

A new benzothiazin-functionalized calix[4]arene-based fluorescent chemosensor for the selective and sensitive detection of Co²⁺ ion

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Abstract

Calixarenes, which have a great place in supramolecular chemistry, has become the most prominent macrocyclic compounds in synthetic organic chemistry due to their easy synthesis and functionalization. In this study, p-tert-butyl calix[4]arene dihydrazide derivative was synthesized and then reacted with 3-oxo-3,4-dihydro-2H-benzo[b][1, 4] thiazin-2-ylideneacetyl chloride to prepare new calixarene based chromophore compound **4**. The structure of the synthesized compound was elucidated by spectroscopic methods such as $^1\text{H-NMR}$ $^{13}\text{C-NMR}$ and FT-IR spectroscopy. Chromogenic and fluorescence properties of compound **4** were evaluated. It was observed from both studies that compound **4** was Co^{2+} selective and shows fluorescence *Switched-off* behavior. Stoichiometry, binding constant and the detection limit was calculated. The stoichiometry between compound **4** and Co^{2+} was found to be 1:1. The binding constant value (K) was calculated as 666.67 M^{-1} using Benesi–Hildebrand equation, while the detection limit for Co^{2+} ion was calculated as $0.0465 \mu\text{M}$.

1. Introduction

Cobalt is an important metal among the transition metal ions, with a considerable role in biological, environmental, and industrial fields [1]. It has essential as well as adverse effects on human health. Cobalt is consumed on daily basis, in the form of breathing air, food, and water [2]. It is a mandatory element for vitamin B12, which is an important chemical to balance the health system [3]. Overtake of intake limits can cause various health issues such as neurological diseases, asthma, thyroid dysfunction [4]. In the latest reports of the environmental protection agency, the permissible limit of Co^{+2} at 0.1 ppm (1.7 mM) has been standardized in groundwater quality [1]. Thus, effective observation and analysis are necessary for cobalt toxicity in different fields of application. For this, there is a dire need of developing a selective and sensitive method to detect Co^{+2} at a low level in environmental samples.

Fluorescence and chromogenic techniques are considered sensitive, selective, and economical methods for the detection of charged or neutral species at a low level [5–7]. Recently, the numbers of fluorophores and chromophores have been developed based on the supramolecular system as well as small molecules [8–17]. Among supramolecular based sensors, Calixarene-based molecules have received intense attention in the last few years in different fields of applications as carriers, sensors, and catalyst [14, 18–24]. They are one of the efficient three dimensional macromolecules with flexible structural property [25, 23]. Synthesized by the simple base-catalyzed reaction of formaldehyde and phenol, they can be functionalized in different positions of choice [26, 27]. Lower polar rim composed of phenolic oxygens has been widely functionalized with active groups to bind ionic species [28]. The designing of calixarene based receptors with cooperative binding sites is an area of interest. These receptors can be of three types: (a) Receptor, which is susceptible to change its spectroscopic properties with interacting analyte of interest; (b) Analyte selective receptor with specific labeling moiety; and (c) third party receptor which connects two active moieties [12, 29].

These receptors further divided into subcategories, based on different working mechanisms. These receptors may follow photo-induced electron/energy transfer (PET) mechanism, metal-ligand charge transfer (MLCT), intramolecular charge transfer (ICT), excimer/exciple formation, imine isomerization, chelation-enhanced fluorescence (CHEF), and fluorescence resonance energy transfer (FRET) [30–32].

In literature, a little amount of work has been carried out on calixarene based sensors for the detection of cobalt ion. For instance, Maity et.al worked on calixarene derivative incorporated with the dithiocarbamate unit and achieved a detection limit of 10^{-12} M for Co(II) [33]. Modi et. al prepared thiacalix[4]arenetetra-(quinoline-8-sulfonate) by condensation of thiacalix[4]arene (TCA) and 8-quinoline sulfonyl chloride for the detection of cobalt.

The detection limit in that study was found to be up to 1.038×10^{-9} M. Hence, it is important to explore new selective and sensitive chromophores for the detection of very important cobalt ion [34].

In this study, we have prepared calixarene based chromophore functionalized with benzothiazin for the detection of cobalt ion at low level concentration. Different parameters were optimized to develop the cobalt detection method with the chromophore.

2. Experiment

2.1 Material

All the chemicals and solvents used in this work were purchased from local vendors and were reagent and analytical grade. Metal perchlorate salts were from Sigma-Aldrich and obtained from local sources. Thin layer chromatography (TLC) was performed on precoated silica gel plates (SiO_2 , PF254, Merck). FT-IR spectra of compounds were recorded on Perkin Elmer spectrum 100 FT-IR spectrometers (ATR). For $^1\text{H-NMR}$ spectra, a 400 MHz Varian NMR spectrometer was used using CDCl_3 and DMSO as solvents. UV /Vis spectra were taken with a Shimadzu UV-1700 spectrophotometer. Fluorescence spectra were recorded with a Perkin Elmer LS 55 spectrometer. All the metal ion solutions (perchlorate salts) were prepared in deionized water.

2.2 Synthesis

Fig.1 and **2** show the synthesis of the fluorophore (C) and calix[4]arene based fluorescence derivative (**4**). The parent compounds depicted in **Fig.1**, were synthesized according to reported methods 32. Compound **1-3** were also prepared according to the literature method [32-34]. The procedure for synthesis of compound **4** is given below: [35]

2.2.1 Preparation of 3-oxo-3,4-dihydro-[1,4]benzothiazin-2-ylidene) acetic acid (B)

0.3 g of compound **A** was refluxed in 10 M NaOH in ethanol for 40 hours. The reaction was monitored by $^1\text{H-NMR}$. The solvent was then evaporated and precipitated with acidic water, filtered and washed with

distilled water and oven dried. Compound **B** was obtained in 80% yield. FT-IR: $^1\text{H-NMR}$ (DMSO) δ (ppm): 6.88 (s, 1H, -CH-), 7.03-7.23 (m, 2H, ArH), 7.21 (t, 1H, $J=7.14$, ArH), 7.40 (d, 1H, $J=7.68$, ArH), 11.5 (s, 1H, Ar-NH-), 11.6 (s, 1H, O=C-OH). Anal. Calc.: $\text{C}_{10}\text{H}_7\text{NO}_3\text{S}$. C, 54.29; H, 3.19; N, 6.33; S, 14.49%. Found: C, 54.33; H, 3.28; N, 6.41; S, 14.51%.

2.2.2 Preparation of 3-oxo-3,4-dihydro-[1,4]benzothiazin-2-ylidene) acetic chloride (C)

0.3 g (1.35 mmol) of the compound **B** was dissolved in 35 ml of benzene. 4 ml of thionyl chloride was added to it and refluxed for 3.5 hours. The solvent was then completely distilled under a vacuum and used in the next step without further purification.

2.2.3 Reaction of compound C with *p*-tert-butylcalix[4]arene dihydrazide derivative (3)

Compound **C** contained in a 250 ml flask was dissolved in 10 ml benzene. 0.534g (0.675mmol) compound **3** was added by dissolving in 10 ml benzene. It was stirred at room temperature. Then 360 mL (1.35 mmol) of pyridine was added. It was stirred at room temperature for 16 hours. The reaction was followed by TLC. The product was washed with water to obtain compound **4**. Yield; 0.454g (85%). $^1\text{H-NMR}$ (DMSO) δ (ppm): 1.10 (s, 18H, but), 1.16 (s, 18H, but), 3.22-3.37 (m, 4H Ar-CH₂-Ar), 4.08-4.29 (m, 4H, Ar-CH₂-Ar), 4.56 (s, 4H, -CH₂-), 7.04-7.39 (m, 18H, ArH_{Oxo}), 8.33 (s, 2H, -NH-). $^{13}\text{C-NMR}$ (DMSO) δ (ppm): 166.8, 149.9, 148.3, 142.3, 133.5, 127.5, 126.4, 126.1, 123.76, 117.4, 116.4, 34.5, 34.1, 31.8, 31.4. Anal. Calc.: $\text{C}_{68}\text{H}_{74}\text{N}_6\text{O}_{10}\text{S}_2$. C, 68.09; H, 6.22; N, 7.01; S, 5.35%. Found: C, 68.13; H, 6.13; N, 7.09; S, 5.37%.

2.2.4 Procedure for UV-visible and fluorescence study

Interaction of metal with ligand was examined by UV-visible and fluorescence spectroscopy. For this, the stock solution of ligand **4** (1.0×10^{-3} M) was prepared in 10 mL of dimethylsulfoxide (DMSO) followed by dilution to 1.0×10^{-4} M into 100 mL for absorption study and 1.0×10^{-7} M for fluorescence study. Metal ion (perchlorate salts) solution (1.0×10^{-3} M) was prepared in a mixed solution of ethanol and water in a 1:1 ratio. Dilution was made according to absorption and fluorescence response. Briefly, 2 mL of ligand (1.0×10^{-4} M) was treated with metal ion solution (1.0×10^{-3} M) using micropipette of 100 μL and absorption was recorded [36]. The emission response of ligand **4** was estimated by titration experiments in DMSO. In 10 mL test tubes, 2 mL of ligand (1.0×10^{-7} M) and 2 mL of metal salt (1.0×10^{-4} M) were mixed together and emission intensities were measured at excitation wavelength 351 nm.

2.2.5 Stoichiometry, binding constant, and limit of detection.

Stoichiometry of ligand and metal was determined by Job's method. For this, an equimolar solution (1.25×10^{-5} M) of ligand and metal ion was prepared in the varying ratios of 1:9 to 9:1 [35]. Stern-Volmer method was applied to analyze the nature of the quenching or enhancement process in the complexation [37,38].

See formulas 1 and 2 in the supplementary files.

3. Results And Discussion

3.1 Synthesis and characterization

As a part of our ongoing studies on the design of calix[4]arene based sensors, in this work, we have prepared benzothiazin anchored calix[4]arene derivative (**4**), depicted in **Fig.2**, due to practical synthesis and high yield. The presence of different electron donor groups on receptors and reporter positions allow the electron deficient metal ions to effectively bind.

The presence of amine, thio and carbonyl group in the receptor aligned in parallel and flexible position may effectively make a complex with the metal ion. Characterization of compound **4** was confirmed with spectroscopic methods. The $^1\text{H-NMR}$ spectra of all compounds are given in Supporting Information (**Fig.S1-7**). $^1\text{H-NMR}$ spectrum of compound **4** was taken in DMSO (**Fig.S6**). The appearance of multiplets at 7.04-7.39 ppm may be due to overlapped aromatic protons. Singlet present at 8.33 ppm maybe correspond to amine proton.

FT-IR spectrum of compound **4** shown in fig. **S2** shows different stretching and bending bands due to the presence of different functional groups. The stretching bands appeared at 3228 cm^{-1} and 2974 cm^{-1} are referred to as $\nu\text{O-H}$, $\nu\text{N-H}$, and $\nu\text{C-H}$, respectively. Broadband appeared at 1655 cm^{-1} may be due to $\nu\text{C=O}$ and 1487 cm^{-1} corresponds to aromatic $\nu\text{C=C}$ bonds.

3.2 UV-visible and Fluorescence study

After thorough characterization of compound **4**, UV-visible and fluorescence studies were performed. **Fig.3** a shows the absorbance behavior of compound **4** ($1.0 \times 10^{-4}\text{ M}$) upon the addition of different metal ions ($1.0 \times 10^{-3}\text{ M}$). It can be seen from spectra that bathochromic shift occurred upon the addition of Co^{2+} ion to the compound **4** solution from 367 nm to 394 nm due to the formation of charge transfer complex between compound **4** and Co^{2+} ion having $n \rightarrow \pi^*$ electronic transition (**Fig.4**).

Similarly, compound **4** displayed a maximum intensity at 412 nm (λ_{ex} . 330 nm) in its fluorescence spectrum that was recorded at neutral pH with a concentration of $1.0 \times 10^{-7}\text{ M}$ (**Fig.5**). It was observed that there is no major change in intensity of compound **4** upon the addition of different metal ions except Co^{2+} ion. This marked quenching due to Co^{2+} ion may be due to electron transfer from non-bonding to low-lying empty d-orbital of Co^{2+} ion. The quenching ability was evaluated from the Stern-Volmer equation (Equation 1). We have also investigated the concentration effect of metal ion on the intensity of compound **4**. There is gradual decrease in intensity of compound **4** upon addition of different concentration of Co^{2+} ion in the range of 0 to 10 equivalent (**Fig.6**), demonstrating "switched off" mechanism and enhanced PET (photoinduced electron/energy transfer) due to electron transfer (**Fig.10**).

3.3 Stoichiometry and binding constant

Fig.7a shows the Job's plot with maximum absorption was observed at 0.6 mole fraction, which indicates 1:1 stoichiometry between compound **4** and Co^{2+} . It can be seen in **Fig.7b**, there is a linear relationship between the concentration of Co^{2+} ion and intensity. In order to determine the stoichiometry of compound **4** and Co^{2+} complex, Job's continual variation method was used. The detection limit for Co^{2+} was calculated to be 0.0465 μM .

The binding constant for the compound **4** and Co^{2+} ion complex was calculated from Benesi-Hildebrand equation (Equation 2). **Fig.8** shows the linear plot for $1/[M]$ against $1/I-I_0$ and the binding constant value obtained as 666.67 M^{-1} , that was calculated from the regression equation obtained from the plot.

3.4 FT-IR study

The recognition mechanism of compound **4** with the Co^{2+} ion was evaluated by FT-IR study. In **Fig.9a**, multiple bands are observed corresponds to the presence of different functional groups present in compound **4**. The stretching vibration peaks of Carbonyl (C=O) of amide linkage can be observed at 1655 cm^{-1} 1387 cm^{-1} , respectively. However, peaks are shifted in the **4-Co²⁺** complex (**Fig.9b**), broad peak at 1655 cm^{-1} split into two small peaks 1667 and 1607 cm^{-1} , respectively, which indicates the formation of the complex between compound **4** and the Co^{2+} ion (**Fig.9**).

As seen in **Fig.10**, the detection properties of **4** against different metal ions, such as Hg^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} , Fe^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} and Ni^{2+} were tested by spectroscopic studies. The addition of the Co^{2+} ion caused the visible color to turn black, while no visible color change was observed by the other metal ions. These results showed the selectivity of **4** towards Co^{2+} ion.

Conclusion

In summary, we have successfully synthesized a new calixarene derivative appended with 3-oxo-3,4-dihydro-2H-benzo [b] [1,4] thiazin-2-ylidene a strong fluorophore. The compound **4** was selective for Co^{2+} ion at very low concentration and exhibited switched behavior upon the addition of Co^{2+} ion. The fluorescent compound (**4**) acts as a selective sensor for Co^{2+} ion in the presence of other metal ions. This compound could be used as a biosensor for the detection of Co^{2+} ion since this ion has an important place in the living body.

Declarations

Author's Contributions

Fatimah Fateh: Conceptualization, Methodology, Investigation, Visualization

Ayşe Yildirim: Conceptualization, Methodology, Investigation, Visualization

Asif Ali Bhatti: Conceptualization, Investigation, Writing - Review & Editing

Mustafa Yilmaz: Conceptualization, Supervision, Funding acquisition, Resources, Writing - Review & Editing.

Data Availability: All data generated or analyzed during this study are included in this published article [and its supplementary information files]

Declaration of Competing Interest

The authors declare that they have no conflict of interest.

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Table

Due to technical limitations, Table 1 is only available as a download in the supplementary files section.

Figures

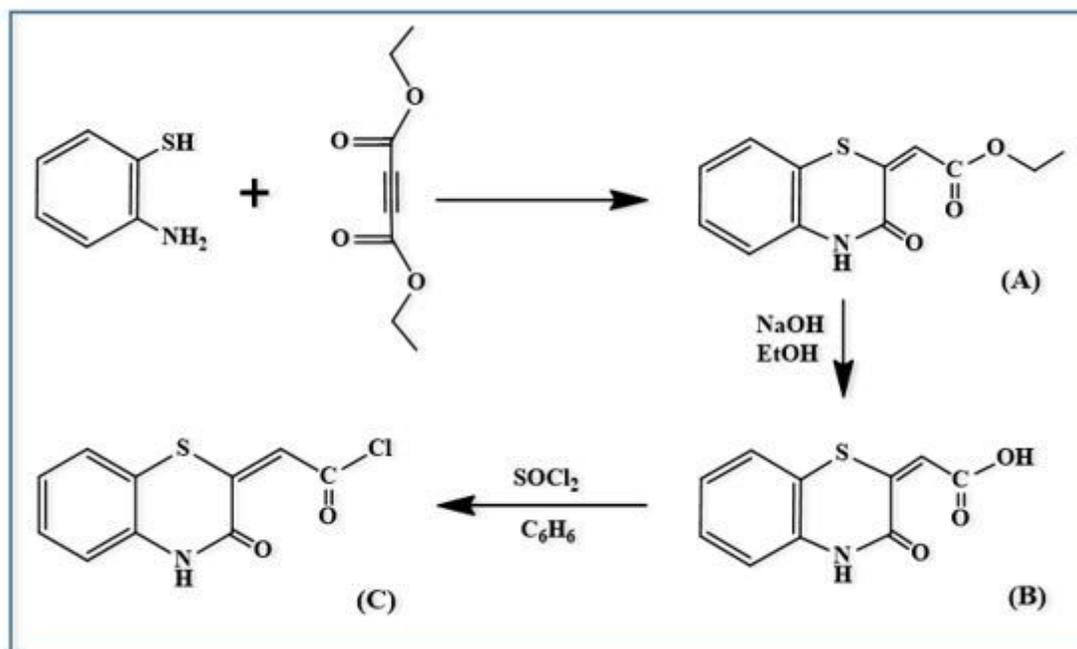


Figure 1

Schematic route for the synthesis of acid chloride derivative.

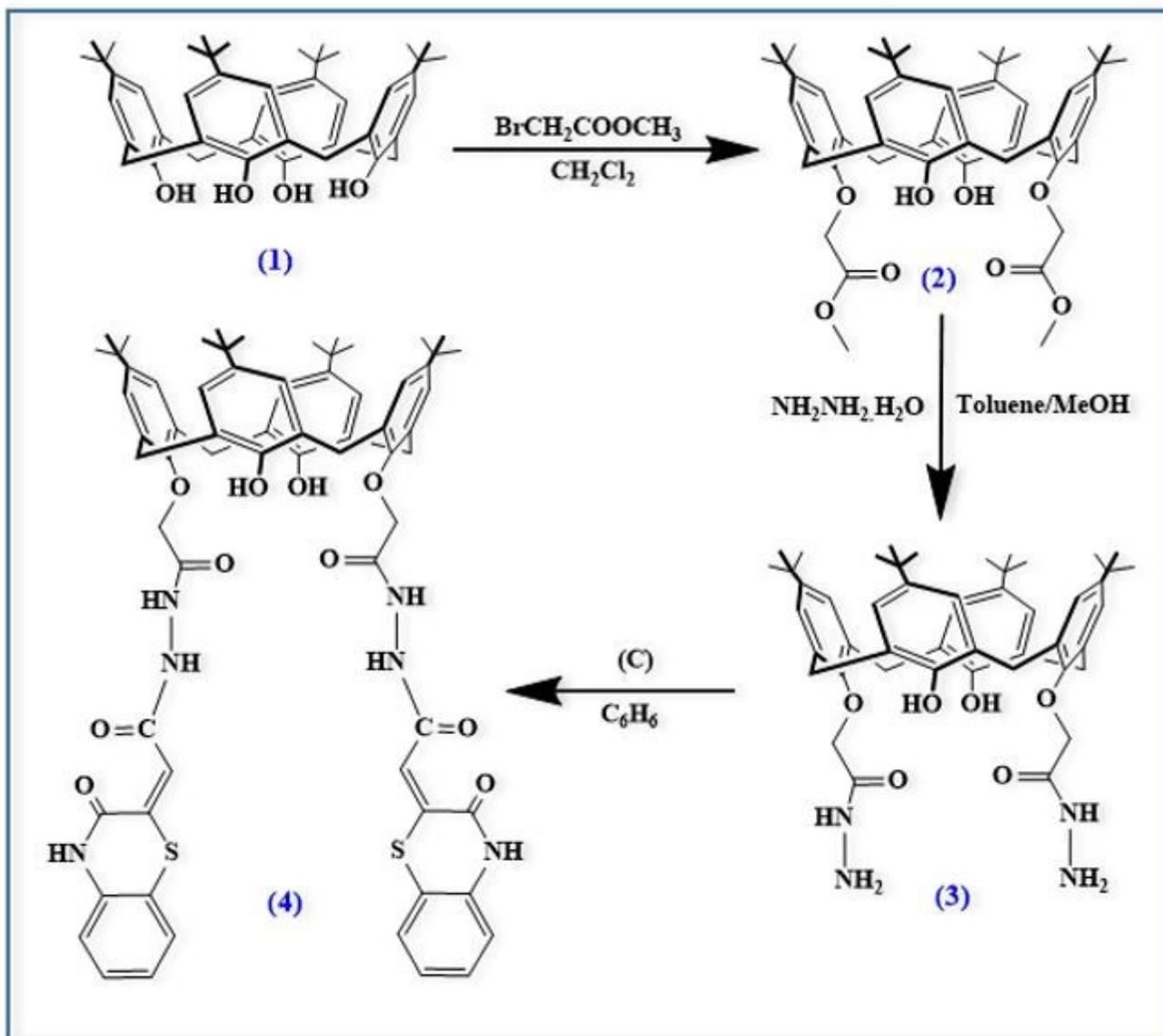


Figure 2

Schematic route for the synthesis of calix[4]arene based fluorescence derivative (4).

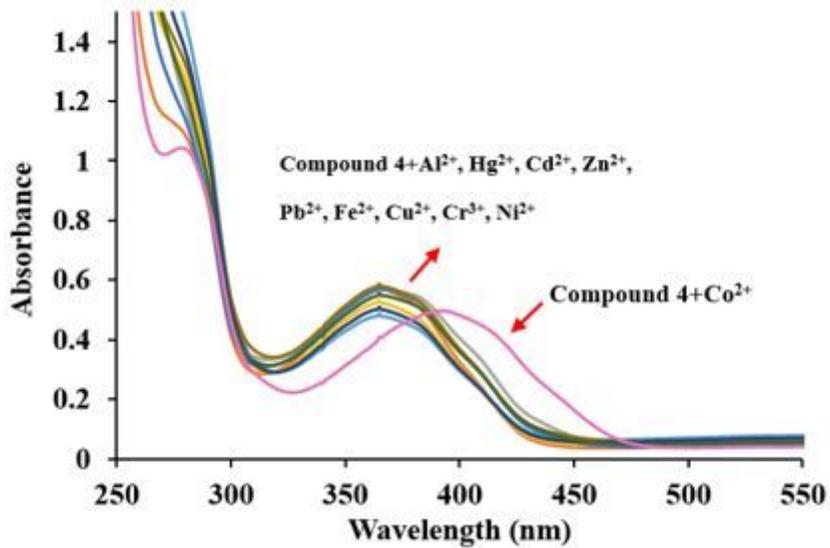


Figure 3

Effect of different metal ions (1.0×10^{-3} M) on compound 4 (1.0×10^{-4} M).

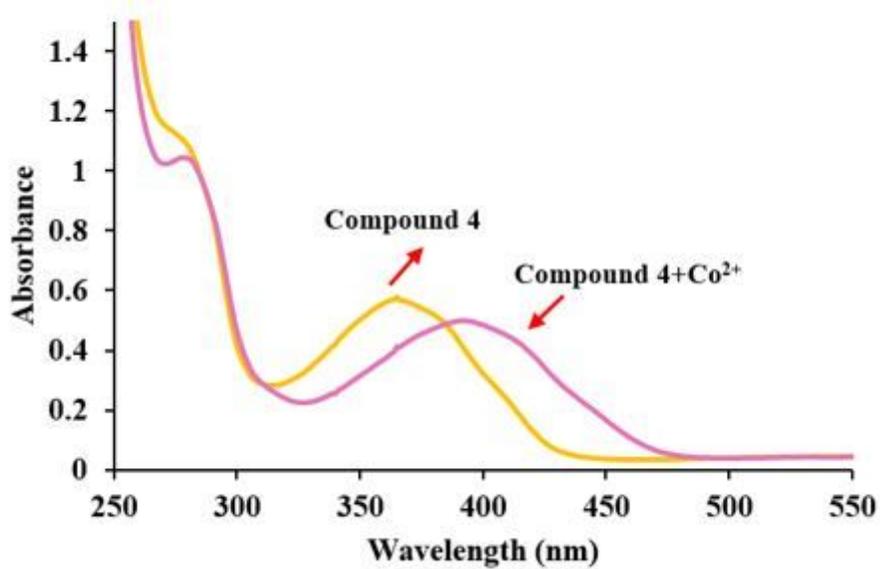


Figure 4

Absorption spectra of compound 4 (1.0×10^{-3} M) after addition of Co²⁺ ion (1.0×10^{-4} M).

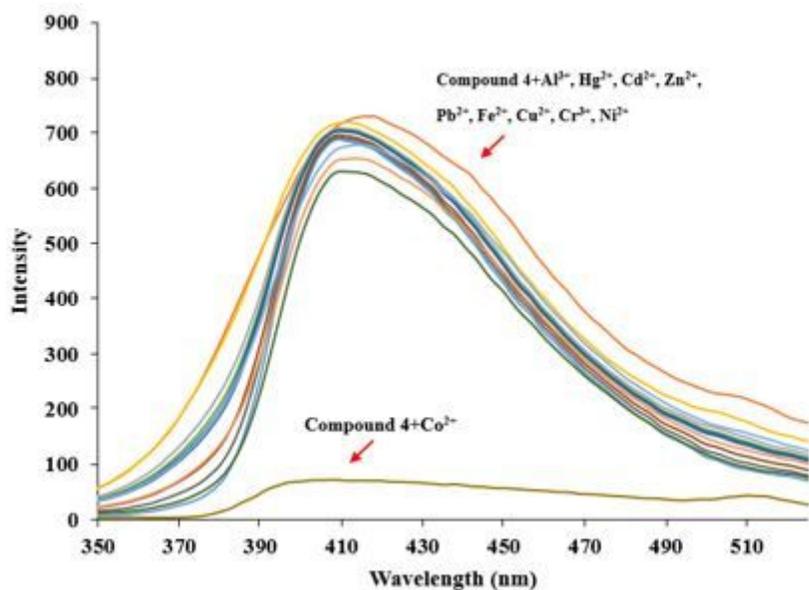


Figure 5

Fluorescence spectrum of compound number 9 ($1.10 \cdot 10^{-7}$ M, DMSO) in the presence of different metal ions ($\lambda_{\text{exc}} = 330$ nm)

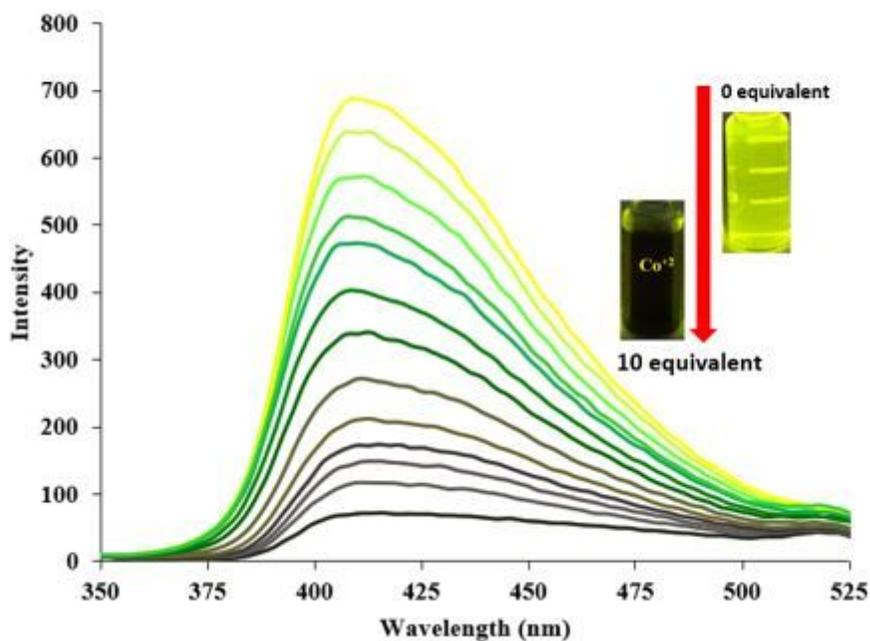


Figure 6

Fluorescence response of compound 4 ($1 \cdot 10^{-7}$ M, DMSO) upon addition of different concentrations of Co²⁺-(0-10 equiv.)

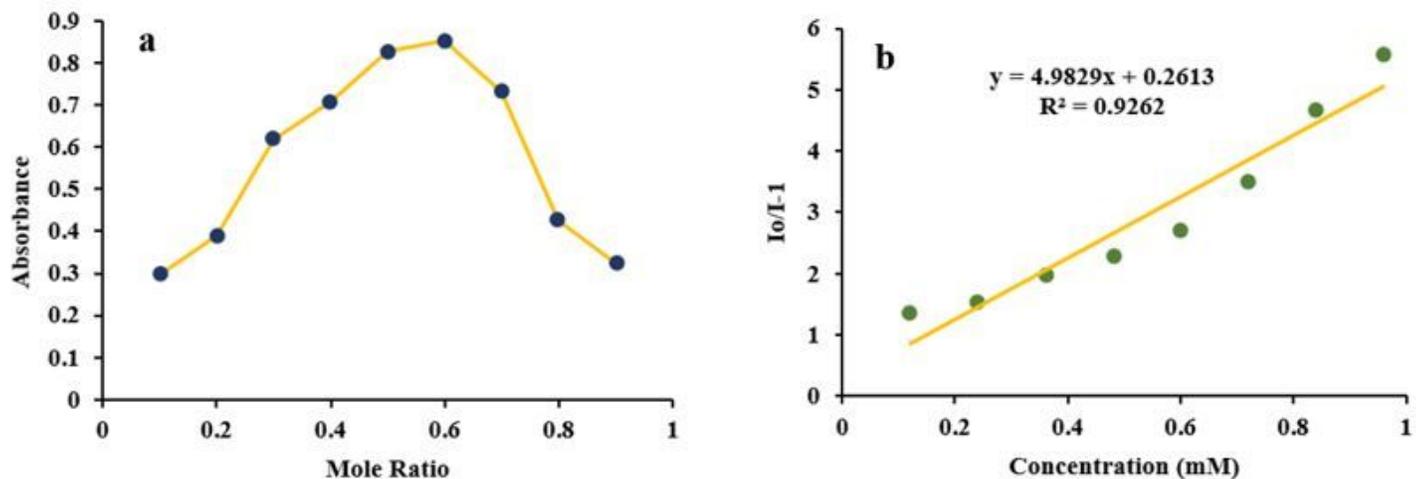


Figure 7

Job's plot for compound 4 and Co^{2+} ion complex (1.0×10^{-4} M) (a). Relationship between the relative fluorescence intensity of compound 4 and Co^{2+} ion (Concentration 0 to 1 mM).

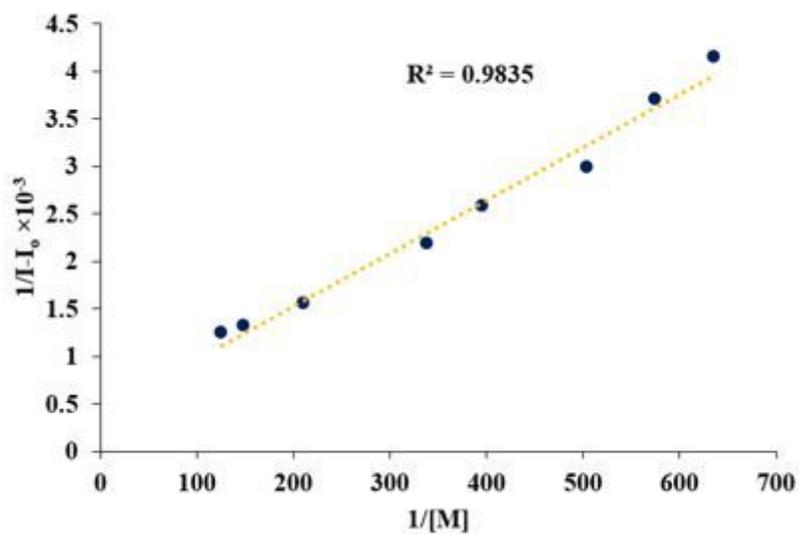


Figure 8

Benesi-Hildebrand plot for the compound 4- Co^{2+} in DMSO. The excitation wavelength was 330 nm and the observed wavelength was 412 nm.

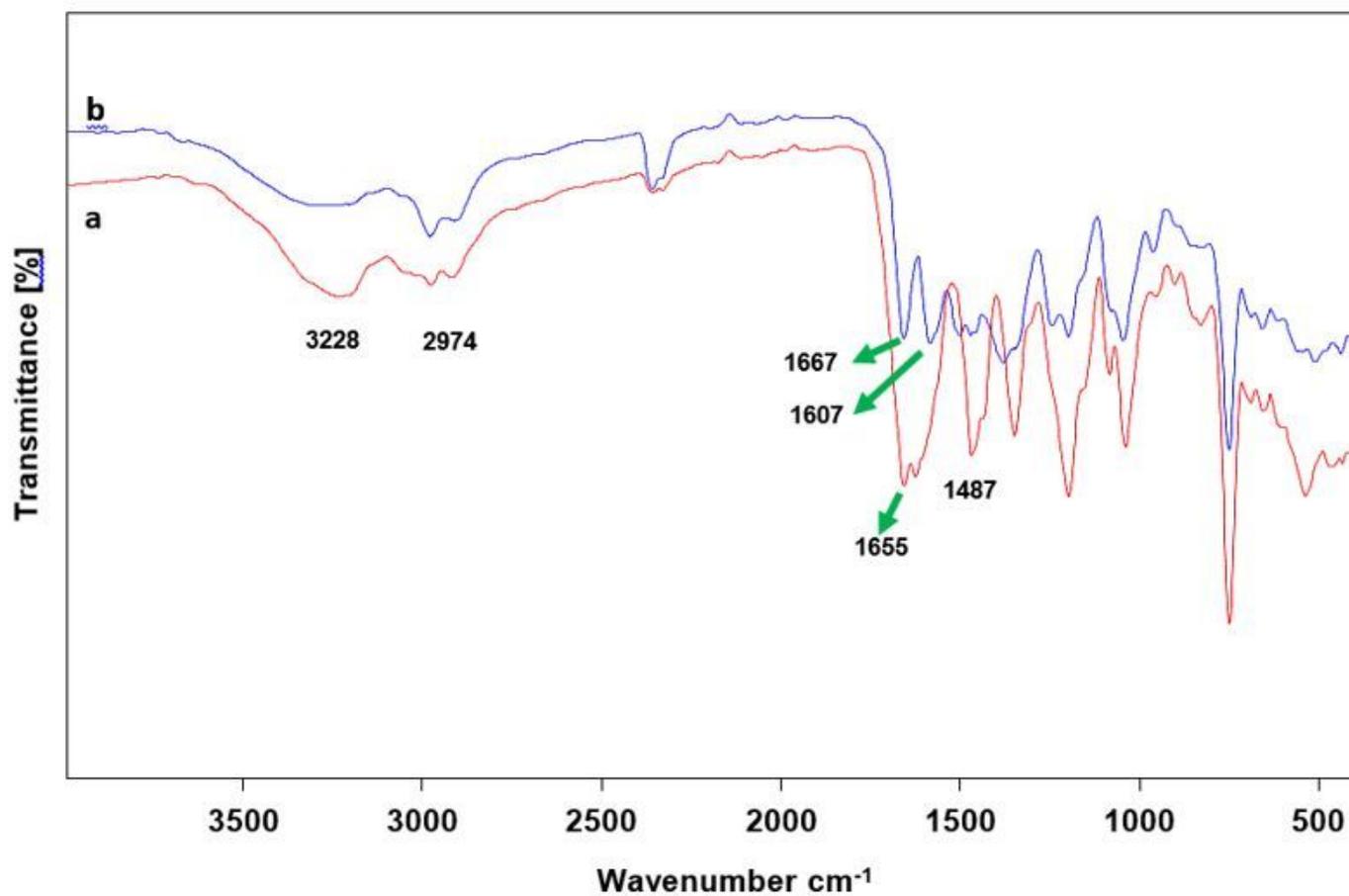


Figure 9

FT-IR spectra of compound 4 (a) and 4-Co²⁺ complex (b)



Figure 10

Naked eye color change of compound 4 upon addition 10 equivalent of Co^{2+} (A) and fluorescence of compound 4 under UV light (B)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [table1.docx](#)
- [formulas.docx](#)