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Triple Action Sensing Behaviour of a Single Receptor for the Detection of Multiple Analytes *via* Different Approaches

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Abstract

The thiosemicarbazide based receptor was synthesized with 4-(diethylamino)salicylaldehyde and N- phenyl-thiosemicarbazide by the simple condensation method and the properties were studied under the naked eye, UV-Vis and fluorescence studies etc. The synthesized receptor detects cyanide, cobalt, and mercury in acetonitrile medium. The observed color changes included colourless to yellow for cyanide, colourless to green for cobalt and colourless to yellow for mercury which were seen under naked eye without the aid of any instruments. Furthermore, the cyanide bound receptor detects Cr^{3+} by the relay recognition method. The detection limit of receptor with cyanide, cobalt & mercury was found to be 5.8×10^{-7} M, 3.6×10^{-7} M and 8.1×10^{-7} M respectively. Experimental results were verified by DFT calculations. Receptor was successfully employed in the construction of INHIBIT and IMPLICATION logic gates.

Keywords Thiosemicarbazide · Turn on-fluorescence · Logic gate · DFT

Introduction

Nowadays, anion & metal ions sensor plays an important role in the field of chemical sensors. Compared to other ions, cyanide is one of the most toxic and dangerous ions to humans and the environment. Food sources such as potatoes, apple seeds, almonds and cassava contain trace amount of cyanide [1]. Still the food samples containing CN⁻ ion may lead to rigorous health problems such as respiratory problems, cardiac arrest, unconsciousness and eventually death [2, 3]. Cyanide ion plays an important role in electroplating, gold mining and polymer processing. The other ion of interest, cobalt, is one of the biologically important trace elements. This ion was responsible for protein synthesis, myelin formation, and production of red blood cells and also used in the high cholesterol treatment [4–7]. Moreover intake of high concentration of cobalt ions leads to DNA damage, cardio toxicity and low cardiac output to human beings [8]. A very limited number of literature reports are available for the

detection of cobalt ion [9]. Mercury is a notorious metal ion that causes many diseases in humans. High levels of mercury poisoning are often associated with pneumonia, respiratory diseases, drug allergies and chronic mercury poisoning, as well as neurological, Parkinson's and chronic psychological problems [10-13]. For these dangerous ions we need a simple and easy method of detection. Many techniques available for the detection of these ions are ascribed with difficult synthesis, poor sensitivity & selectivity and also interference of other ions like F⁻, AcO⁻. Chemical sensors have many amazing unique advantages in overcoming these shortcomings, as well as many other advantages such as high sensitivity and selectivity, making it easy to see target ions visually and at a low cost [14]. For cyanide ion detection, Chemchem and coworkers reported the receptor for cyanide ion detection in the DMSO / H₂O medium, which detects cyanide ions through a deprotonation and ICT mechanism [15]. Wang and co-workers developed a receptor with coumarin derivative with benzothiazole Schiff base moiety which sense cyanide ion by nucleophilic addition mechanism [16]. In cobalt ion detection, Vashisht and co-workers achieved the colorimetric receptor with coumarin moiety for the selective detection of Co²⁺ ion in near aqueous medium by ICT (intramolecular charge transfer) [17]. Jeong Na and co-workers developed a novel receptor for the selective detection of cobalt ions in a near perfect aqueous solution through LMCT (ligand-to-metal

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achieving a new and simple fluorescent receptor bearing mono-sulfur and tetra-sulfur tetrahydro dibenzo phenanthridine derivatives for the selective sensing of Hg²⁺ ion by twisted intramolecular charge transfer (TICT) mechanism [19]. Tripathy and co-workers reported a receptor based on styrylpyridinium donor- π -acceptor (D- π -A) chromophore containing NS₂O₂ binding site for the selective sensing of mercury ion via ICT mechanism [20]. All the above cases, a single receptor detect single metal ions only. Generally due to its biological and analytical application thiosemicarbazide and its derivatives are very important and also get immense interest in anticancer, antiHIV, antibacterial, antiviral and antifungal activities. They play an important role in the regulation of plant growth. Some literature review based on thiosemicarbazide moiety are, Harikrishnan et al. reported the thiosemicarbazide based receptor which detects F⁻, CN⁻ and Cu²⁺ ion through deprotonation followed by hydrogen bonding [21]. Islam et al. reported the thiosemicarbazide based receptor which detects cyanide, fluoride and acetate ion by deprotonation [22]. Udhayakumari et al. reported thiosemicarbazone based sensors that detect the transition metal ions in aqueous media due to photon induced electron transfer mechanism [23]. Lei et al. reported the receptor with thiosemicarbazide moiety for the selective detection of mercury ion by aggregation induced emission.[24]. Amuthakala et al. reported the thiosemicarbazide based chemosensor which detects manganese, cobalt, nickel, copper and zinc cations, and fluoride anion through deprotanation [25]. Sahu et al. reported the pyridine appended thio-semicarbazide based receptor for the selective detection of Cu²⁺ and Ag⁺ ions via ICT process [26]. All the above cases, a single receptor detect multiple ion with a single approach. Herein we report the application of the thiosemicarbazide based receptor synthesized from 4-(N,N-diethylamino) salicylaldehyde and N- phenyl-thiosemicarbazide. Though this thiosemicarbazide is known for quite a few years and have been well studied for its biological activities no report is available on the application of this molecule as chemosensor. This is the first time this receptor was used to detect ions using chemosensor method.

charge-transfer) [18]. Marimuthu and co-workers were

Fig. 1 Colorimetric detection of receptor $(5.0 \times 10^{-5} \text{ M in ACN})$ with all anions $(1 \times 10^{-4} \text{ M in ACN})$

Herein we report the receptor with thiosemicarbazide moiety for multiple ion detection with different approaches. The proposed receptor was also applicable in DFT and logic gate application.

Materials and Instruments

Required chemicals like 4-(N,N-diethyl amino)salicylaldehyde, N-phenylthiosemicarbazide, tetra butyl ammonium salts of AcO⁻, F⁻, I⁻, Cl⁻, CN⁻, Br⁻, H₂PO₄⁻,HSO₄⁻, NO₃⁻, OH⁻ and metal ions such as Mn (OAc)₂, CoCl₂, Cu (NO₃)₂, ZnCl₂, Cd (CH₃COO)₂, HgCl₂, NiCl₂, CrCl₃, FeCl₃ and AlCl₃ were purchased from Sigma Aldrich and used without any purification or modification. Using Bruker 500 MHz NMR spectrometer, ¹H and ¹³ C NMR spectra were recorded with tetramethylsilane (TMS) as an internal standard and CDCl3 as a solvent. IR-spectra were recorded by the KBr pelletization method using a Thermo Fisher Nicolet FT-IR spectrometer. Shimadzu UV-2600 was used to measure the UV-Vis spectrum. Shimadzu-RF-5301PC spectrofluorometer was used to run the fluorescence spectra. For all UV and PL titrations, 5×10^{-5} M solution in ACN medium was taken as a standard. 0 equ. -2.0equ. of the analyte was used for the incremental addition.

Receptor Synthesis

As per the literature report [27] the receptor was synthesized with 98 % yield (Scheme 1). The melting point was 145°C; (The reported melting point was 147°C) [28]. ¹H NMR (CDCl₃, 500 MHz, δ ppm) 10.3 (s, 1H, O-H proton) 9.6 (s,1H,NH-Proton) 8.0 (s,1H,imine proton) 8.3 (s,1H, NH-proton) 7.6 (d, 2H J = 7.5 Hz) 7.4 (t, 2H, J = 8 Hz) 7.3 (s,1H,) 7.0 (d,1H, J = 9 Hz) 6.27 (d,1H, J = 8.5 Hz) 6.25 (d,1H, J = 8.5 Hz) 6.1 (d,1H, J = 8.5 Hz) 2.4 (m,4H, CH₂-proton) 1.19 (t, 6H, CH₃-proton) ¹³ C NMR (CDCl₃, 125 MHz, δ ppm) 12.6, 44.6, 97.7, 104.5, 105.3, 124.9, 126.4, 128.8, 133.4, 137.7, 148.8, 151.3,159.6,174.4.





Fig. 3 (a) UV-Vis spectral studies of the receptor $(5.0 \times 10^{-5} \text{ M in ACN})$ with all anions $(1 \times 10^{-4} \text{ M in ACN})$ (b) UV-Vis Incremental addition of the receptor with CN⁻ ion $(1 \times 10^{-4} \text{ M in ACN})$

Results and Discussion

Naked Eye Detection of Anions and Cations

The sensitivity of the receptor was tested with various anions and cations by naked eye detection in acetonitrile medium. By adding cyanide ion to the receptor it changed from colorless to yellow. However there is no visible color change for other ions (Fig. 1). The colour change of the receptor was associated with the large red shift of 443 nm in UV-Vis spectra upon the addition of cyanide ion. However, by the addition of 2.0 equ.of cyanide ion into the receptor its get saturated. Large bathochromic shift and observed color change are responsible for the strong hydrogen bonding and the deprotonation of the NH protons by the $\rm CN^-$ ions in solution.

Visual detection in acetonitrile medium was performed to examine the selective detection of receptor towards different cations. As shown in Fig. 2, the receptor showed a significant color change from colourless to light green for cobalt and colourless to yellow upon the addition of Hg^{2+} ions. In the presence of Co^{2+} ions, the absorption band at 375 nm apparently decreased and a new absorption band appeared at 400 nm. At the same time adding Hg^{2+} ions to the receptor solution reduces the band at 375 nm to form a new band at 393 nm. Other cations did not show any significant spectrum and color changes.



Fig. 4 a Spectral studies of receptor $(5.0 \times 10^{-5} \text{ M in ACN})$ with all cations in $1 \times 10^{-4} \text{ M in H}_2\text{O}$. **b** Incremental titration of receptor with Co^{2+} ions $(1 \times 10^{-4} \text{ M in H}_2\text{O})$.



Fig. 5 (a) PL-studies of receptor $(5.0 \times 10^{-5} \text{ M in ACN})$ with various anions $(1 \times 10^{-4} \text{ M in ACN})$ (b) Incremental addition of CN⁻ ion $(1 \times 10^{-4} \text{ M in ACN})$ with receptor

Spectral Studies of Receptor with All Anions

To examine the sensitivity of the receptor, UV-visible studies of the receptor with all ions were carried out in acetonitrile medium. Anions like CN⁻, Br⁻, F⁻, Γ , Cl⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, and NO₃⁻ and OH⁻ are taken in the form of their tetrabutyl ammonium salts. By the addition of all anions into the receptor, only the cyanide ion got a colour change from colourless to yellow with red shift. By adding cyanide ion into the receptor, the peak at 375 nm get decreases and formed the new peak at 445 nm. (Fig. 3a). The new peak is due to the ICT band between the receptor (>NH/CN⁻) and signalling benzene units. As the CN⁻ ion in the receptor solution increases, the CN⁻ ion peak gradually increases, eventually becoming saturated. Moreover there is an isosbestic point at 404 nm which indicates the stable complex formation of the receptor-cyanide complex.

Spectral Studies of Receptor with All Cations

The sensitivity of the receptor was further examined by UV-Vis spectroscopic titration in ACN medium. For cation

studies, Mn(OAc)₂, CoCl₂, Cu(NO₃)₂, ZnCl₂, Cd (CH₃COO)₂, HgCl₂, NiCl₂ CrCl₃, FeCl₃ and AlCl₃ were taken in aqueous media. By the addition of all cations into the receptor solution Co²⁺ and Hg²⁺ ion only got a colour change and it changes its colour into light green for cobalt and yellow for mercury. By the addition of cobalt ion, the receptor peak at 375 nm get decreases and formed a new peak with two clear isosbestic points. The two isosbestic point at 330 nm and 400 nm indicates the stable complex formation between the receptor and cobalt ion. At the same time by the addition of mercury ion into the receptor the absorbance band of the receptor at 375 nm get decreases and the new band get increase with a clear isosbestic point at 393 nm which was depicted in (Fig. 4a). In incremental addition of receptor with these two cations get saturated by the addition of 0 equ. to 2.0 equ. which is shown in (Fig. 4b and c).

Fluorescence Studies of All Anions with Receptor

To find out the emission properties of the receptor with all anions the fluorescence titration was done with the help of spectrofluorometer with slit width as 5 nm and the excitation



Fig. 6 a PL-studies of receptor $(5.0 \times 10^{-5} \text{ M in ACN})$ with various cations $(1 \times 10^{-4} \text{ M in H}_2\text{O})$. **b** Incremental addition of Co²⁺ ion $(1 \times 10^{-4} \text{ M in H}_2\text{O})$ with receptor. **c** Incremental addition of Hg²⁺ ion $(1 \times 10^{-4} \text{ M in H}_2\text{O})$ with receptor

Fig. 7 Competitive titration studies of receptor with all anions with CN^{-} ion



wavelength as 350 nm. By the addition of all anions into the receptor, only cyanide ion got a fluorescence enhancement with slight red shift from 439 nm to 471 nm (Fig. 5a). By the ongoing addition of cyanide ion into the receptor upto 2.0 equ. its intensity got gradually enhanced which was depicted in (Fig. 5b). This is due to the deprotonation take place in the hydroxyl O-H and the NH group in the receptor.

Fluorescence Studies of All Cations with Receptor

To find out the emission properties of cations with receptor, addition of all cations were added into the receptor solution. Only Co^{2+} and Hg^{2+} gave a fluorescence enhancement whereas all the other cations did not give any fluorescence change (Fig. 6a). For the addition of Co^{2+} and Hg^{2+} ion into the



Fig. 8 Interference studies of receptor with all cations with Co^{2+} ion





receptor solution the emission maxima of Co^{2+} and Hg^{2+} ion are 433 nm & 434 nm respectively. On adding either Hg^{2+} or, Co^{2+} ion, remarkable fluorescence enhancement was observed (Fig. 6b and c). This turn-on fluorescence is due to the inhibition of PET (photo induced electron transfer).

Interference Studies of Cyanide with All Anions

The plausible interference study was done and it was observed by UV–Vis spectra. Initially by the addition of all anions into the receptor, and then followed by adding CN^- ion. The results suggested that, the receptor is highly sensitive and selective towards cyanide ion over other ions. There was no interference of other anions (Fig. 7).

Competitive Titration Studies of Co²⁺ with All Cations

One of the important features of the chemical sensor is its high selectivity towards the specific metal ion and its resistance to other interfering ions. To evaluate the selectivity of the receptor for the detection of Co^{2+} in the presence of other metals, it should not be disturbed by the presence of other metal ions

Table 1 $\,$ Binding ratio, association constant and limit of detection of receptor with CN $^{-},$ Co $^{2+}$ and Hg $^{2+}$

Sl.No	Ions	Binding ratio	Binding constants	Limit of detection
1	CN ⁻	1:1	$\begin{array}{c} 1.6\!\times\!10^5\ M^{\!-\!1} \\ 1.9\!\times\!10^5\ M^{\!-\!1} \\ 1.0\!\times\!10^5\ M^{\!-\!1} \end{array}$	$5.8 \times 10^{-7} \text{ M}$
2	Co ²⁺	1:1		$3.6 \times 10^{-7} \text{ M}$
3	Hg ²⁺	1:1		$8.1 \times 10^{-7} \text{ M}$

simultaneously in the solution shown in Fig. 8. Thus the chemosensor has a better selectivity towards Co^{2+} .

Competitive Interaction Studies of Hg²⁺ with All Cations

Achieving the best selection for specific analysis of competing species remains a challenge in the development of sensors. To evaluate the selectivity of the receptor in practice, competitive tests were also performed in which the receptor was added to the solution of Hg^{2+} in the presence of other individual cations as shown in Fig. 9. This observation further confirms that these ions do not exhibit obvious interference with Hg^{2+} detection, and that selective detection of Hg^{2+} is not affected by the presence of common metal ions. However, since the Hg^{2+} and Co^{2+} ions in the UV-Vis and PL spectra both induce the same effect, it cannot completely rule out the interference of the Co^{2+} ion.

Job's Plot, Benesi–Hildebrand Plot and Limit of Detection of CN^- , Co^{2+} and Hg^{2+} ions

Job's plot studies show the stoichiometry of receptor + cyanide ion interaction. The interaction follows 1: 1 binding stoichiometry (Supplementary data-S1). By plotting the straight line using $1/\Delta A$ and $1/[CN^-]$, the Benesi–Hildebrand plot (Supplementary data-S2) Similarly the detection limit was calculated using the formula $3^* \sigma/m$. The limit of detection of receptor with cyanide ion is displayed in (Supplementary data-S3). The significant bathochromic shift induced by CN⁻ is most probably due to the deprotonation of the hydroxy



Fig. 10 1 H NMR titration studies of receptor with CN⁻ ion (0.equ - 2.0 equ.) in CDCl₃ solvent

group and NH-group in the receptor. The resultant change in the electronic environment of the receptor is readily transmitted across the conjugated circuit, which leads to an extension of π -conjugation, giving rise to the color change.

In Job's plot studies, the binding ratio of the receptor with cobalt ion shows 1:1 ratio which is shown in (Supplementary data-S4). Binding constant and LOD was depicted in

(Supplementary data-S5 and S6). Further Job's plot studies shows the receptor with mercury ion describe the binding ratio as 1: 1 (Supplementary data-S7). The association constant and limit of detection was revealed in (Supplementary data-S8) & (Supplementary data-S9). The stoichiometric ratio, Benesi– Hildebrand plot and LOD value of receptor with CN^- , Co^{2+} and Hg²⁺ ions are revealed in (Table 1).





¹H NMR Titration Studies of Receptor with CN⁻ ion

The interaction and binding behavior of CN^- with receptor was studied by ¹H NMR titration using $CDCl_3$ as a solvent with TMS act as an internal standard. The free receptor shows the OH-peak at 10.3 ppm and the NH- proton peak at 9.65 ppm and imine proton resonance at 8.3 ppm. Upon addition of 2.0 equ. of CN^- ion into receptor, the peak at 10.3 ppm and 9.65 ppm get vanished and also the intensity of the imine proton get decreases this is due to the deprotonation take place and also the CN^- ion go to attack the N-H moiety and followed by the electron density on phenyl protons is increased, resulting in an upfield shifting in NMR signals. This was shown in Fig. 10. and this mechanism was shown in Scheme 2.

Possible Binding Mechanism of Receptor with $\operatorname{Co}^{2+} \& \operatorname{Hg}^{2+}$ Ion

Cobalt's binding pattern can further confirm the possibility of ICT and PET occurring between the electron-releasing amino group at thiourea and, as mentioned above, the carbonyl group at salicylaldehyde, which causes the receptor to turn off condition [29]. Changes in charge density at the N-binding sites of the receptor after complexation with Co^{2+} inhibit the PET and ICT processes, so that a fluorescence with a slight red-change is activated as a result. Photo-induced electron transfer (PET) from a donor (D) to acceptor (A) leads to the formation of a charge-separated state with donor radical cation and acceptor

radical anion [30, 31]. The molecular structure of the receptor consists of a D-group (thiourea) and an A-group (salicylaldehyde) and completes the generally accepted mechanism of an endogenous PET fluorescent receptor (D-A) [32, 33]. The mechanism for the detection of cobalt ions by the receptor is shown in Scheme 3. The formation of Co^{2+} complex was observed while adding the CoCl₂ to the receptor and the formation was discussed in the mechanism. Complexation has happened between the nitrogen donor atoms in the receptor, in which imine nitrogen was coordinated to cobalt metal via neutral fashion and the remaining N-H moiety of the receptor was coordinated through anionic mode. The ratio of receptor and cobalt was 1:1 in the complex. Based on the above results and literature [34] cobalt can be bound as shown in Scheme 3. Similarly, receptor can coordinate to mercury through anionic mode [35-38]. The proposed binding method of the receptor with cobalt and mercury is shown in Scheme 3. To prove this mechanism IR- spectrum for free receptor, receptor with Co²⁺ ion and receptor with Hg²⁺ ion were taken. In the IR spectral data, the intense band in the region 1628-1634 cm^{-1} associated with C = N stretching vibration of free receptor and it is shifted to lower frequencies (1588-1598 cm^{-1}) in the spectra of corresponding to metal complexes (Co²⁺, Hg²⁺). This indicated the coordination of azomethine nitrogen to the metal ion [39]. phenolic O-H disappeared in the IR spectra of the complexes in the region $3279-3360 \text{ cm}^{-1}$, suggesting deprotonation proceeding to coordination to metal ion. In addition, a band appeared in the region 1268–1300 cm⁻¹ due to phenolic C-O stretching in the



Fig. 12 a UV-Vis spectroscopic changes of receptor with CN^- ion $(1 \times 10^{-4} \text{ M in ACN})$ and cations in $(1 \times 10^{-4} \text{ M in water})$; b Photoluminescence studies of receptor with CN^- in $(1 \times 10^{-4} \text{ M in ACN})$ and cations in $(1 \times 10^{-4} \text{ M in water})$

Table 2 Truth table of inhibition and implication logic gates of the receptor, receptor + CN^{-3+} ions

Sl.No	Input-1 CN [−] ion addition	Input-2 Cr ³⁺ ion addition	Output- 1 375 nm	Output- 2 445 nm
1	0	0	1	0
2	1	0	0	1
3	0	1	1	0
4	1	1	1	0

free ligand has been shifted to $1310-1344 \text{ cm}^{-1}$ in the IR spectra of the complexes indicating the coordination through phenolic oxygen atom [40]. IR spectrum showed two NH-bands at 3406 and 3470 cm⁻¹. These bands remained unaltered in the spectrum of the corresponding metal complexes revealing non participation of NH₂ in coordination [41]. A band which appeared in the region 3127–3175 cm⁻¹ due to N-H proton disappeared on complexation this was shown in Supplementary data-S10.

Relay Recognition Studies

In cascade recognition studies, metal ion such as Cu^{2+} , Ni²⁺,Co²⁺, Hg²⁺, Mn²⁺, Cd²⁺, Zn²⁺, Cr³⁺, Al³⁺ and Fe³⁺ are used. Conversely, receptor showed no color change and spectral change with chromium. In the presence of cyanide ion, it shows an admirable answer for Cr³⁺ ion, which changes its vellow colour to colourless while notable change was not observed for other ions. The reason is Cr³⁺ ion reacts more rapidly with receptor than other ions and also the interaction between hard acids and hard bases is mainly electrostatic, increasing the stability of complexes containing hard acids and hard bases as the positive charge of the metal ion increases and its radius decreases [42, 43]. For this reason the receptor interacts with Cr³⁺ion than other cations. This naked eye observation was exposed in Fig. 11. And this was confirmed by UV-Vis and PL-studies. With the addition of the cyanide ion, the fluorescence is enhanced, while the emission is quenching by the addition of the Cr^{3+} ion to the reaction mixture

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(receptor + CN^{-}). (Supplementary-data. S11). Upon addition of Cr^{3+} ion into the [receptor + CN^{-}] solution spectrum of receptor was revitalized (Fig. 12a and b).

Logic Gate Application

Theoretically, implication and inhibition logic gates could be developed from an integrated study that effectively detects CN^- and Cr^{3+} ions. Two absorptions are specified, indicating that the absorbance at 375 nm, the implication logic gate is in the "switch-on" position. Conversely, the inhibition gate is in 'switch-off' position, while the absorption at 445 nm is in the "switch-on" position. Instead the implication gate is in the "switch off" position. The input signals are CN^- (input 1) and Cr^{3+} (input 2). Absorption at 375 nm and 445 nm are output 1 and output 2, respectively as shown in (Table 2).

Absorption at 375 nm, the receptor is in colorless, indicating that the implication gate is in the 'on' position. The addition of cyanide ion to the receptor solution changes its color from colorless to yellow, indicating that the inhibition logic gate is 'switched on' with absorption at 445 nm. The receptor changes its color from yellow to colorless by adding Cr³⁺ ion to the solution, while at 375 nm the implication gate is 'switched on. Although the Cr³⁺ ions are added to the receptor-CN⁻ ion complex, the implication logic gate is 'switched on' again, which is seen under the naked eye (Fig. 13a). This change was further confirmed by the UV-Vis spectroscopic studies (Fig. 13b). By the addition of 2.0 equ.of cyanide ion and chromium ion in to the receptor solution colourlessvellow-colourless cycle was repeated. The reason is Cr^{3+} ion minimizes the synergy within the cyanide ion and the receptor. Based on the repeating cycle we have developed another logic gate namely memory machine. Here we use two input signals 'set' (adding cyanide ion) & 'reset' (adding chromium ion). IMP and INH are two output signals, taken as two logic gates (Fig. 14a). The memory machine is executed depending on the output signal. The logic circuit i.e. 'write-read-deleteread' cycles is derived from the repetitive functions of the 'onoff' process (Fig. 14b). The truth table of the memory machine is illustrated in (Table 3).







Fig. 14 a Implication and Inhibition logic circuits for molecular gates; b Memory machine logic circuits for the corresponding ions

 Table 3
 Truth table for memory machine device

Sl.No	Set CN ⁻ addition	Reset Cr ³⁺ addition	Output (Absorbance in 445 nm)
1	0	0	0
2	1	0	1
3	0	1	0
4	1	1	0

DFT Calculations of Receptor with CN⁻ Ion

To find out more details about the inclination of the receptor and CN^- , the structure of the receptor and its complex with CN^- were discretely optimized in acetonitrile solvent, using DFT-B3LYP/6-311G (d,p). Figure 15 shows the optimized configuration of the receptor with CN^- ion in ground state. The structural parameters of the optimized structures of the receptor and its CN^- complex were performed using Gaussian 09 program. The energy gap of HOMO-LUMO of receptor was 3.27 eV and the receptor-cyanide complex energy gap was 1.74 eV.The energy gap of HOMO-LUMO of receptor with cyanide ion is reduced. The reason was when the energy gap decreases automatically the wavelength increases. That's

Fig. 15 DFT-calculation of the optimized structure of receptor, and its complex with CN^{-1} ion

why our receptor got a color change from colourless (375 nm) to yellow (445 nm).

DFT Calculations of Receptor with Co²⁺ Ion

To find out the detail information about the interaction of receptor with cobalt ion, structure of the receptor and its complex were optimized using Gaussian 0.9 program with the parameter of B3LYP/6-311G (d,p) in solvent medium. Using DFT- calculation the binding of receptor with cobalt ion may be calculated. Here the experimental energy gap of receptor and receptor with cobalt ion as 3.27 eV and 0.27 eV respectively which was shown in (Fig. 16). Thus the energy gap of receptor with cobalt ion decreases due to the bathochromic shift occurs in the UV-Vis spectrum. From this evidence it is clear that if the wavelength increases automatically the energy gap decrease that's why our receptor got a color change from colourless (375 nm) to light green (400 nm) in UV-Vis spectrum.

DFT Calculations of Receptor with Hg²⁺ Ion

To find out the detail information about the interaction of receptor with mercury ion, structure of the receptor and its



Fig. 16 DFT-calculation of the optimized structure of receptor, and its complex with Co^{2+} ion



complex were optimized using Gaussian 0.9 program with the parameter of B3LYP/6-311G (d,p) in solvent medium. Using DFT- calculation the binding of receptor with mercury ion may be calculated. Here the experimental energy gap of receptor and receptor with mercury ion as 3.27 eV and 1.72 eV respectively which was shown in (Fig. 17). Thus the energy gap of receptor with mercury ion decreases due to the bathochromic shift occurs in the UV-Vis spectrum. From this evidence it is clear that if the wavelength increases automatically the energy gap decrease that's why our receptor got a color change from colourless (375 nm) to yellow (393 nm) in UV-Vis spectrum.

Conclusions

In summary, we have developed the receptor for the selective and sensitive detection of cyanide, cobalt and mercury in acetonitrile medium. The synthesized receptor shows colorimetric transitions from colourless to yellow for cyanide, colourless to light green for cobalt ion and colourless to yellow for mercury. The strong hydrogen bonding between the amino groups of the receptor and CN^- ions and / or the deprotonation of the -NH proton by CN^- ions caused large bathochromic shift and observed color change. Furthermore, the cyanide bound receptor detects Cr^{3+} by relay recognition





method. The limit of detection of cyanide, cobalt and mercury as 5.8×10^{-7} M, 3.6×10^{-7} M and 8.1×10^{-7} M respectively which were lower than the permissible level given by World Health Organization (WHO). Job's pot titration shows 1:1 binding ratio for cyanide, cobalt and mercury. The receptor was effectively applicable in the construction of logic gates.

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Author Contributions G. punithakumari synthesised the molecule and did all the experiments, data collection and first draft of the manuscript. Dr. S. Velmathi has funded the project, conceptualised the idea, and corrected the manuscript and overall coordinator of the work.

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Data Availability Job Plot, Binding constant, Detection limit plots IR spectra of complexes and other associated data are available as supporting information.

Code Availability Not applicable.

Declarations

Conflict of Interest Authors declare no conflict of Interest.

Ethics Approval Not Applicable.

Consent to Participate All authors have agreed for participation.

Consent for Publication All authors have agreed for publication.

References

- Burns AE, Bradbury JH, Cavagnaro TR, Gleadow RM (2012) Total cyanide content of cassava food products in Australia. J Food Compos Anal 25:79–82
- Bin Cheng X, Li H, Zheng F, Lin Q, Yao H, Zhang YM, Wei TB (2016) A simple chemosensor for the dual-channel detection of cyanide in water with high selectivity and sensitivity. RSC Adv 6: 27130–27135
- Gong W, Zhang Q, Shang L, Gao B, Ning G (2013) A new principle for selective sensing cyanide anions based on 2-hydroxynaphthaldeazine compound. Sens Actuators B Chem 177:322–326
- Little C, Aakre S, Rumsby MG, Gwarsha K (1982) Effect of Co²⁺ substitution on the substrate specificity of phospholipase C from bacillus cereus during attack on two membrane systems. J Biochem 1:117–121
- Kolattukudy PE, Dennis M (1992) A cobalt-porphyrin enzyme converts a fatty aldehyde to a hydrocarbon and CO. Proc Natl Acad Sci 89:5306–5310
- Walker KW, Bradshaw RA (1998) Yeast methionine aminopeptidase I can utilize either Zn²⁺ or Co²⁺ as a cofactor: a case of mistaken identity? Protein Sci 7:2684–2687
- Maret W, Vallee BL (1993) Cobalt as probe and label of proteins. Methods Enzymol 226:52–71

- James H, Gibb HJ (2006) Cobalt and Inorganic Cobalt Compounds : Concise International Chemical Assessment Document 69. World Health Organization, Geneva
- Zeng Z, Jewsbury RA (1998) The synthesis and applications of a new chromogenic and fluorescence reagent for cobalt (II). Analyst 123:2845–2850
- Nolan EM, Lippard SJ (2008) Tools and tactics for the optical detection of mercuric ion. Chem Rev 108:3443–3480
- D'ltri PA, D'ltri FM (1978) Mercury contamination: a human tragedy. Environ Manag 2:3–16
- Renzoni A, Zino F, Franchi E (1998) Mercury levels along the food chain and risk forexposed populations. Environ Res 77:68–72
- Czarnik AW (1993) Fluorescent chemosensors for ion and molecule recognition. American Chemical Society, Washington DC
- Isaad J, El A (2011) Colorimetric sensing of cyanide anions in aqueous media based on functional surface modification of natural cellulose materials. Tetrahedron 67:4939–4947
- Chemchem M, Yahaya I (2018) A novel and synthetically facile coumarin-thiophene-derived Schiff base for selective fluorescent detection of cyanide anions in aqueous solution: Synthesis, anion interactions, theoretical study and DNA-binding properties. Tetrahedron 74:6897–6906
- Wang K, Feng W (2016) A coumarin derivative with benzothiazole Schiff's base structure as chemosensor for cyanide and copper ions. Inorg Chem Comm 71:102–104
- Vashisht D, Kaur K (2019) Colorimetric chemosensor based on coumarin skeleton for selective naked eye detection of cobalt (II) ion in near aqueous medium. Sens Actuators B Chem 280:219–226
- Na YJ, Choi YW (2016) A novel selective colorimetric chemosensor for cobalt ions in a near perfect aqueous solution. Sens and Actuators B Chem. 223:234–240
- Ponram M, Balijapalli U (2018) Development of paper-based chemosensor for the detection of mercury ions using mono- and tetra-sulfur bearing phenanthridines. New J Chem 42:8530–8536
- Tripathy M, Subuddhi U (2020) A styrylpyridinium dye as chromogenic and fluorogenic dual mode chemosensor for selective detection of mercuric ion: Application in bacterial cell imaging and molecular logic gate. Dyes Pigments 174:108054
- Harikrishnan VK, Basheer SM (2017) Colorimetric and fluorimetric response of salicylaldehydedithiosemicarbazone towards fluoride, cyanide and copper ions: Spectroscopic and TD-DFT studies. Acta A Mol Biomol Spectrosc1825:160–167
- 22. Islam M, Hameed A (2018) Receptor-spacer-fluorophore based coumarin-thiosemicarbazones as anion chemosensors with "turn on" response: spectroscopic and computational (DFT) studies . ChemistrySelect 3:7633–7642
- Udhayakumari D, Suganya S (2013) Thiosemicabazone based fluorescent chemosensor for transition metal ions in aqueous medium. J Lumin 141:48–52
- Lei F (2016) A novel thiosemicarbazone Schiff base derivative with aggregation-induced emission enhancement characteristics and its application in Hg²⁺ detection. Sensors Actuators B Chem. 237: 563–569
- Amuthakala S, Bharathi S, Kalilur Rahiman A (2020) Thiosemicarbazone-based bifunctional chemosensors for simultaneous detection of inorganic cations and fluoride anion. J Mol Struct 1219:128640
- Sahu M , Manna AK, Rout K, Mondal J (2020) A highly selective thiosemicarbazone based Schiff base chemosensor for colorimetric detection of Cu²⁺ and Ag⁺ ions and *turn-on* fluorometric detection of Ag⁺ ions. Inorg Chim Acta 508:119633
- I.Dilovic M, Rubcic (2008) Novel thiosemicarbazone derivatives as potential antitumor agents: Synthesis, physicochemical and structural properties, DNA interactions and antiproliferative activity. Bioorg Med Chem 16:5189–5198

- Priyarega S, Kalaivani P (2011) Nickel (II) complexes containing thiosemicarbazone and triphenylphosphine: Synthesis, spectroscopy, crystallography and catalytic activity. J Mol Struct 1002:58–62
- Liu YL, Yang L (2019) A new fluorescent chemosensor for cobalt(II) ions in living cells based on 1,8-naphthalimide. Molecules 24:3093
- Balzani V (ed) (2001) Electron transfer in chemistry. Wiley-VCH, Weinheim
- Natali M, Campagna S, Scandola F (2014) Photoinduced electron transfer across molecular bridges: electronand hole-transfer superexchange pathways. Chem Soc Rev 43:4005–4018
- Daly B, Ling J, De Silva AP (2015) Current developments in fluorescent pet (photoinduced electron transfer) sensors and switches. Chem Soc Rev 44:4203–4211
- Stennett EMS, Ciuba MA, Levitus M (2014) Photo physical processes in single molecule organic fluorescent probes. Chem Soc Rev 43:1057–1075
- Zhang YZ, Lu SZ, Sha CM, Xu DM (2015) A single thioureaappended 1,8-naphthalimide chemosensor for three heavy metal ions: Fe³⁺, Pb²⁺, and Hg²⁺. Sensors Actuators B Chem 208:258– 266
- Lu W, Jiang H (2011) A novel chemosensor based on FE(III)complexation for selective recognition and rapid detection of fluoride anions in aqueous media. Tetrahedron 67:7909–7912
- 36. Chang HQ, Wang Y (2017) A highly sensitive colorimetric and offon fluorescent chemosensor for Cu2 + based on rhodamine 6G hydrazide bearing thiosemicarbazide moiety. J Photochem Photobiol A 335:10–16

- Li Y, Shi W (2017) A novel optical probe for Hg²⁺ in aqueous media based on mono-thiosemicarbazone Schiff base. J Photochem Photobiol A 338:1–7
- Calatayud DG, Torres EL (2013) A fluorescent dissymmetric thiosemicarbazone ligand containing a hydrazonequinoline arm and its complexes with cadmium and mercury. Eur J Inorg Chem :80–90
- 39. Muthu Tamizh M, Mereiter K, Kirchner K, Bhat BR, Karvembu R (2009) Synthesis, crystal structures and spectral studies of square planar nickel(II) complexes containing an ONS donor Schiff base and triphenylphosphine Polyhedron 28:2157–2164
- Muthu Tamizh M, Varghese B, Endo A, Karvembu R (2010) NMR (1D and 2D) and X-ray crystallographic studies of Ni(II) complex with N- (2-mercaptophenyl) -4 methoxysalicylide neimine and triphenylphosphine. Spectrochim Acta Part A 77:411–418
- Boghaei DM, Mohebi S (2002) Synthesis, characterization and study of vanadyl tetradentate Schiff base complexes as catalyst in aerobic selective oxidation of olefins. J Mol Catal A: Chem 179: 41–51
- 42. Ayers PW (2005) An elementary derivation of the hard/soft-acid/ base principle. J Chem Phys 122:141102
- Pearson RG (1963) Hard and soft acids and bases. J Am Chem Soc 85:3533–3539

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