state and the ground state. As the solvent polarity increased, electron-transfer reaction between



Scheme 1 Synthesis procedures of fluorescence sensor 5.

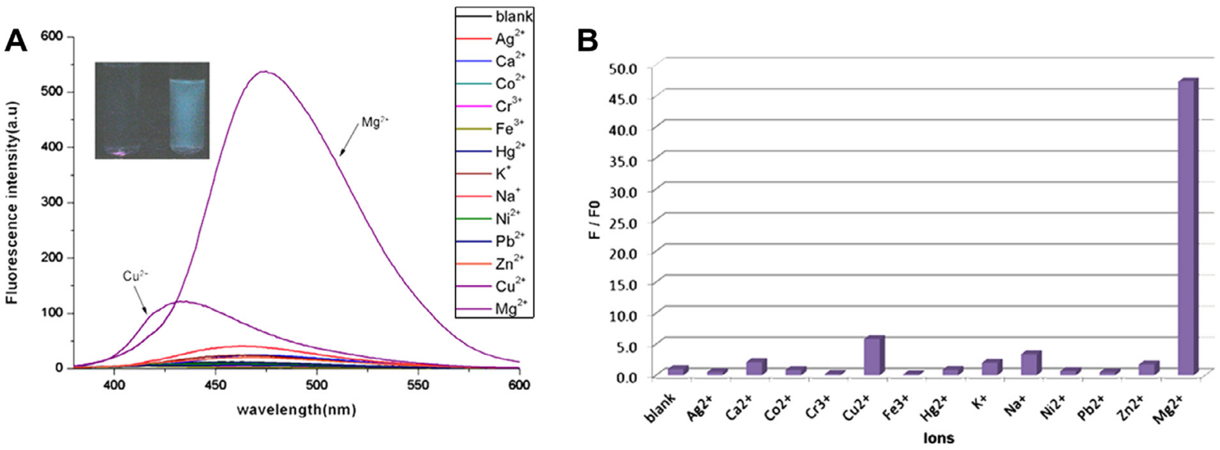


Figure 1 Fluorescence spectra (A) and intensity at 474 nm (B) of SU-CM (10 μM) with various different ions. λ_{ex} = 372 nm. The solution turned blue after the addition of Mg^{2+}.

metal ions and the ligands raised the dipole moment to the excited state, resulting in fluorescence enhancement and a progressive red shift (Azab et al., 2010; Chakraborty and Panda, 2011).

Secondly, high sensitivity is also essential for the selective ion probe. We further tested the fluorescence emission spectra of SU-CM in the presence of various amounts of Mg^{2+}. The fluorescence titration of SU-CM with Mg^{2+} is presented in Fig. 2A. In the absence of Mg^{2+}, SU-CM had only weak fluorescence. With increasing concentrations of Mg^{2+}, the fluorescence intensity showed a gradual enhancement and reached its maximum when the concentration of Mg^{2+} was one equiv of SU-CM. Then the fluorescence intensity was saturated although the amount of Mg^{2+} continues to rise (Fig. 2B). Therefore, a 1:1 stoichiometry was the most likely binding model between SU-CM and Mg^{2+}.

Next, a fluorescence-based Job's plot was created and shown in Fig. 3. The regression equations were $y = 1.4768 + 12.0599x$ ($R^2 = 0.9499$) and $y = 11.4021 - 11.041x$ ($R^2 = 0.9847$), respectively. The intersection at 0.43 indicated that the maximum amount of the SU-CM-Mg^{2+} complex was formed when

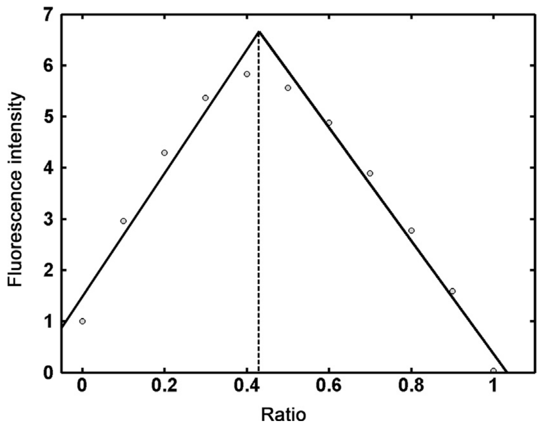


Figure 3 Job's plot of SU-CM with Mg^{2+} obtained by fluorescence measurements (λ_{ex} = 372 nm, λ_{em} = 474 nm). The total concentration of SU-CM and Mg^{2+} is 10 μM. Ratio = $[Mg^{2+}]/([Mg^{2+}] + [SU\text{-}CM])$.

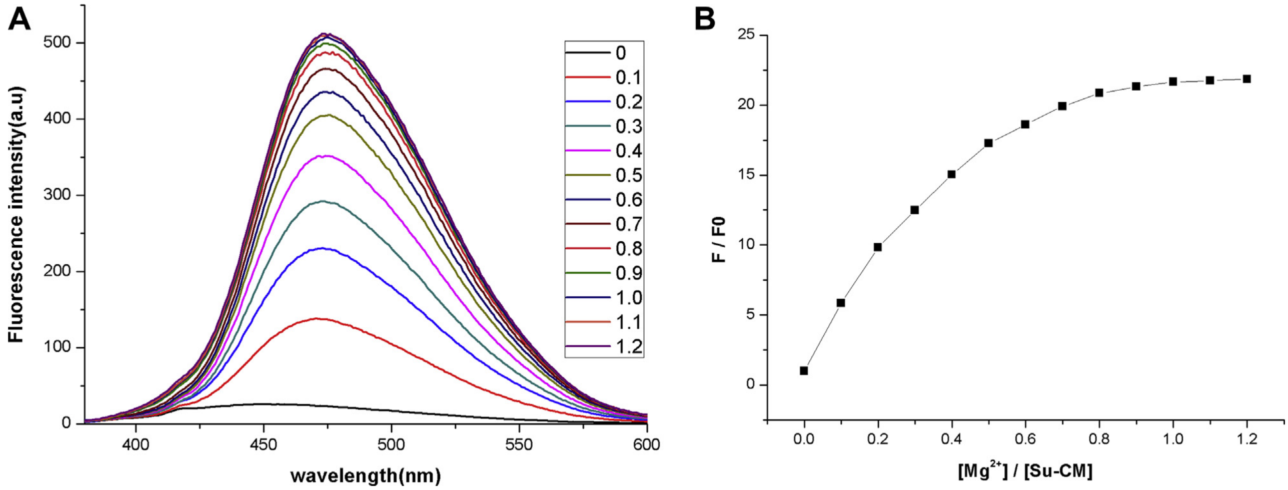


Figure 2 (A) Fluorescence spectra of SU-CM (10 μM) in isopropyl alcohol solution in the presence of different amounts of Mg^{2+}. (B) Fluorescence intensity at 474 nm as a function of different Mg^{2+} concentration. λ_{ex} = 372 nm.

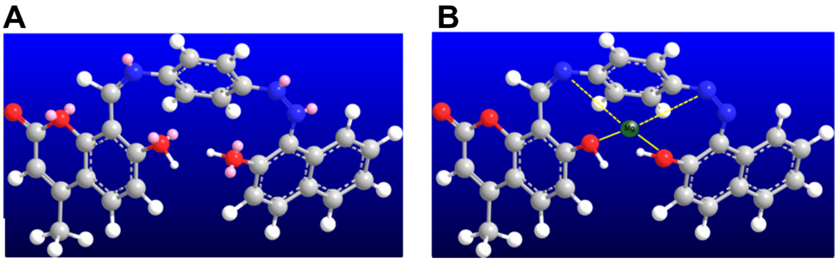


Figure 4 Schematic illustration of the structure of SU-CM in the absence of Mg^{2+} (A) and after addition of Mg^{2+} (B). Carbon atoms (ash black), oxygen atoms (red), nitrogen atoms (blue), magnesium atom (green) and long pair (pink) were also marked.

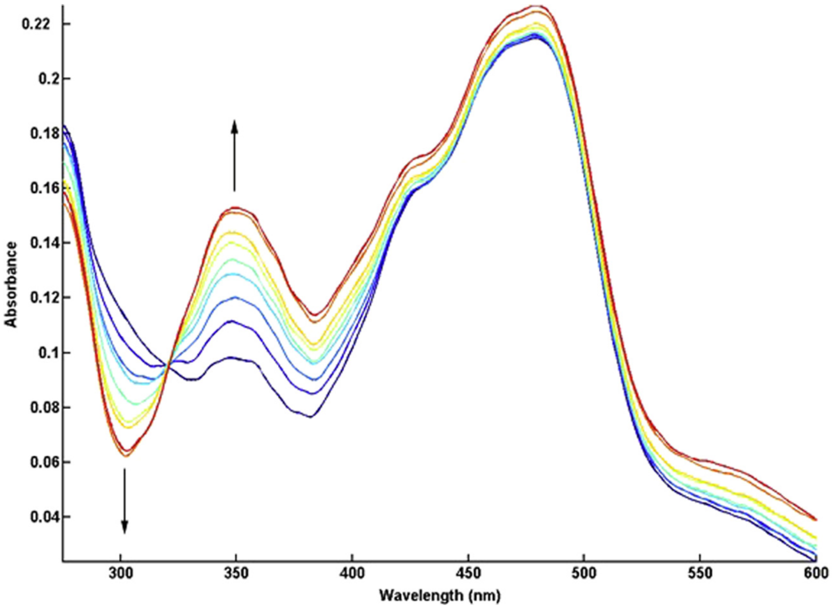


Figure 5 The UV–vis spectrum absorbance of SU-CM-Mg^{2+} complex.

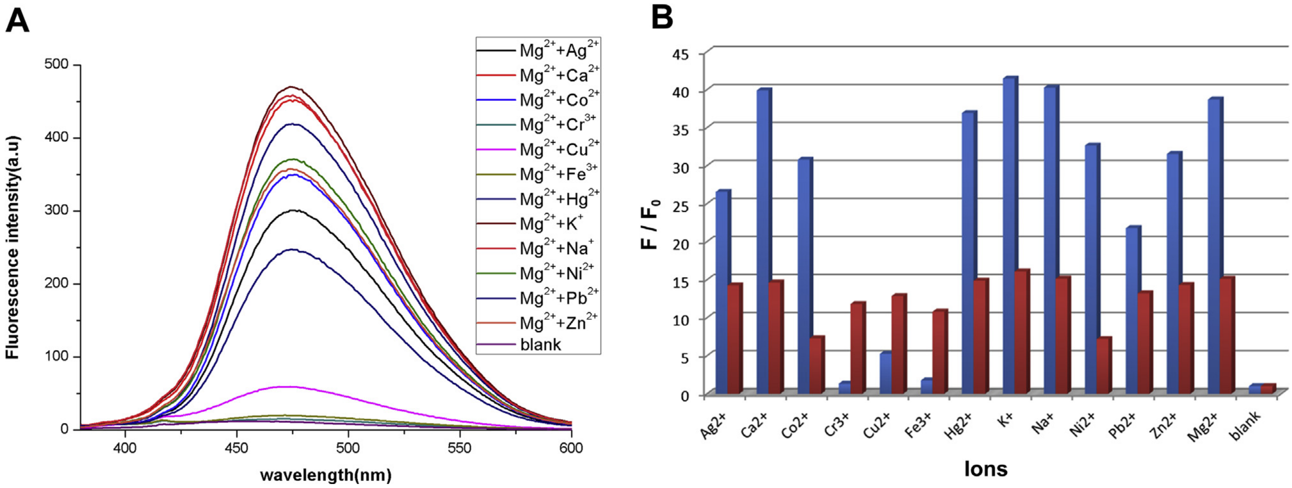


Figure 6 The selectivity of SU-CM for Mg^{2+} in the presence of various metal ions. (A) Fluorescence spectra of SU-CM (10 μM) with various different ions in the presence of Mg^{2+}. (B) Fluorescence intensity at 474 nm in the presence of 1.0 equiv of Mg^{2+} followed by other metal ions of interest in DMF (red bars) and isopropyl alcohol (blue bars).

the concentrations of Mg^{2+} and SU-CM were 4.3×10^{-6} M and 5.7×10^{-6} M, respectively. Therefore, this Job's plot confirmed that the SU-CM-Mg^{2+} complex existed with 1:1 stoichiometry.

The possible sensing mechanism of SU-CM to Mg^{2+} could be ascribed to the following reasons: firstly, from the 3-dimensional structure of SU-CM (Fig. 4A), due to the isomerization of the C=N bond and intramolecular charge transfer (ICT), there was almost no fluorescence emission of SU-CM in the absence of Mg^{2+} (Wu et al., 2007). After adding Mg^{2+}, however, a classic Salen ligand (Cozzi, 2004) with four coordinating sites, was formed (Fig. 4B), and then this served to lower the HOMO of the conjugated segment of the ligand when the Salen-based N_2O_2 receptor was coordinated with Mg^{2+} (Liu et al., 2007; Pina-Luis et al., 2008). Secondly, the formation of a new π-chemical bond bridge between SU-CM and Mg^{2+} may inhibit ICT effect. In this process, the hydroxyl group in SU-CM indeed played an important role in the course of binding with Mg^{2+} (Yu et al., 2011). Upon binding Mg^{2+}, a coordination-enhanced fluorescence process occurred and therefore an enhancement in the emission spectrum could be observed (Liu et al., 2009; Wang et al., 2010; Zhang et al., 2008). Additionally, the UV–vis spectrum of Su-CM-Mg^{2+} complex was also characterized (Fig. 5).

Since a sensor with the high specificity for the analyte and strong anti-jamming capability is the prerequisite in complex samples. We next examined the fluorescence response of SU-CM to Mg^{2+} in the presence of other metal ions. The Mg^{2+} response of SU-CM was almost not affected by some metal ions including Ag^{2+}, Ca^{2+}, Co^{2+}, Hg^{2+}, K^+, Na^+, Ni^{2+} and Zn^{2+}. Only Cr^{3+}, Cu^{2+} and Fe^{3+} may weaken the fluorescence in isopropyl alcohol (Fig. 6A). Compared with the fluorescent characteristics of SU-CM-Mg^{2+} complex in isopropyl alcohol solution, almost all ions involved had no significant effect on the fluorescence response of SU-CM to Mg^{2+} in DMF (Fig. 6B). These results were consistent with the solvent effect aforementioned and shown that the differential fluorescence may be exhibited in different solvents.

4. Conclusions

In summary, a novel fluorescence probe SU-CM for Mg^{2+} detection using aminated Sudan I dyes based on Schiff base ligand was designed and synthesized. The low concentration of SU-CM displayed a good sensitivity to Mg^{2+} and an approximately 47-fold enhancement in fluorescence response for Mg^{2+} selective chelation was observed in isopropyl alcohol when excited at 372 nm. The possible mechanism may be due to the formation of Salen-based N_2O_2 receptor coordinated with Mg^{2+}. Meanwhile, SU-CM also exhibited high specificity even with the interference of other metal ions such as Ag^{2+}, Ca^{2+}, Co^{2+}, Hg^{2+}, K^+, Na^+, Ni^{2+}, Zn^{2+}, Cr^{3+}, Cu^{2+} and Fe^{3+}. In addition, strong fluorescence intensity of SU-CM was still maintained in water-isopropyl alcohol solution, which will enable it as a potential excellent fluorescence chemosensor for rapid Mg^{2+} detection with high selectivity and sensitivity.

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Appendix A. Supplementary data

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