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ORIGINAL ARTICLE

Coumarin Derived "Turn on" Fluorescent Sensor for Selective Detection of Cadmium (II) Ion: Spectroscopic Studies and Validation of Sensing Mechanism by DFT Calculations

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Abstract

A novel coumarin based Schiff base sensor probe **1**, was synthesized and structural elucidation was carried out by FTIR, UV–vis, ^{1}H and ^{13}C NMR and MS spectroscopy. The optical properties of the sensor probe were investigated by employing absorption and fluorescence titrations which showed specific recognition behaviour being highly selective towards Cd^{2+} over the other 3d transition metal ions. The strong fluorometric response of probe **1** towards Cd^{2+} ion is attributed to inhibition of C=N isomerization effect upon coordination of the metal ion. The binding stoichiometry was determined by Job's plot and the probable sensing mechanism of the probe towards Cd^{2+} was investigated by employing FTIR spectra analysis and ^{1}H NMR titration experiments. Computational validation of the sensing mechanism in various modes towards Cd^{2+} was also performed by carrying out the DFT studies which were found to be in good concordance with the experimental results. The reversible nature of the probe was studied by EDTA titration indicating that it can be reused. Interaction studies of the sensor probe with the BSA showed the practical applicability for the quantitative determination of Cd^{2+} concentration in the blood plasma. The lower detection limit of the probe upto 0.114 μM further proves its practical application in the sensing phenomenon.

Keywords Fluorescence · C=N isomerization · Reversible · Cadmium · DFT studies

Introduction

The design and development of small molecules that can act as highly sensitive and efficient fluorosensor for detecting heavy metal ions such as Cadmium, is a topic of ever increasing concern for human health [1, 2]. Cadmium which is a toxic metal ion is widely used in chemical industries and agricultural fields as alloy material, in batteries, quantum dots and phosphate fertilizer. Substantial amount of cadmium is discharged into the environment as food contaminants, industry effluents and pollutants resulting in contamination of soil, air and water resources [3]. Being toxic and carcinogenic, Cadmium requires monitoring, as it is found to accumulate within the human body causing serious diseases such as destruction of mucous membrane of lungs, pneumonitis, renal dysfunction, bone defects and prostate cancer [4–8]. However, the major challenge while detecting cadmium ion is offered by Zn^{2+} resulting in interference due to similar spectral properties upon coordination with the sensor molecule [9]. Only a few fluorescence based sensors for detecting the cadmium ion in aqueous solution have been reported which are commercially available till date [10–12]. In lieu of this, it is desirable to develop a sensitive and low cost fluorescent sensor for quantitative measurement of cadmium ion in real samples offering selectivity over other metal ions.

Fluorescent sensors are not only advantageous over the traditional methods [13, 14] but are attractive due to high sensitivity, fast response time, ease of handling and for determining the presence of metal ions in their aqueous solutions [15, 16]. Coumarin is frequently used chromophore in the

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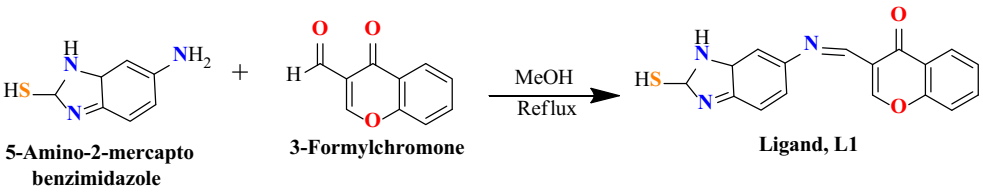
Scheme 1 Reaction pathway for the synthesis of probe **1**



5-Amino-2-mercapto benzimidazole

3-Formylchromone

Ligand, L1

synthesis of fluorescence based sensors owing to their tunable photophysical properties, less toxicity, good water solubility and fluorescent properties in the visible region [17–19]. Literature reports reveal many coumarin based fluorescent sensors which are known to selectively detect Cd^{2+} in presence of various metal ions [20, 21]. Schiff base probes which are recognized as sensing molecules are weakly fluorescent or non–fluorescent in the absence of any metal ion due to free rotation around the C=N bond. But it was observed that addition of the metal ion results in chelation which restricts C=N isomerization and the emission intensity is greatly enhanced due to the formation of chelated complex [22–24]. Herein, we have designed and synthesized a novel coumarin derived Schiff base probe **1** as a "turn on" fluorescent sensor exhibiting high selectivity for detecting cadmium ion in aqueous media. The binding stoichiometry and modes of probe **1** towards Cd^{2+} ion were confirmed by FTIR spectra, ^{1}H NMR titration and Job's plot. The experimental observations for probable binding modes were further justified by computational studies employing DFT calculations.

Experimental Section

Reagents and Instruments

3–formyl chromone (Sigma–Aldrich), 5–amino–2–mercaptobenzimidazole (Sigma–Aldrich), $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $ZnCl_2$, $NiCl_2.6H_2O$, $FeCl_2.2H_2O$, $MnCl_2$ and $CdCl_2$ metal salts (Merck) were utilized as received. Absorption spectra were recorded on UV–1700 PharmaSpec UV–vis spectrophotometer (Shimadzu) using cuvettes of 1 cm path length and collected data were reported in λ_{max}/nm. Fluorescence spectra were measured using Shimadzu RF–5301PC Spectrofluorophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance AVII–300 MHz spectrometer. The High–resolution mass spectrum (HRMS) was measured on an Agilent ESI–Q–TOF mass spectrometer.

Synthesis of the Probe 1

The probe **1** was prepared by condensation of 5–amino–2–mercaptobenzimidazole with 3–formylchromone in a 1:1 stoichiometry in methanolic solution under reflux condition. A bright yellow solid product was obtained, filtered and dried in vacuo. The synthesized ligand was spectroscopically characterized by employing UV–vis, FT–IR, Mass and ^{1}H and ^{13}C NMR studies. [$C_{17}H_{13}N_3O_2S$], **1**: Yield: 80%, M.P: 185 °C, FTIR: 1604 ν(HC=N), 1641 ν(C=O), 1442 ν(C − N), 847 ν(C − S). UV − vis (λ_{max}, nm): 237, 277 (π − π*). ^{1}H NMR (ppm): 12.39 (−SH), 9.26 (HC=N), 7.9–6.9 (Ar − H). ^{13}C NMR (ppm): 180.09 (C=O), 168.61 (C=N), 156.10 (C − N), 135.45–112.20 (Ar − C). ESI − MS (*m*/*z*): 323 $[C_{17}H_{13}N_3O_2S]^+$, 321 $[C_{17}H_{13}N_3O_2S–2H]^+$.

Sample Preparation and Titration

The stock solutions of the metal ions (Cu, Co, Ni, Fe, Mn, Zn and Cd) were prepared in double distilled water with a concentration of 1.0×10^{-3}M and further diluted to a

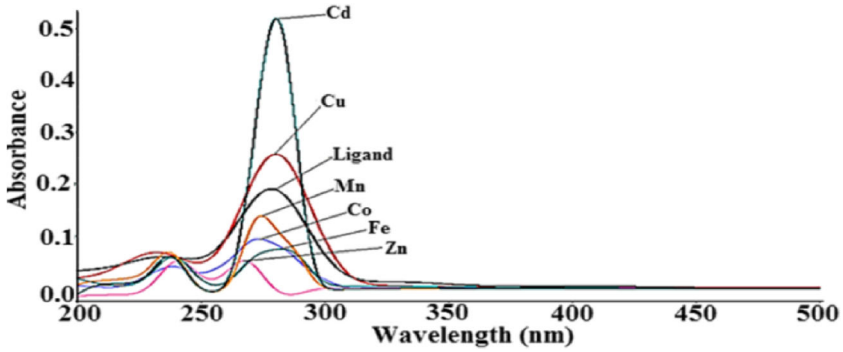


Fig. 1 Ion selective profile of the probe in presence of various divalent metal ions

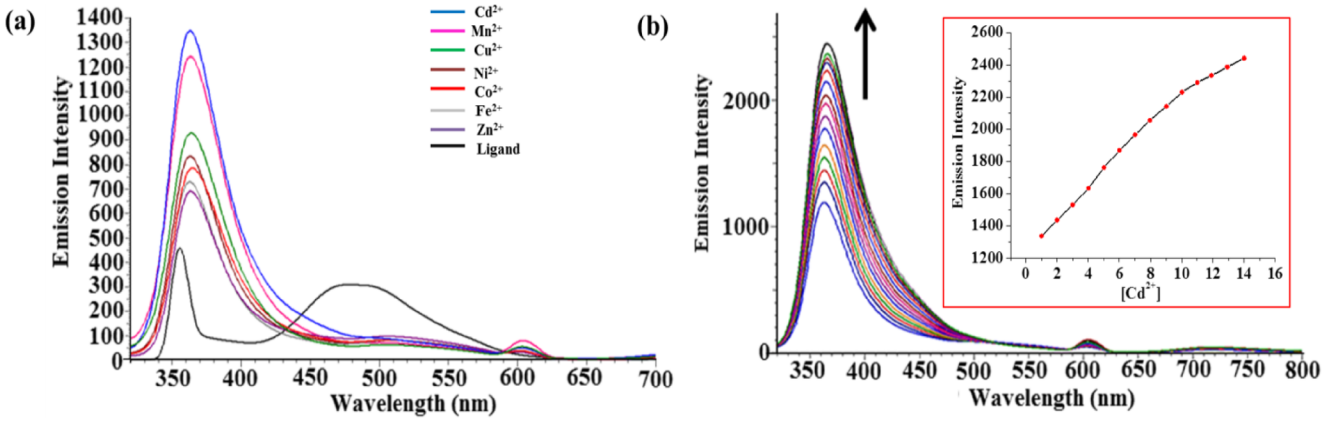


Fig. 2 **(a)** Fluorescence emission spectrum of probe **1** with different metal ions **(b)** Changes in the emission spectrum of the probe with increasing amount of Cd^{2+} [$\lambda_{ex} = 300$]

concentration of 1.0×10^{-5} M. The ligand **L1** stock solution was prepared at a concentration of 1.0×10^{-3}M in THF and further diluted to 1.0×10^{-5}M for carrying out the titration experiments. The stock solution of BSA was prepared using Tris-HCl buffer (pH = 7.4) in which the concentration is 1.5×10^{-6} mol/L. All the spectra measurements were carried out at room temperature.

Optical Studies

The sensing behaviour of the probe **1** towards various metal ions were studied by employing UV-vis and fluorescence spectroscopy in THF: H_2O (1:1 *v*/v) system. The fluorescence spectra of probe **1** were recorded with the excitation wavelength at 300 nm and a slit width of 5 nm.

Computational Studies

The theoretical calculations were carried out by employing Density Functional Theory (DFT) on deMon2k program [25]. The PBE functional with DZVP basis set and non–relativistic effective core potential (ECPS) CD (ECP20 SD) were assigned to the metal ion and the optimized structures of the probe and coordinated metal complex were determined based on energy minimized structures. The frontier molecular orbitals (HOMO and LUMO) and IR spectrum of the chemosensor alone and the metal bound complex were obtained and visualized using the Molden software (http://cheminf.cmbi.ru.nl/molden/).

Results and Discussion

Synthesis and Characterization

The probe **1** was synthesized by condensation reaction in which the π bond conjugation was extended *via* linking 4–oxo–4H–chromene–3–carbaldehyde with 6–amino–2,7a–dihydro–1H–benzo[d]imidazole–2–thiol through an imine bond (Scheme 1). The probe is structurally characterized by several spectroscopic techniques including FTIR, ^{1}H and ^{13}C NMR and mass spectroscopy (Fig. S1 and S2). The results were found to be in good agreement with the proposed structure of the chemosensor.

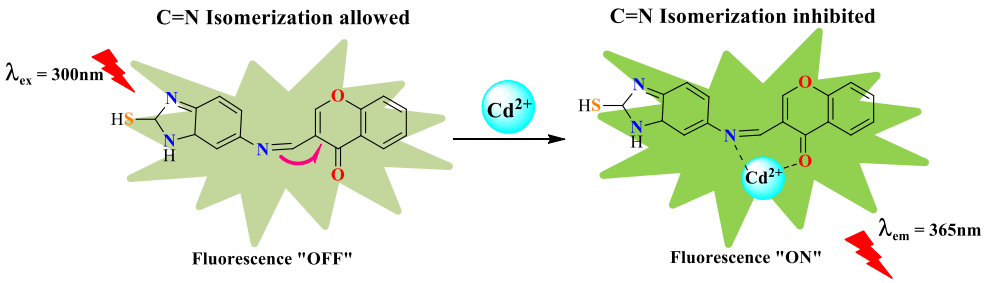


Fig. 3 TURN-ON/OFF fluorescence mechanism for the sensor probe **1** in presence of Cd^{2+}

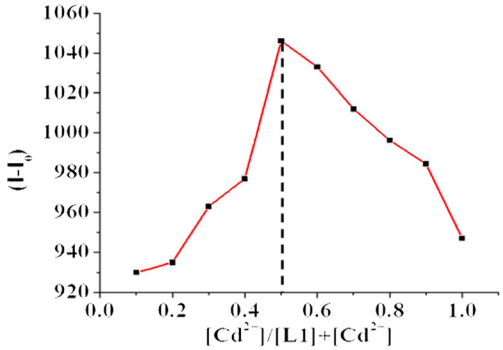


Fig. 4 Job's plot of the sensor probe with Cd^{2+} ion

Electronic Absorption Spectral Studies

The spectral properties and the selectivity of the probe towards various metal ions were studied in a 1:1 mixture of THF: H_2O. The electronic spectrum of the ligand probe (1.0×10^{-5}) exhibited an absorption band centered at 237 nm and 277 nm which could be assigned to π–π* transitions of the azomethine chromophore present in the ligand system (Fig. 1). Upon addition of Cd^{2+} ion a red shift of ~ 5 nm was observed with a significant enhancement in the absorption intensity, however, it does not lead to any appreciable color change in the probe solution. In presence of other metal ions a blue shift was observed with a slight decrease in the absorption intensity relative to the free ligand except for Cu^{2+} where the absorption intensity is found to increase. However, no change in the solution color was observed upon addition of these metal ions.

Fluorescence Spectral Studies

The fluorescence spectra of the probe alone displayed no significant emission after excitation at a wavelength of 300 nm however, addition of Cd^{2+} induces significant increase in the emission intensity. The fluorescence intensity also increases upon addition of other metals ions viz., Fe^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} but the enhancement is less as compared to Cd^{2+} ion except for Mn^{2+} (Fig. 2a). The noticeable "turn–on" response is ascribed to the binding of Cd^{2+} with the N atom of imine bond (–C=N) and carbonyl oxygen atom inhibiting C=N isomerization which results in chelation enhanced fluorescence effect (CHEF) [26] (Fig. 3). Further, titration experiments with Cd^{2+} in the range of 1–15 μM were carried out which resulted in a significant increase as evidenced in Fig. 2b. The plot of emission intensity versus increasing concentration of Cd^{2+} ion shows a linear relationship and these results indicate that the chemosensor could be utilized for the quantitative determination of Cd^{2+} in the aqueous solutions.

The stoichiometry of **1**–Cd^{2+} complex was determined by Job's plot [27] which showed that the emission maxima was obtained at a molar ratio of 0.5 indicating a 1:1 stoichiometry for the complexation (Fig. 4). The detection limit was calculated as low as 0.114 μM with a linear relationship according to the equation 3σ/S [28].

On the basis of 1:1 stoichiometric ratio of the **1**–Cd^{2+} complex as determined by Job's plot, the association constant K_a, was calculated with the help of Benesi–Hildebrand equation as written below [29]:

$$1/I–I_o = 1/I_{max}–I_o + 1/K_a(I_{max}–I_o)\left[Cd^{2+}\right]$$

The K_a was found to be 3.3×10^5 M^{-1} with a good nonlinear relationship (R = 0.9917) obtained by employing nonlinear curve fitting model [30].

Effect of Probe Concentration and Time on Emission Intensity

The effect of probe concentration on the emission spectrum of the **1**–Cd^{2+} complex was studied by incremental addition of the probe in the concentration range of 1–15 μM. As shown in Fig. 5a, a gradual decrease with the increasing probe

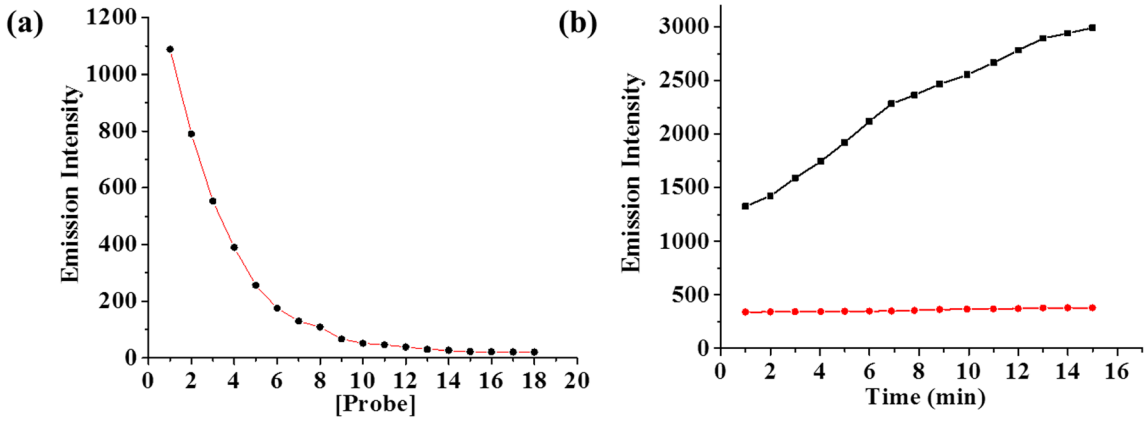


Fig. 5 **(a)** Emission intensity of **1**–Cd^{2+} complex as a function of probe concentration **(b)** Time dependant plot for emission intensity of chemosensor in the absence (red) and presence of Cd^{2+} (black)

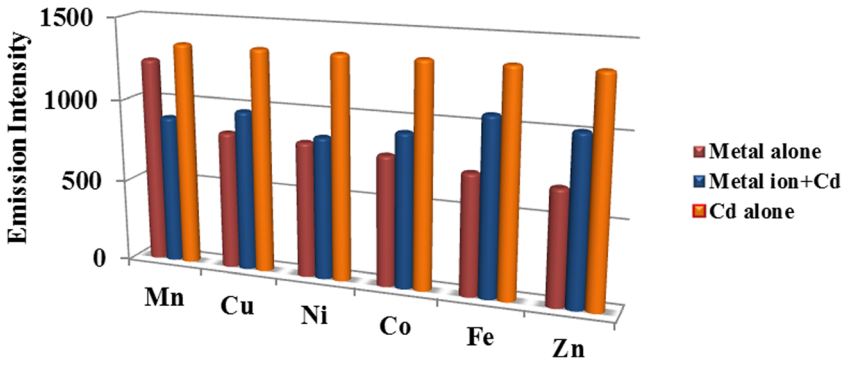


Fig. 6 Fluorescence response of the sensor probe **1** towards various metal ions in presence of Cd^{2+}

concentration was observed but it becomes constant at higher concentration. The response time of the fluorescent sensor was measured in the presence and absence of Cd^{2+} in a time interval of 1–15 min (Fig. 5b). No appreciable change in the fluorescence intensity was observed in the absence of Cd^{2+} however, the fluorescent emission intensity turns on remarkably upon addition of aqueous solution of Cd^{2+} suggesting rapid response of the ligand towards the metal ion. For higher Cd^{2+} concentration the ligand shows a fast response time indicating that the recognition process was accomplished instantaneously without any delay in time.

Competitive Binding Studies with Metal Ions

The practical applicability of the probe **1**, as a selective fluorescent probe for Cd^{2+} was monitored in presence of various competitive metal ions. As shown in Fig. 6 fluorescence enhancement caused by the Cd^{2+} ion remained unaffected and no significant interference was observed for fluorescent recognition in presence of different metal ions. Consequently, the probe **1** could be employed as a sensitive fluorescence based sensor for the detection of Cd^{2+} in presence of different metal ions.

Reversibility Studies with EDTA

The reversibility is an important criterion to examine the chemical reusability of the sensor for its practical application.

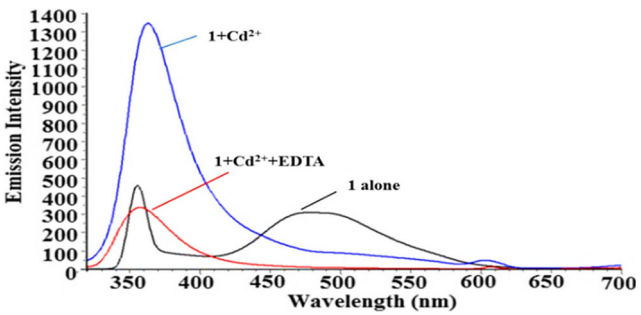


Fig. 7 Variation in the emission intensity of the **1**–Cd^{2+} upon addition of an equivalent amount of EDTA

To determine whether the formation of **1**–Cd^{2+} is reversible in nature, emission titration were carried out with EDTA (Fig. 7). Upon addition of an equivalent amount of EDTA to the probe solution containing Cd^{2+} quenching is observed and the fluorescence intensity becomes comparable to that of the probe alone which could be ascribed to the removal of Cd^{2+} by EDTA. This clearly indicates that the chemosensor **1** could be restored for repeated use.

Probable Binding Mode of 1 with Cd^{2+}

The interaction between **1** and Cd^{2+} was studied by employing FTIR and ^{1}H NMR spectroscopy. The IR spectrum of the probe in presence of Cd^{2+} revealed a red shift in

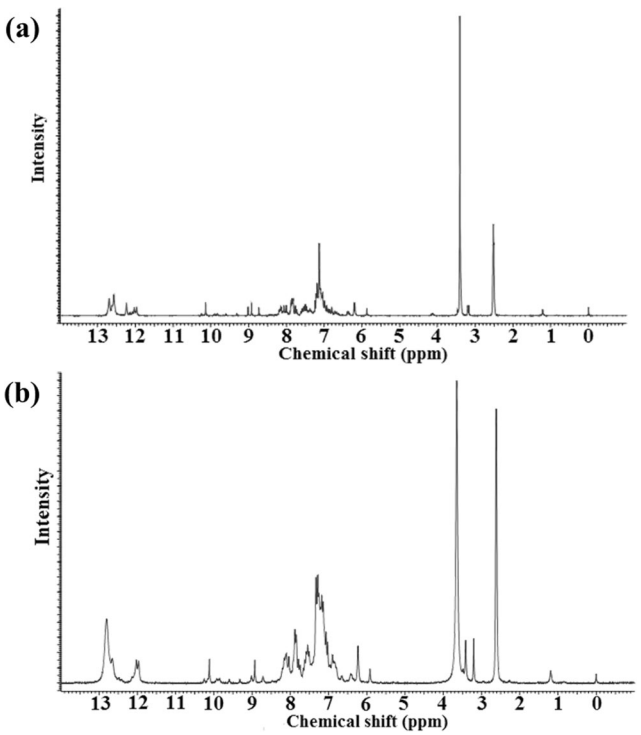


Fig. 8 ^{1}H NMR spectra for the **(a)** probe **1** alone and **(b)** in presence of 1.0 equivalent of Cd^{2+}

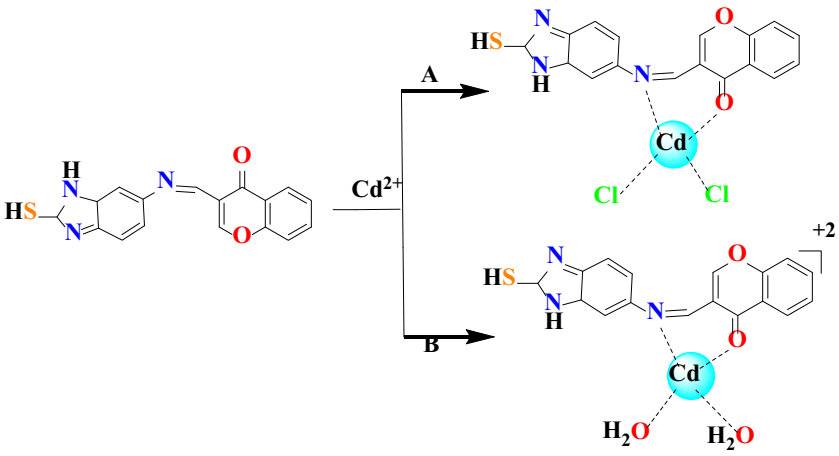


Fig. 9 Probable modes of interaction for sensor probe **1** with Cd^{2+}

the imine nitrogen band as well as for the carbonyl stretching frequency. The band centered at 1604 cm^{-1} attributed to (–N=CH) for the probe **1** is observed at 1607 cm^{-1} after complexation while the band for (–C=O) at 1641 cm^{-1} is shifted to 1647 cm^{-1}. In the ^1H NMR it was observed that upon addition of 1 equivalent of Cd^{2+}, the imine proton (–N=CH) and the aromatic protons which appears at 9.26 ppm and 7.9–6.9 ppm were shifted to downfield suggesting that the imine nitrogen atom and carbonyl oxygen atom of the chromone moiety are involved in binding with the Cd^{2+} ion (Fig. 8).

Validation of Sensing Mechanism by DFT Calculations

To elucidate the electronic structure of the sensor probe and to further validate the sensing mechanism of the probe towards Cd^{2+}, DFT calculations were performed using deMon2k software package. The optimized structure of probe alone and upon complexation with Cd^{2+} (Fig. S3) reveals that the central metal ion adopts a tetrahedral geometry in coordination with the imine nitrogen, carbonyl oxygen and possibly two aqua or chloro ligands (Fig. 9). The frontier orbital analysis shows that for the probe alone the HOMO orbital is centered at 5-–aimno–2–mercapto benzimidazole moiety while the LUMO spreads over the coumarin ring (Fig. S4). Upon coordination with the Cd^{2+} the HOMO electron density is centered on the chlorine atom coordinated to the Cd (II) metal centre in case of mode **A** while it is located around imine bond and benzimidazole ring in case of mode **B**. The LUMO orbitals are localized over the whole ligand molecule for mode **A** however, for mode **B** it is mainly distributed over the coumarin unit (Figs. 10 and 11). Furthermore, the DFT studies showed that the energy gap for HOMO and LUMO in the probe **1** ($\Delta E = 0.0757$) is considerably lowered upon coordination of

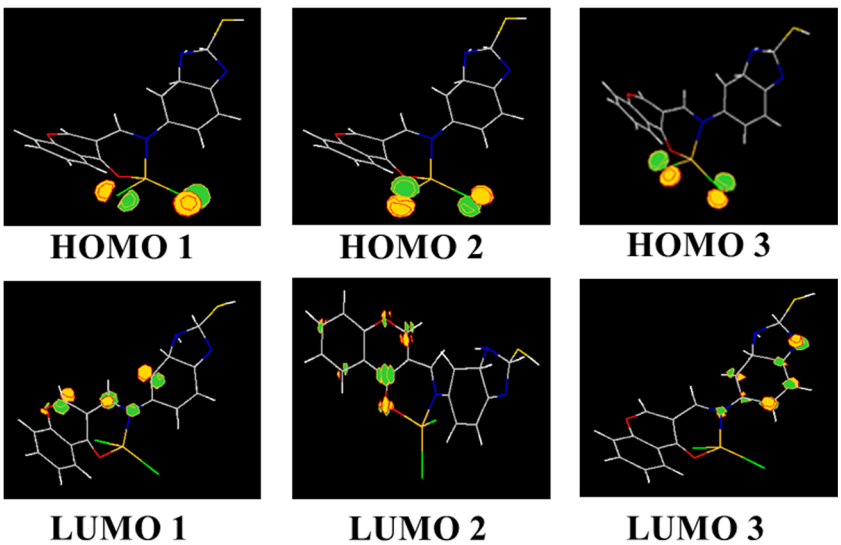


Fig. 10 HOMO and LUMO molecular orbitals of the **1**–Cd^{2+} complex in mode A

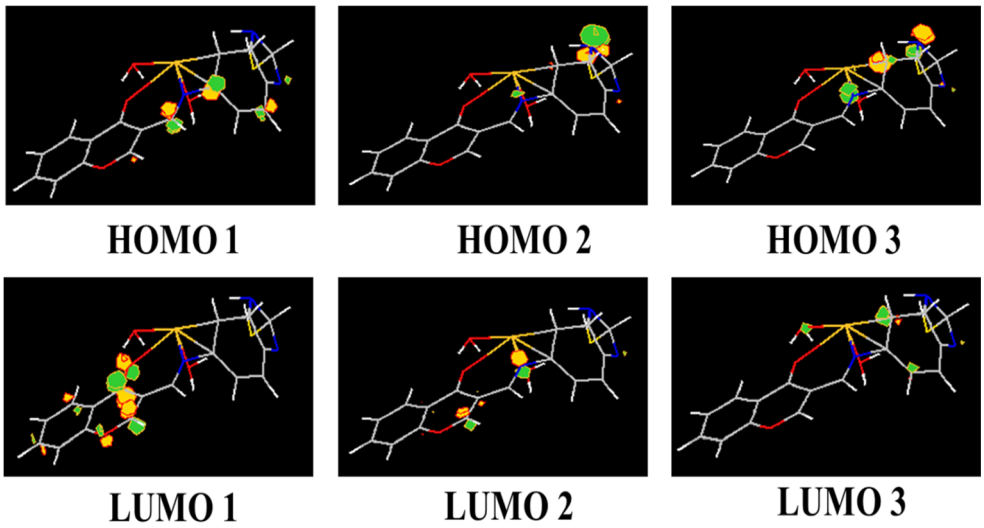


Fig. 11 HOMO and LUMO molecular orbitals of the **1**–Cd^{2+} complex in mode B

Cd^{2+} ion. However, the energy values in case of mode **A** ($\Delta E = 0.0244$) is found to be higher than the energy gap in mode **B** ($\Delta E = 0.0202$), suggesting the higher stability of Cd^{2+} aqua complex and the probable binding of the probe **1** occurs *via* complexation through mode **B** (Table S1). Therefore, it was concluded that Cadmium ion binding will result in the lowering of the HOMO orbital of the ligand probe leading to the "turn on" sensing mechanism of the metal ion. The observed results showed that the the electron transfer process was significantly arrested upon coordination of Cd^{2+} ion to **1** and leads to increment in the fluorescence intensity.

The IR spectra of the probe and **1**–Cd^{2+} complex were also calculated for different modes by employing the optimized structures (Fig. S5–S7). The theoretically observed spectral behaviour correlates well with the experimentally obtained FTIR spectrum with similar spectral shift (Table S2). The bond angles and bond distances have also been measured for the probe alone and after coordination with the Cd^{2+}. From the optimized geometry of the probe **1**, the bond length for –C=N and –C=O were found to be 1.269 Å and 1.217 Å, respectively which are stretched out to 1.367 Å and 1.254 Å upon coordination to Cd^{2+}. Similarly, the binding of Cd^{2+} triggered the change in the bond angles corresponding to C—O=C and C—N=C from 121.03° and 130.72° to 124.30° and 117.65° respectively. These observed changes in the bond length and bond angles of the probe atoms after coordinating with the metal ion further validates the binding with Cd^{2+} via N atom of imine bond and the carbonyl oxygen atom.

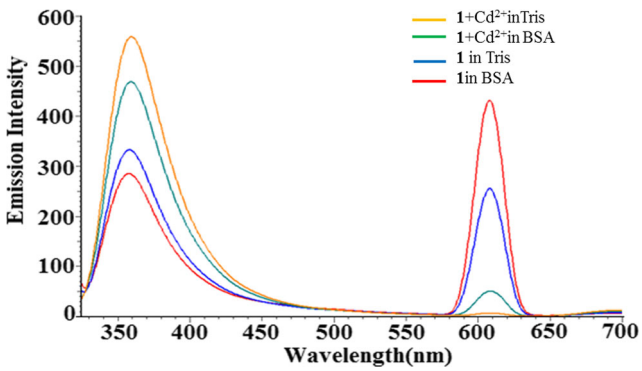


Fig. 12 Fluorescence detection of Cd^{2+} (1.0 equivalents) in Tris buffer (pH = 7.4) and BSA media

Detection of Cd^{2+} in BSA Media and Molecular Docking Studies

For the quantitative detection of Cd^{2+} ions by probe **1** in the biological systems, the fluorescence spectral studies were performed in presence of bovine serum albumin (BSA). The probe **1** shows weak fluorescence upon addition of an equivalent concentration of BSA and also in presence of Tris buffer. However, the emission intensity of the ligand probe increases upon addition of Cd^{2+} (red shift of ~2 nm) in Tris buffer which is more as compared to the enhancement observed in BSA media (Fig. 12). Titration experiments of the probe **1** with increasing Cd^{2+} concentration in the BSA media reveals a gradual increase in the fluorescence intensity (Fig. 13) with a considerable red shift from ~10 nm. No significant enhancement in the emission intensity after addition of 1.5 equivalents of the Cd^{2+} was observed and the plot shows a linear relationship at low concentration suggesting the quantitative determination of metal ion in BSA media thus, possibly allowing its assessment in the human blood plasma.

Molecular docking studies were carried out to determine the preferential binding site and favourable energy changes upon introduction of the metal ion in the probe system. The resulting docked pose shows that the binding energy for the probe alone

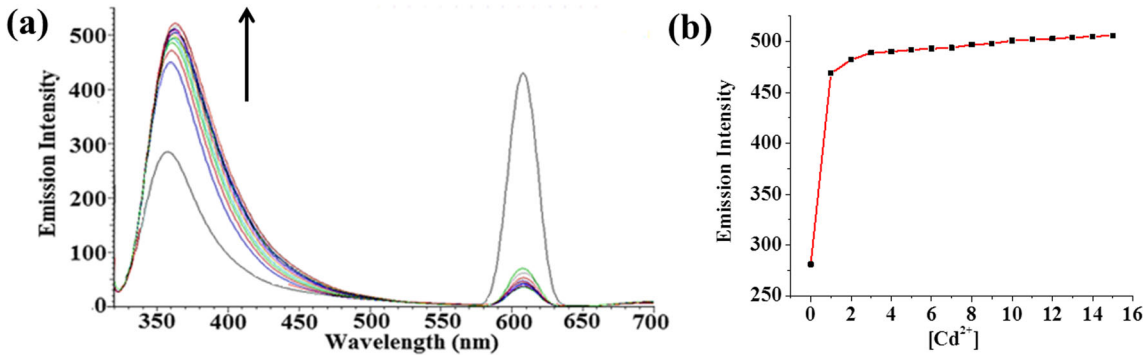


Fig. 13 **(a)** Fluorescence titration of probe **1** with Cd^{2+} (0–15 μM) in BSA media. (**b**) Plot of emission intensity as a function of [Cd^{2+}]

was found to be – 64.91 KJ/mol which was further lowered to – 78.33 KJ/mol validating that the interactions are energetically favourable in presence of metal ions within the cavity of Sudlow site II present in the protein structure (Fig. S8).

Comparison of the Reported Sensor with Previous Literature Reports

A comparative study of the synthesized probe with some previously reported fluorescence based sensors for the detection of Cd^{2+} shows that it exhibits a comparable or higher analytical performance with them (Table S3). Thus, we can say that the synthesized probe could be employed as an efficient chemosensor for selectively detecting the micromolar concentration of Cd^{2+} in the environmental and biological samples as well.

Conclusions

In summary, we have designed and synthesized a new coumarin derived Schiff base ligand (3)–((2–mercapto–2,7a–dihydro–1H–benzo[d]imidazol–6–yl)imino)methyl)–4H–chromen–4–one as a sensor probe which showed excellent sensitivity for the selective detection of cadmium ion in presence of other competing metal ions. The "turn on" fluorescent mechanism in presence of Cd^{2+} is attributed to the restricted C=N isomerization resulting due to chelation enhanced fluorescence effect. The 1:1 binding stoichiometry was determined by employing Job's plot with an association constant of 3.3×10^5 M^{-1}. The reversibility of the probe was ascertained by EDTA experiment. The sensing phenomenon of the probe as proposed by the experimental results including FTIR and ^{1}HNMR titrations is further supported by DFT based computational studies. Titration experiments of the probe **1** with increasing Cd^{2+} concentration in the BSA media were performed and the preferential binding sites were determined by molecular docking studies. Because of its lower detection limit, as low as 0.114 μM, the sensor could be employed to detect lower concentrations of Cd^{2+} in biological and environmental samples for its practical application.

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