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Selective naked-eye detection of Magnesium (II) ions using a coumarin-derived fluorescent probe☆

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ABSTRACT

A simple 4-Methyl-7-hydroxy-8-formyl Coumarin (CS) serves as a selective chemosensor for Mg^{2+} in the presence of alkali and alkaline earth metal ions. It showed a significant fluorescence enhancement towards Mg^{2+}. The receptor CS exhibited a good binding constant and lowest detection limit for Mg^{2+}. The variation of emission signal exists via of reversible chelation enhanced fluorescence (CHEF) with this inherent quenching metal ion.

1. Introduction

Magnesium is the fourth most abundant cation in the human body, most abundant divalent cation within cells and plays an important physiological role in many of its functions [1]. Also magnesium found in the bone and plays an active role in bone remodelling and skeletal development [2,3]. On the other side, magnesium is the eighth most abundant element on earth crust [4]. Magnesium deficiency can result from a variety of causes including gastrointestinal and renal losses, can cause a wide variety of features including cardiac, hypokalaemia, hypocalcaemia and neurological manifestations. A number of chronic diseases, such as diabetes, osteoporosis, hypertension and coronary heart disease have been associated with chronic low magnesium [5,6]. Detection of Mg^{2+} in the presence of other alkali and alkaline earth metal ions, like as Ca^{2+}, Na^{+} and K^{+} is of particular significance. Serum magnesium and the magnesium tolerance test are the most widely used. There are no easy and readily available methods to assess magnesium status.

The design of fluorescent chemosensors is an active field of research for analytical as well as environmental and biological problems [7–11]. Typically, chemosensors are small molecules and are able to bind selectively and reversibly the analyte of interest with a change in the sensing system property, such as absorption, emission and redox potentials, which may allow naked eye detection of the analyte without resorting to the use of any expensive instruments. Of the various kinds of chemosensors, the fluorescent based chemosensors present many advantages. Fluorescence measurements are usually very sensitive, low cost, easily performed, capability of real-time detection and versatile [12–17].

Till now, various families of fluorescent probes for Mg^{2+} have been developed. These probes have receptor groups based upon moieties including diaza-18-crown-6 [18], benzo-15-crown-5 [19], calix[4]arene [20], Benzo chromene [21], Imidazo-1,10-phenanthroline [22] and other [23–27]. Most of the reported fluorescent probes for Mg^{2+} demonstrate poor selectivity for Mg^{2+} over Ca^{2+} and are useful only where the Mg^{2+} ion concentrations are much higher than those of Ca^{2+} ion.

We now report the ability of 4-Methyl-7-hydroxy-8-formyl Coumarin (**CS**) as a fluorescent probe to serve as an effective chemosensor for Mg^{2+} in the presence of other alkali and alkaline earth metal ions. Our particular interest is to investigate how Mg^{2+} affects the fluorescent behaviour of fluorophore upon complexation.

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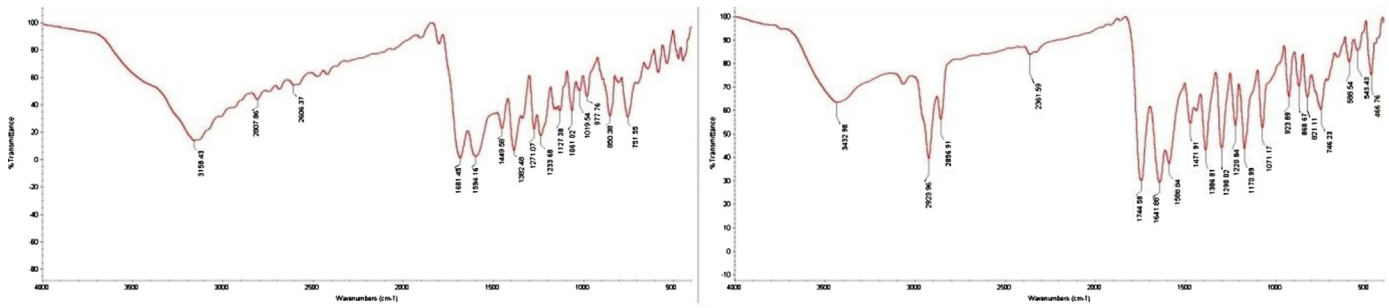
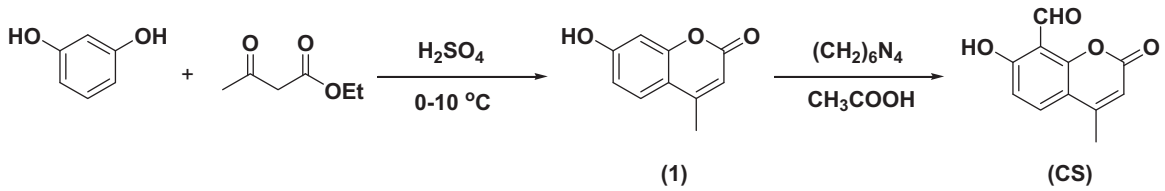


Fig. 1. FT-IR Spectrum of **1** and **CS.**



Scheme 1. Synthetic route for **CS**.

2. Experimental

2.1. Reagents and apparatus

All the commercially available chemicals were purchased from Merck and Aldrich and used without further purification. The IR spectra were recorded on a Nexus FT-IR (Illinois, USA) spectrometer in the range 4000–400 cm^{-1} with KBr. The NMR spectra were measured by using Bruker 500 MHz (USA), TMS as an internal standard, DMSO-d6, $CDCl_3$ and CD_3OD are taken as solvents. The mass spectra were recorded on a Bruker-micrOTOF II (USA). The UV–vis absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer (Japan) and the Fluorescent spectra were recorded by using Shimadzu RF-5301PC spectrofluorophotometer (Japan). Differential Pulse Voltammetric experiments were performed using a CHI760E electrochemical workstation (USA) with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum wire counter electrode, and an aqueous $Ag/AgNO_3$ reference electrode. The pH was measured with a Eutech CyberScan pH 510 (Singapore).

2.2. Synthesis and characterisation

The synthetic route of Chemosensor (**CS**) was outlined in Scheme 1. Chemosensor was prepared by following the literature method [28,29] and the structure was characterised by FT-IR, ^1H NMR and HRMS spectra (Figs. 1–3).

2.2.1. Synthesis of 4-Methyl-7-hydroxy Coumarin (*1*):

Concentrated sulphuric acid (20 mL) was cooled at 0–5 °C in an ice bath. A solution of resorcinol (20 mmol) in ethyl acetoacetate (30 mmol) was added to sulphuric acid under constant stirring at 0–5 °C. The reaction mass was stirred about 2–3 h under the same conditions and poured in to crushed ice under vigorous stirring. Obtained solid was filtered and recrystallised from

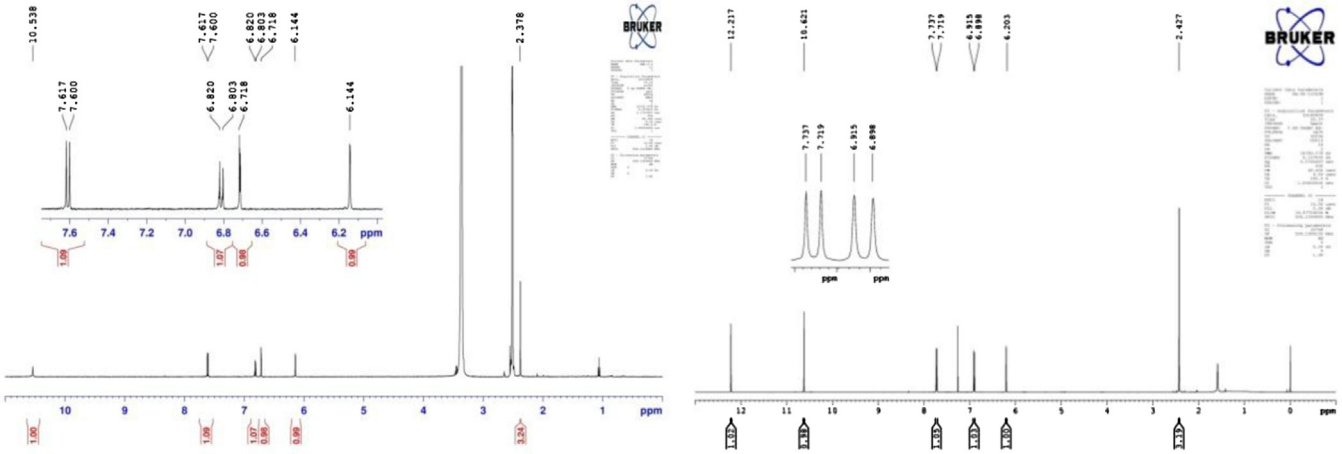


Fig. 2. ^1H NMR Spectrum of **1** and **CS.**

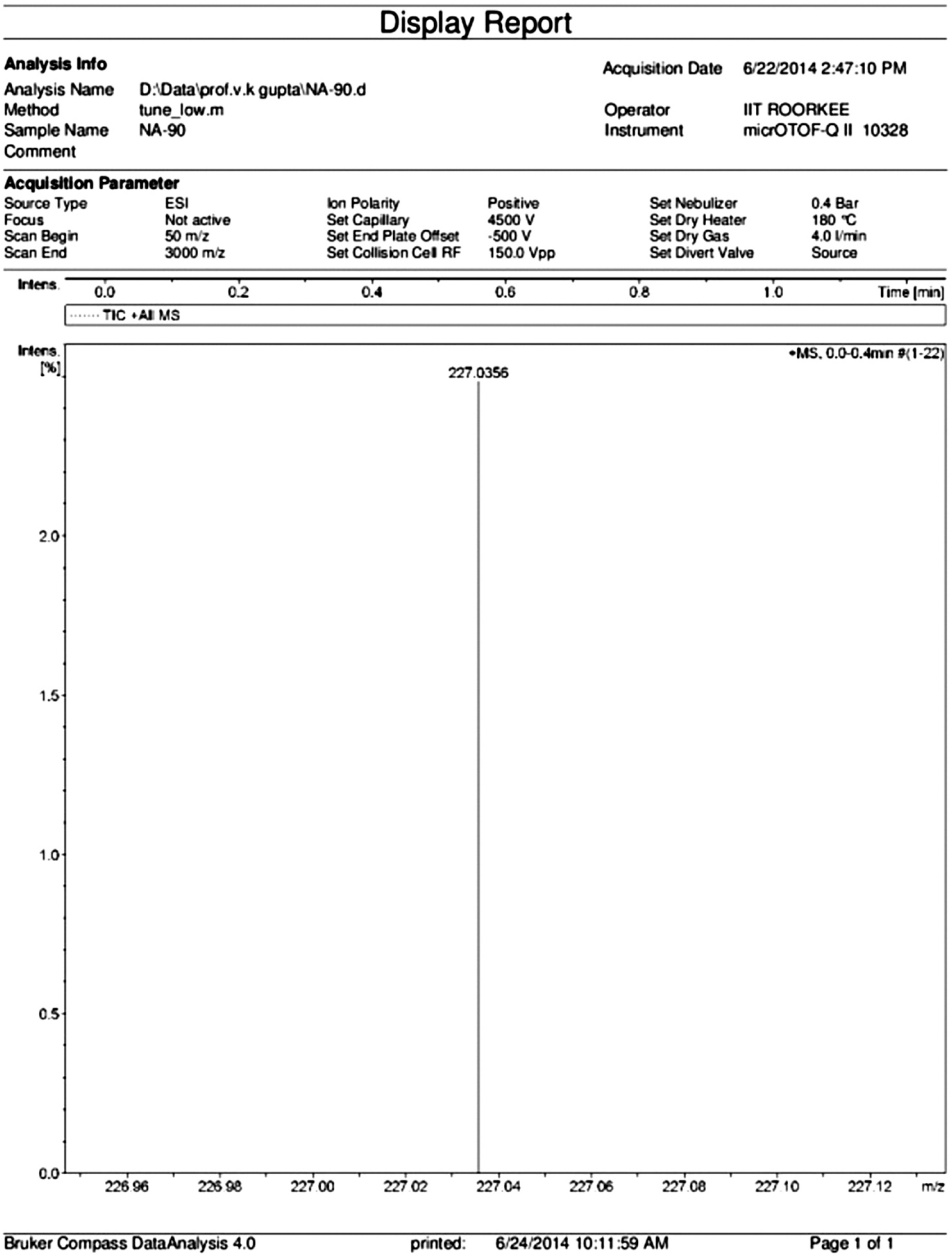


Fig. 3. HRMS Spectrum of **CS.**

methanol. Yield: 2.8 g (79%); color: White crystals; m.p. 179–181 °C; FT-IR (KBr), ν, cm^{-1}: 3158 (O—H), 1681 (C=O), 1594 (C=C), 1382, 1234 (C—O); ^1H NMR (DMSO-d6), δ, ppm (*J*, Hz): 2.38 (s, 3H), 6.14 (s, 1H), 6.72 (s, 1H), 6.81 (d, *J* = 8.5, 1H), 7.61 (d, *J* = 8.5, 1H), 10.54 (s, 1H).

*2.2.2. Synthesis of 4-Methyl-7-hydroxy-8-formyl Coumarin (**CS**):*

The mixture of 7-hydroxy-4-methyl-coumarin (10 mmol), hexamethylene tetramine (30 mmol) in glacial acetic acid (20 mL) was refluxed for 4–5 h in a water bath. Then, 20% HCl (25 mL) was added and further heated for 30 min, cooled to room temperature and extracted with diethyl ether. Solid was obtained on evaporation of solvent. Yield: 0.37 g (18%); color: pale yellow solid; m.p. 175–177 °C; FT-IR (KBr), ν, cm^{-1}: 3433 (O—H), 2924 (OC—H), 1745 (HC=O), 1642 (C=O), 1589 (C = C), 1387, 1298 (C—O); ^1H NMR ($CDCl_3$), δ, ppm (*J*, Hz): 2.43 (s, 3H), 6.20 (s,1H), 6.91 (d, *J* = 8.5, 1H), 7.73 (d, *J* = 9.0, 1H), 10.62 (s, 1H), 12.22 (s, 1H). ESI calcd for $C_{11}H_8O_4$ $(M + Na)^+$: 227.0320, found: 227.0356.

2.3. UV–vis and fluorescent studies

All measurements of UV–vis absorption and fluorescence emission spectra were carried out in 1.0 cm path length quartz cuvettes in alcoholic medium (MeOH) at room temperature. Absorption and emission spectra of the chemosensor in the presence of various metal ions were measured in the concentration of 50 μM (for absorption spectra), 10 μM (for emission spectra). Stoichiometry, binding constant of sensing probe–Mg^{2+} complex and limit of detection of Mg^{2+} were calculated by using spectrofluorophotometer. For all the measurements, excitation wavelength was 350 nm,

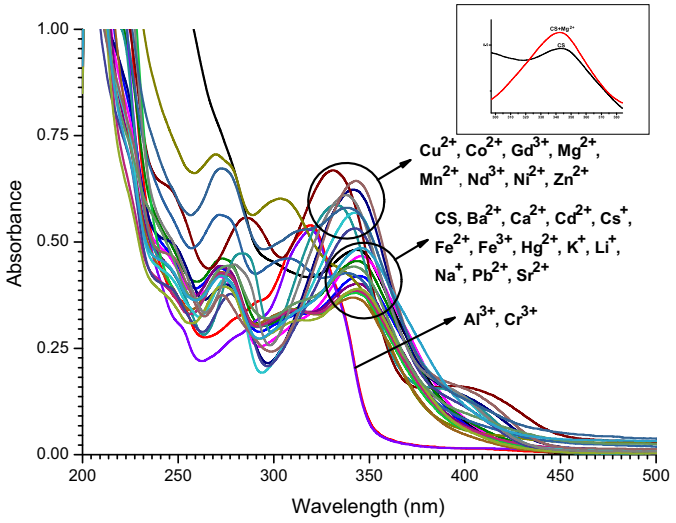


Fig. 4. UV–vis absorbance spectra of **CS** (50 μM) in the presence of 1.0 equiv. of various metal ions in MeOH.

and both the excitation and emission slit widths were 3 and 5 nm, respectively.

3. Results and discussion

The binding ability and mode of chemosensor towards Mg^{2+} were investigated through absorption, emission, electrochemical and ^1H NMR spectroscopic experiments.

3.1. Absorption spectroscopic studies

The binding ability of probe (50 μM) against cations (50 μM), such as Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cs^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Gd^{3+}, Hg^{2+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Nd^{3+}, Ni^{2+},Pb^{2+}, Sr^{2+} and Zn^{2+} was carried out by UV–vis absorption spectroscopic studies in methanol. The free ligand **CS** exhibited a single absorption band at about 343 nm, hyperchromic shift was observed when added to Co^{2+}, Cu^{2+}, Gd^{3+}, Mg^{2+}, Mn^{2+}, Nd^{3+}, Ni^{2+} and Zn^{2+} ions (Fig. 4). It showed a blue shift accompanied by a hyperchromic shift in the presence of Cr^{3+} and Al^{3+} metal ions. The other cations Ba^{2+}, Ca^{2+}, Cd^{2+}, Cs^{+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, K^{+}, Li^{+}, Na^{+}, Pb^{2+} and Sr^{2+} did not show

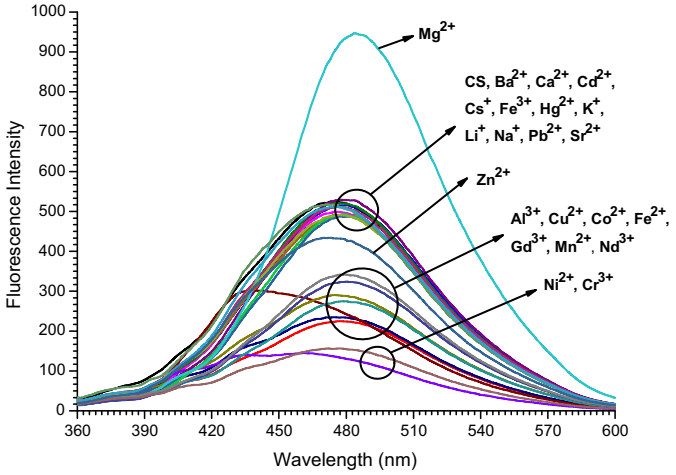


Fig. 5. Fluorescence emission spectra (λ_{ex} = 340 nm) of receptor **CS** (10 μM) in the presence of 1.0 equiv. of various metal ions in MeOH.

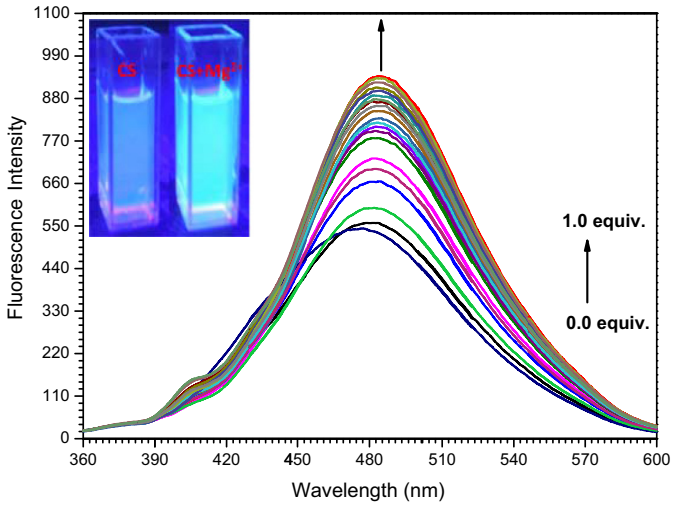


Fig. 6. Fluorescent spectral changes of **CS** (10 μM) upon titration with $MgCl_2$ in MeOH. Inset, changes in the fluorescence intensity of **CS** with Mg^{2+} under 365 nm UV-light.

any significant spectroscopic change even when added in excess (10 equiv.).

3.2. Fluorescence emission studies

The fluorescence emission spectral behaviour of sensor **CS** (10 μM) upon addition of various metal ions (10 μM) has been investigated in methanol. Chemosensor alone showed a single emission band at 473 nm with an excitation of 350 nm. **CS** showed a chelation enhanced fluorescence (CHEF) only with Mg^{2+}, even though there was a relatively chelation enhanced fluorescent quenching (CHEQ) effect with Al^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Gd^{3+}, Mn^{2+}, Nd^{3+}, Ni^{2+} and Zn^{2+} (Fig. 5).

The sequential addition of Mg^{2+} ions from 0 to 1.0 equiv. to the solution of **CS** showed a gradual increase in emission accompanied by a small red shift of 12 nm from 473 to 485 nm (Fig. 6). Under a UV lamp, the solution of **CS** in the presence of Mg^{2+} showed a dramatic color change from dull fluorescent blue to bright fluorescent blue, which could easily be detected by the naked-eye (Fig. 6, inset). Furthermore, to explore the binding mechanism, the Job's plot of fluorescence emission titration of Mg^{2+} was revealed in Fig. 7. A maximum emission was observed when the molar fraction reached

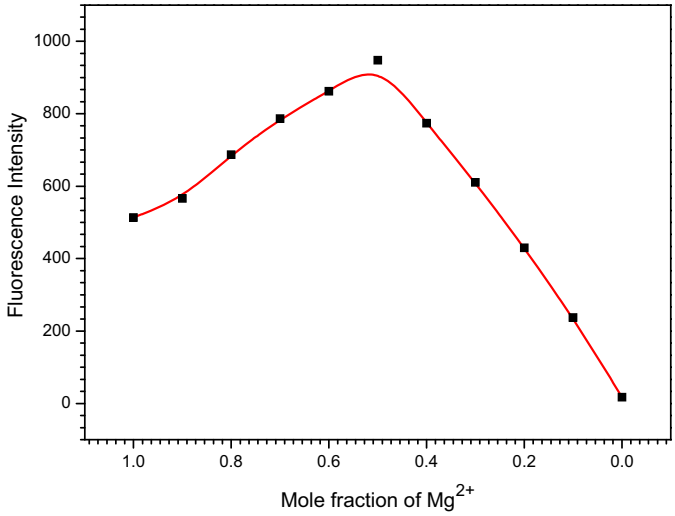


Fig. 7. Job's plot, Fluorescence intensity at 485 nm was plotted as a function of the molar ratio.

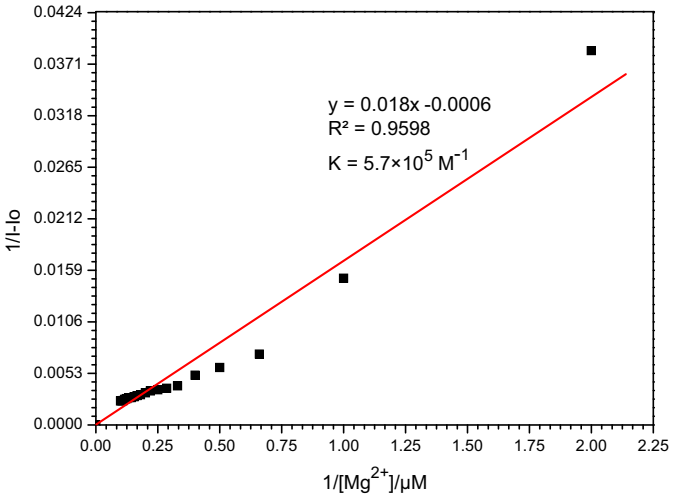


Fig. 8. Benesi–Hildebrand plot, fluorescence intensity at 485 nm.

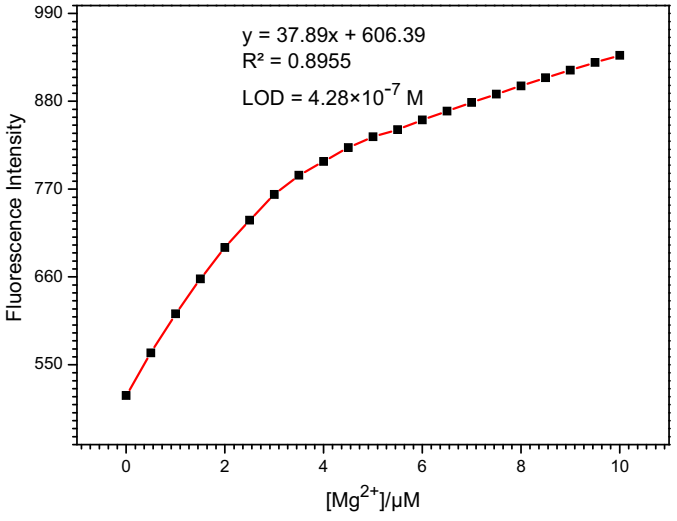


Fig. 9. The linear relation for fluorescent intensity of **CS** (10 μM) toward Mg^{2+} concentration in the range of 0–10 μM.

0.5, which is indicative of a 1:1 stoichiometry complexation for the newly formed species of **CS**–Mg^{2+}.

From the Fluorescence titration profiles, linear relationship was obtained for the plot measured $[1/(I - I_0)]$ at 485 nm as a function of $1/[Mg^{2+}]$ using the well-known linear Benesi– Hildebrand expression [30]. The binding constant of the newly formed complex (**CS**–Mg^{2+}) in MeOH was determined as $5.7 \times 10^5\ M^{-1}$ (Fig. 8). The detection limit was calculated based on the fluorescence titration of Mg^{2+} as 0.43 μM based on S/N = 3 (Fig. 9).

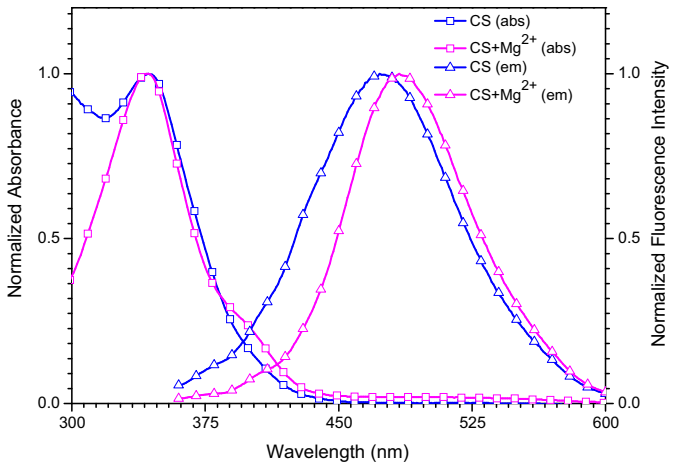


Fig. 11. UV–vis absorption and fluorescence emission spectra of **CS** and **CS**–Mg^{2+} recorded in methanol.

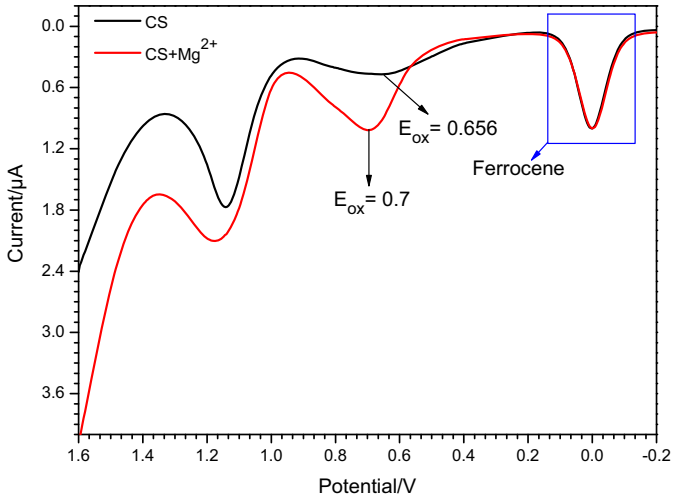


Fig. 12. Differential pulse voltammograms recorded for the probe **CS** and the corresponding Mg^{2+} addition product in methanol.

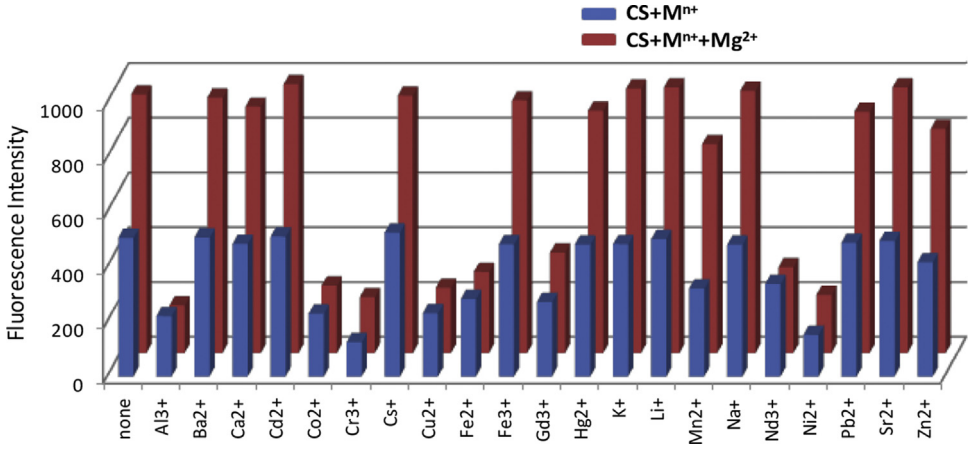


Fig. 10. Selectivity of the probe **CS** toward various metal ions (1.0 equiv.) in the absence and presence of Mg^{2+} (1.0 equiv.), fluorescence intensity at 485 nm.

In addition, the selectivity of **CS** towards Mg^{2+} over other metal ions was investigated by the competition experiment. As shown in Fig. 10, probe **CS** (10 μM) was treated with 1 equiv. of Mg^{2+} in the presence of other metal ions of the same concentration. Relatively low interference levels were observed for the detection of Mg^{2+} in the presence of alkali (Li^+, Na^+, K^+ and Cs^+), alkaline earth (Ca^{2+}, Sr^{2+} and Ba^{2+}), p-block (Pb^{2+}) and d-block (Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}) metal ions. The receptor **CS** responses for Mg^{2+} in the presence of Al^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Gd^{3+}, Nd^{3+} and Ni^{2+} are relatively low. Thus probe **CS** can be used as a selective fluorescent chemosensor for Mg^{2+} in the presence of most competing metal ions especially alkali and alkaline earth metal ions.

3.3. Electrochemical measurement

As shown in Fig. 11, the corresponding wavelength to the band gap energy can be calculated from the cross point of absorption and emission onset lines. The corresponding wavelength for **CS** is 396 nm and **CS** + Mg^{2+} is 415 nm which are equal to 3.13 eV (for **CS**) and 2.99 eV (for **CS** + Mg^{2+}) band gap energy.

Fig. 12 shows the current–voltage curve for **CS** and **CS** + Mg^{2+} regarding to Differential Pulse Voltammetric experiments. Based on results, **CS** shows E_{ox} = 0.656 V which is equal to E_{HOMO} = −5.46 eV and **CS** + Mg^{2+} shows E_{ox} = 0.7 V which is equal to E_{HOMO} = −5.5 eV [31–42]. By addition of Mg^{2+} ion increased the oxidation potential of **CS**, due to decrease in electron releasing nature of **CS** – Mg^{2+} complex. LUMO energy levels (for **CS** is −2.33 eV, for CS + Mg^{2+} is −2.51 eV) were estimated from HOMO and band gap energies.

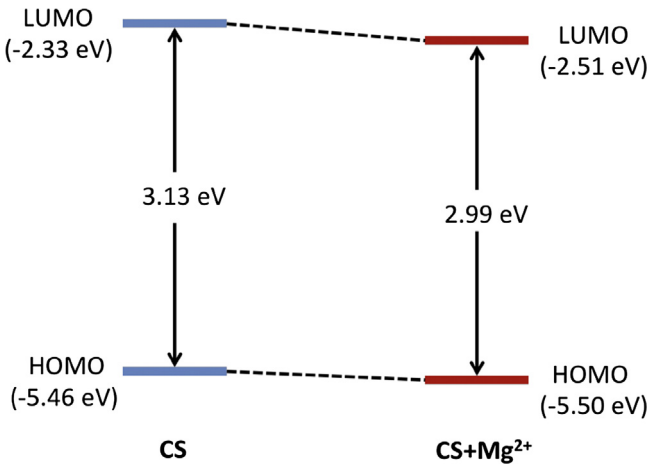


Fig. 13. Energy level diagram of the probe **CS** and the corresponding Mg^{2+} addition product.

This experiment proves that, increase in oxidation potential and decrease in band gap due to the interaction between **CS** probe and magnesium ion. Fig. 13 shows the energy diagram with HOMO/LUMO levels of **CS** and **CS** + Mg^{2+}.

3.4. ^1H NMR titration

To further clarify the bonding mode of sensing probe (**CS**) towards Mg^{2+}, ^1H NMR titration experiments were carried out in

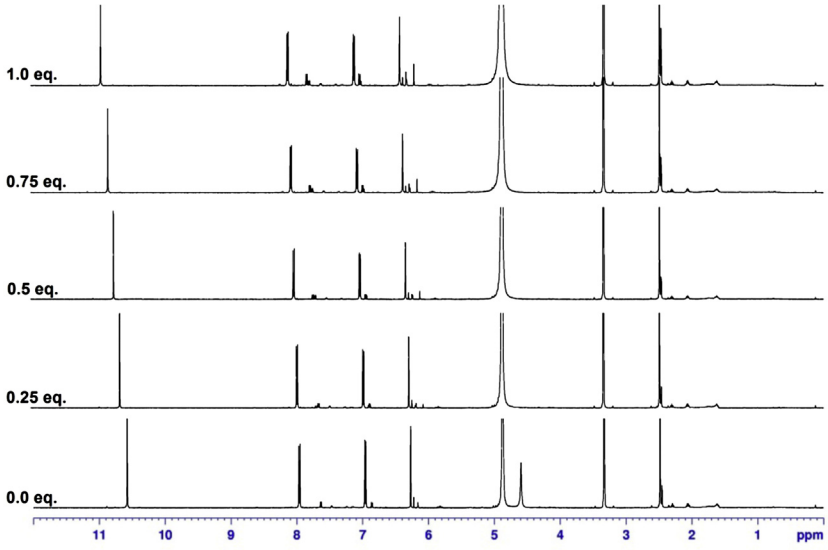
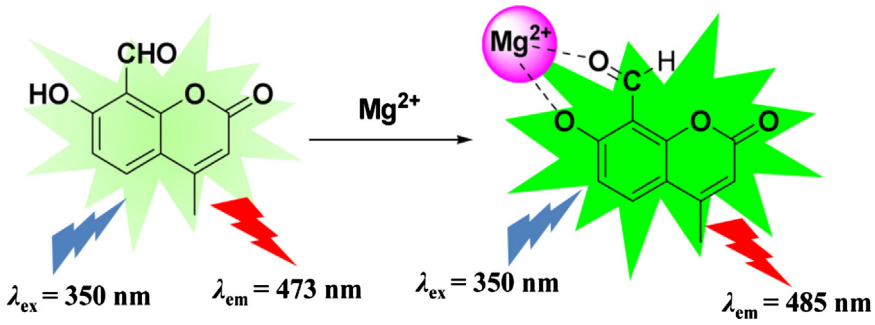


Fig. 14. ^1H NMR titration plot of receptor **CS** with Mg^{2+} in CD3OD.



Scheme 2. Schematic representation of binding mode of receptor with Mg^{2+}.

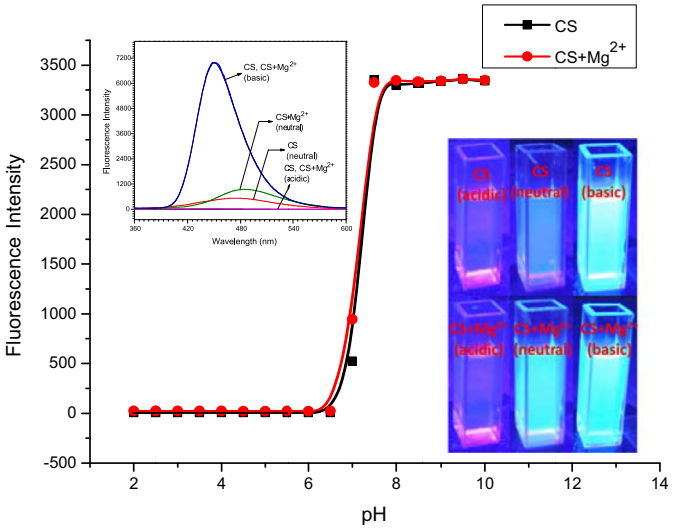


Fig. 15. Fluorescence intensities of **CS** (10 μM) at 485 nm in the presence of Mg^{2+} (10 μM) under different pH conditions. Inset: Spectral changes of **CS**–Mg^{2+} as a function of pH (left), photographs of **CS** and **CS**–Mg^{2+} in different pH media under a UV lamp (right).

both absence and presence of magnesium ion in various concentrations in methanol-d4 at room temperature. As depicted in Fig. 14, the aldehyde proton of **CS** at around 10.58 ppm was shifted downfield toward 10.98 ppm upon addition of Mg^{2+}. The hydroxyl proton was disappeared in CD_3OD solvent. On the other hand, the aromatic protons were shifted downfield by 0.02–0.17 ppm followed the addition of Mg^{2+}. The results suggested that the binding of probe (**CS**) to Mg^{2+} forms a rigid system by a chelation with the phenolic OH and the oxygen atom of carbonyl group (Scheme 2).

3.5. pH effect

The pH-dependent response of **CS** was carried out to investigate a suitable pH range for Mg^{2+} sensing. As shown in Fig. 15, the fluorescence emission changes were observed at 485 nm with pH variation. After mixing **CS** with Mg^{2+} in the basic pH range, exhibited a rapid fluorescence enhancement accompanied by a blue shift of 37 nm from 485 to 448 nm. The emission intensity of **CS**–Mg^{2+} complex was quenched in the acidic conditions. For pH < 7, the decreased fluorescence intensity at 485 nm indicates that the protonation of coumarin prevents the formation of **CS**–Mg^{2+} complexes in acidic condition. The chemosensors **CS** in the presence of Mg^{2+} showed a dramatic color changes in the different pH conditions, which could easily be detected by the naked-eye (Fig. 15, inset) under a UV lamp. The same fluorescence emission changes were observed for **CS** alone in acidic and basic conditions.

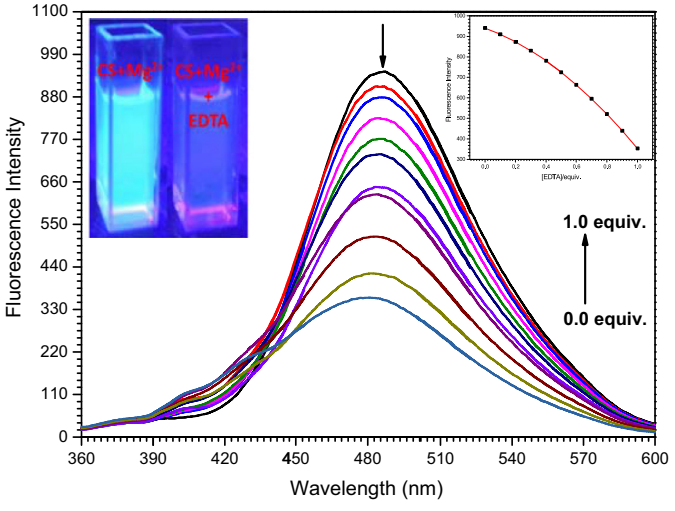


Fig. 16. The variation in Fluorescence emission spectra of **CS**–Mg^{2+} (10 μM) upon addition of EDTA in methanol. Inset: The color changes of **CS**–Mg^{2+} upon addition of EDTA (1 equiv.) (left), fluorescence spectral changes at 485 nm as a function of the amount of EDTA (right).

3.6. Reversibility of complexation of probe–Mg^{2+}

To establish the reversibility binding of **CS**–Mg^{2+}, EDTA titration was conducted. This experiment was performed by the addition of EDTA to the mixture of **CS** (1equiv.) and Mg(II) (1equiv.). Therefore, the addition of EDTA to a mixture of receptor **CS** and Mg^{2+} resulted in quenching of the fluorescence intensity at 485 nm, which indicated the regeneration of the free receptor **CS** (Fig. 16). The fluorescence was recovered by the addition of Mg^{2+} again. These results show that **CS** is suitable to be used as a reversible fluorescent chemosensor to detect Mg^{2+}.

4. Conclusion

In summary, we have found a coumarin based sensitive probe **CS** to Mg^{2+} which fluorometrically selective with Mg^{2+} ions and makes it a dual probe for naked eye detection of Mg^{2+} through change in color and fluorescence. The limit of detection of Mg^{2+} was found to be much lower as 0.43 μM. The binding ability and mode of sensor **CS** towards Mg^{2+} were investigated through UV–vis absorption, fluorescence emission, electrochemical and ^1H NMR spectroscopic techniques. Thus, our chemosensor can be used as a practical sensor for detection of Mg^{2+} in analytical as well as environmental and biological samples.

Acknowledgements

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