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ORIGINAL ARTICLE

Hydrazone Based Dual – Responsive Colorimetric and Ratiometric Chemosensor for the Detection of Cu^{2+}/F^{-} Ions: DNA Tracking, Practical Performance in Environmental Samples and Tooth Paste

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Abstract

Colorimetric sensors have attracted wide scope of attentions due to its fascinating advantages, like handy, equipment-free and naked eye detections. In this investigation, a new and novel hydrazone based dual-responsive ratiometric/colorimetric chemosensor have been developed for highly selective and sensitive detection of Cu^{2+} and F^{-} ions in dimethyl sulfoxide (DMSO) solvent. The probe showed highly selective sensing towards Cu^{2+} and F^{-} ions by exhibiting a color change from pale yellow to yellowish green and pale yellow to yellowish brown respectively., in DMSO without any interference of other ions at same concentration. These experimental results have also substantiated by the NMR, HR-MS, UV-Vis spectroscopic, cyclic voltammetry, differential pulse voltammetry techniques and DFT calculations. The detection limits are found to be 5.8 μM for Cu^{2+} and 0.025 μM for F^{-} ions which is far below to the values recommended by WHO. The stoichiometric ratios between NAPCBH and Cu2+/ F- ions were confirmed from the Job's plots and ^{1}H NMR titration experiments which are found to be 2:1 and 1:1 respectively. The tracking ability of the DNA with NAPCBH-Cu^{2+} was studied by UV-Vis titration and Cyclic voltammetry measurements. It shows efficient affinity towards DNA with NAPCBH-Cu^{2+}. The probe can also quantitatively determine the Copper and fluoride ions present in environmental samples & toothpaste. The NAPCBH was promptly recovered by utilizing very low concentration of HCl, showing that was found feasible and re-usable sensor for the convenient detection of Cu^{2+} and F^{-} ions.

Keywords Colorimetric sensor · Ratiometric sensor · Selective/sensitive probe · Naked eye detection

Introduction

Recent developments in colorimetric chemosensors showed special interests due to their utilization in analytical, environmental, therapeutic fields, as well as in industry based sectors [1–3]. This detection technique was identified to be cost-effective, rapid and facile with wide range of applications [4, 5]. In comparison to fluorescent chemosensors, the colorimetric sensors have promising features in the detection of metal ions and anions. The precise and expedient discovery for the detection of Cu^{2+} ion using hydrazone based Schiff base by the naked eye without utilizing massive instruments were created. Among all, copper ion is one of the important micronutrients for human existence. It serves as a vital cofactor via constituting the lively element in a huge variety of enzymes along with superoxide dismutase, cytochrome c oxidase and tyrosinase [6–8]. Therefore, day by day ingestion of copper is integral for human health [9]. However, unregulated overloading of

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Highlights

- A new hydrazone based chemosensor NAPCBH was synthesized via simple synthetic process.
- Dual-response of NAPCBH towards Cu^{2+} and F^{-} ions in an organic medium was developed.
- The Cu^{2+} and F^{-} ions detection are highly selective and sensitive.
- ICT mechanism was confirmed for both NAPCBH with Cu^{2+} and F^{-} ions through Job's plot, ^{1}H NMR titration and DFT studies.
- DNA tracking ability was also studied for NAPCBH-Cu^{2+} successively.
- The probe can also quantitatively determine the Copper and fluoride ions present in environmental samples & toothpaste.
- The NAPCBH was readily regenerated at lower concentration of HCl, showing its feasibility to be a re-usable sensor for the convenient detection of Cu^{2+} and F^{-} ions.

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copper ions can result in extreme neurodegenerative illness inclusive of alzheimer's, parkinson's, prion, stomach and gastro intestinal disturbance, liver or kidney damage, loss of cognition, Wilson's disease and etc. [10–15] On the other hand, copper deficiency is associated with myelopathy [16]. Furthermore, copper ion is a considerable environmental pollutant due to its great usage. The World Health Organization (WHO) has set the safe restriction of copper in drinking water at 2 ppm (31.5 μM) [17]. Thus, the advancement of detecting copper ion with higher sensitivity, low detection limit and quick response is an extraordinary process in high demand.

DNA is a giant cellular target of several metallodrugs for the treatment of various pathologies, including cancer, and it assumes a vast role in revealing the capability of metal binding destinations with either electron rich nucleobases or phosphate oxygen of the DNA [18, 19]. Typical nucleic acid probes distinguish and identify nucleic acids on the basis of intercalation [20], groove binding [21], electrostatic interaction [22] and hydrogen bonds [23]. Thus, DNA tracking is essential in the advancement of chemical tools for the biologically relevant metallic ions. Very recently there are a number of DNA tracking strategies for the fluorescent probes with metal ions [24, 25]. To the best of our knowledge and understanding very few reports on the tracking of DNA in colorimetric sensor particularly for Cu^{2+} ions [26]. It appears strongly that such applications will bloom in the forthcoming months and years for sure.

Furthermore, biological and environmental strategies have been given the importance of anions and triggered interests. Among the anions, some of the features of fluoride ions are exhibits unique chemical properties, extensively used in tooth paste, pharmaceutical dealers use them for the prevention of dental carriers, teeth demineralization at the same time as carrying orthodontic appliances and remedy for osteoporosis [27, 28]. It has been shown that fluoride ions can cause dental, bone fluorosis and sickness including gastric and kidney issues, urolithiasis and even loss of life [29–31]. Therefore, the detection of fluoride ions in ingesting water and dwelling organs attracted a great attention in chemistry and bio-inorganic chemistry [32–34]. Hence, many chemical sensors have been reported towards the detection of F^- ions [35, 36]. In addition, variety of fluorescent and chemical sensors based on hydrogen bonding interactions and fluoride ion induced chemical reactions have also been reported for fluoride ion sensors [37, 38].

In recent years, plenty of analytical techniques are commercially employed to recognize metal ions and anions such as atomic absorption spectroscopy [39], inductively-coupled plasma mass spectroscopy [40] and fluorescence techniques [41], however, these methods are costly [42], require sophisticated instrumentation set up, tedious sample preparative methods and trained operators [5]. Therefore, efforts are being devoted by researchers to develop most attractive and effective over other techniques based on colorimetric sensors which allows the naked eye detection of the color change without using the luxurious methods [43–45] and on other hand, it offers many advantages such as high sensitivity, specificity, simplicity, low cost, rapid monitoring of analytes in biological, toxicological and environmental samples [42, 46–48]. Therefore, the development of a simple and efficient colorimetric sensor for the detection Cu^{2+} and F^- ions might be useful for chemists and biologists.

Schiff bases possessing π electrons in the imine group and nitrogen analogues in the aromatic rings provide an opportunity for chelation with the metal ions and anions. The chelation could decorate intramolecular charge transfer (ICT) transition or cause the ligand to metal charge transfer (LMCT) transition which will be used for the detection of metal ions and anions [44, 49]. Although several studies have been reported for the colorimetric detection of copper ion and fluoride ion in various media they suffer from many complications like involving tedious synthetic processes, complicated structure and etc. [50–52]

In view of the above necessities, we endeavored to design an easy and efficient probe based on the conjugation of 2-hydroxy-1-naphthaldehyde and chlorobenzylidene hydrazine which leads to the formation of hydrazone moiety. Hydrazone probe are one of the best and promising agents in preventing many diseases. In addition, NAPCBH possess hydroxyl and imine moieties which can facilitate metal ions, anions binding and DNA tracking [53, 54]. The sensing capability of NAPCBH was examined towards diverse cations and anions. The experimental results have shown that the probe shows an effective and colorimetric detection of $Cu^{2+}$and F^- ions in organic medium without involving any complicated processes. The applications and potential of the developed sensor were examined by DNA tracking, practical performance in environmental samples and tooth paste.

Materials and Methods

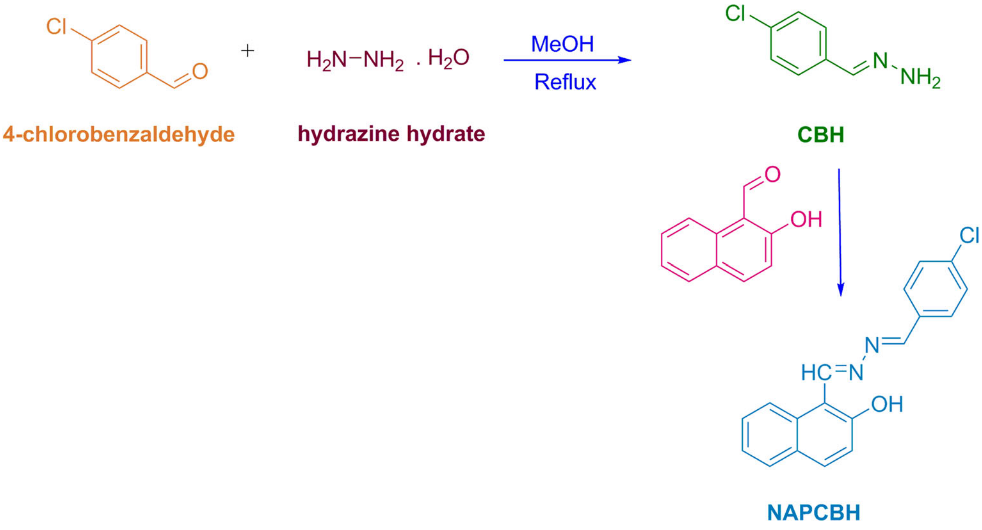
Materials

4-Chlorobenzaldehyde, hydrazine hydrate, 2-hydroxy-1-naphthaldehyde, tetrabutylammonium perchlorate, metal salts, all solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich, Merck respectively and used as obtained without any purification.

Instrumentation

^1H NMR and ^{13}C NMR were recorded on a BRUKER 300 and 400 MHz. Chemical shifts are mentioned in ppm, Tetramethylsilane as standard and DMSO-d^6 used as solvent. Electronic absorption spectral measurements were recorded in

Scheme 1 Synthetic procedure of NAPCBH



solution using JASCO V-550 UV-Visible spectrophotometer with a quartz cuvette (cell length 1 cm). Cyclic voltammetry, Differential pulse voltammetry studies were carried out at room temperature using a CH Instruments Electrochemical Workstation (Model-760D), HR-MS was analyzed in Q – Tof mass spectrometer and DFT calculations were also performed using Gaussian 09 software.

Preparation of Stock Solutions

Stock solution of probe (1-((E)-(((E)-4-chlorobenzylidene)hydrazono)methyl)naphthalen-2-ol) NAPCBH was prepared in the concentration of 1×10^{-3} M in DMSO and the solution of metal ions were prepared from their chloride salts except silver nitrate, lead nitrate and the solution of anions were prepared from their tetra-n-butyl ammonium and sodium salts in the concentration of 1×10^{-2} M using double distilled water. The stock solution of NAPCBH (30 µl) was diluted with 2 ml DMSO to a final concentration of 15 µM which was further used for all the experiments carried out at room temperature.

Synthesis of CBH

A methanolic solution of 4-chlorobenzaldehyde (100 mg, 1 mmol) was refluxed in an excess amount of hydrazine hydrate for 3 h. The white solid product (E)-(4-chlorobenzylidene)hydrazine (CBH) was obtained from ice cold water and recrystalized from the hot methanolic solution. (Yield 97%) ^{1}H NMR (300 MHz, DMSO) δ 5.17 (s, 1H), 4.91

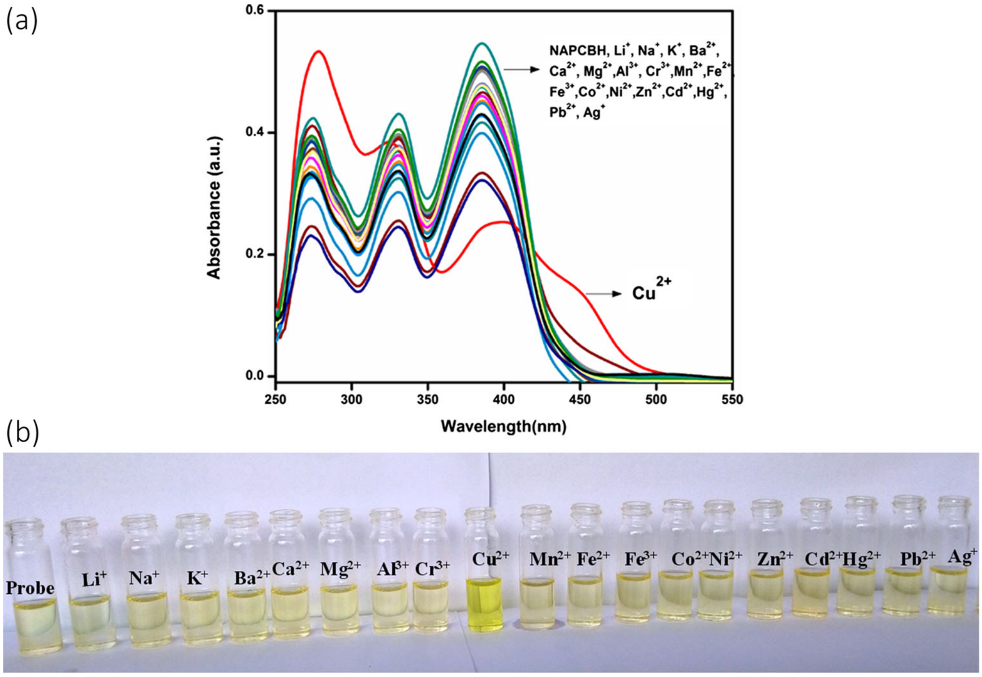


Fig. 1 **a** UV-Vis spectra of NAPCBH (15 µM) in the presence of various metal ions in DMSO; **b** The color changes of NAPCBH (15 µM) upon addition of various metal ions (15 µM) in DMSO

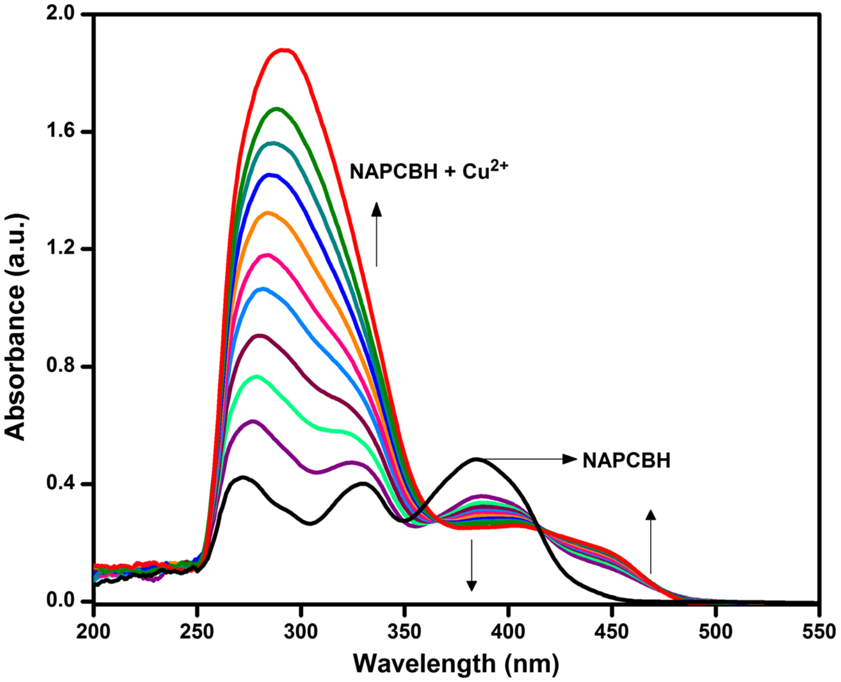


Fig. 2 UV-Vis spectral changes of NAPCBH (15 µM) upon addition of Cu^{2+} ion in DMSO. Insert zoomed UV-Vis spectral changes from 350 nm -500 nm

(dd, *J* = 36.3, 8.4 Hz, 1H), 4.39 (s, 1H), 0.99 (s, 1H), −0.00 (s, 1H) (Fig. S1). ^{13}C NMR (75 MHz, DMSO) δ 137.65, 136.19, 132.39, 129.33, 127.50, 41.10, 40.99–40.14, 39.86, 39.45, (Fig. S2). HR-MS (calculated 154.60, Found 155.07) (Fig.S5).

Synthesis of NAPCBH

A methanolic solution of 2-hydroxy-1-naphthaldehyde (50 mg, 0.2 mmol) was refluxed with CBH (30 mg, 0.2 mmol) for 2 h. A yellow color solid product 1-((E)-(((E)-4-chlorobenzylidene)hydrazono)methyl)naphthalen-2-ol (NAPCBH) was obtained and recrystalized from the hot methanolic solution. (yield 96%). ^1H NMR (300 MHz, DMSO) δ 10.53 (s, 1H), 7.27 (s, 1H), 6.40 (s, 1H), 6.05 (d, *J* = 8.6 Hz, 1H), 5.55–5.37 (m, 2H), 5.11 (d, *J* = 8.4 Hz, 1H), 4.94 (d, *J* = 7.2 Hz, 1H), 4.75 (d, *J* = 9.0 Hz, 1H), 0.87 (s, 5H). (Fig. S3). ^{13}C NMR (75 MHz, DMSO) δ 162.21, 161.53, 160.43, 138.15, 135.15, 133.18, 132.54, 130.31, 129.76, 128.55, 128.32, 123.86, 120.37, 119.59, 108.75(Fig. S4).HR-MS (calculated 308.77, found 309.08) (Fig.S6).

Colorimetric Response of NAPCBH

The colorimetric response of NAPCBH dissolved in DMSO to a final concentration of 15 µM in the presence of diverse cations and anions dissolved in double distilled water and DMSO respectively was seen through naked eye detection.

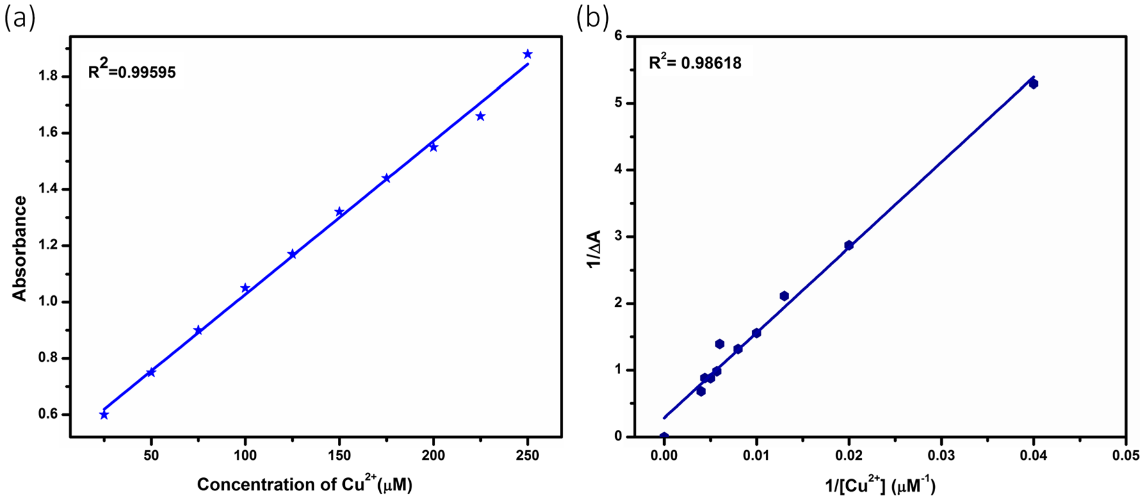


Fig. 3 **a** Linear fit and (**b**) Benesi-Hilderbrand plot obtained from the UV-Vis titration of Cu^{2+} ions

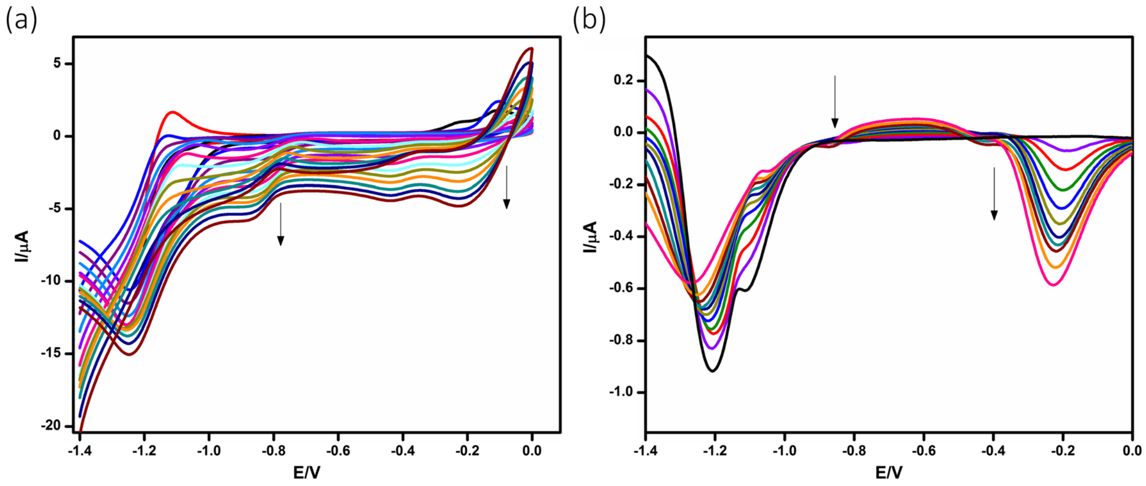


Fig. 4 **a** Cyclic voltammetry titration of NAPCBH with Cu^{2+} ions and (**b**) Differential pulse voltammetry titration of NAPCBH with Cu^{2+} ions

After mixing them for few seconds, UV-Vis spectra were recorded at room temperature. Further, UV-Vis spectra were also recorded to determine the selectivity, sensitivity and competitive sensing studies.

UV-Vis Titration Measurements of NAPCBH with Cu^{2+} Ions

The probe NAPCBH concentration of 15 μM was prepared and to this solution an aqueous copper solution of 10^{-2} M was gradually added and UV-Vis spectral changes were monitored at room temperature after each addition.

UV-Vis Titration Measurements of NAPCBH with F^{-} Ions

The probe NAPCBH final concentration of 15 μM was measured and fluoride ions of 10^{-2} M in DMSO was gradually added to this solution and UV-Vis spectral changes were monitored at room temperature after each addition.

Electrochemistry Measurements of NAPCBH with Cu^{2+} and F^{-} Ions

Cyclic voltammetry and differential pulse voltammetry measurements were measured for the probe NAPCBH at concentration of 10^{-4} M. Copper and fluoride ion concentrations of 10^{-4} M were gradually added to NAPCBH and their electrochemical changes were monitored at room temperature. In addition, the diverse cations and anions changes were monitored. The glassy carbon, Ag/AgCl electrode and platinum electrode were used as working, reference and counter electrode respectively. Tetrabutylammonium perchlorate was used as supporting electrolyte.

Calculation of the Limit of Detection and Binding Constant

The limit of detection was calculated using the formula, 3σ/s, where σ is the standard deviation of the blank titration curve.

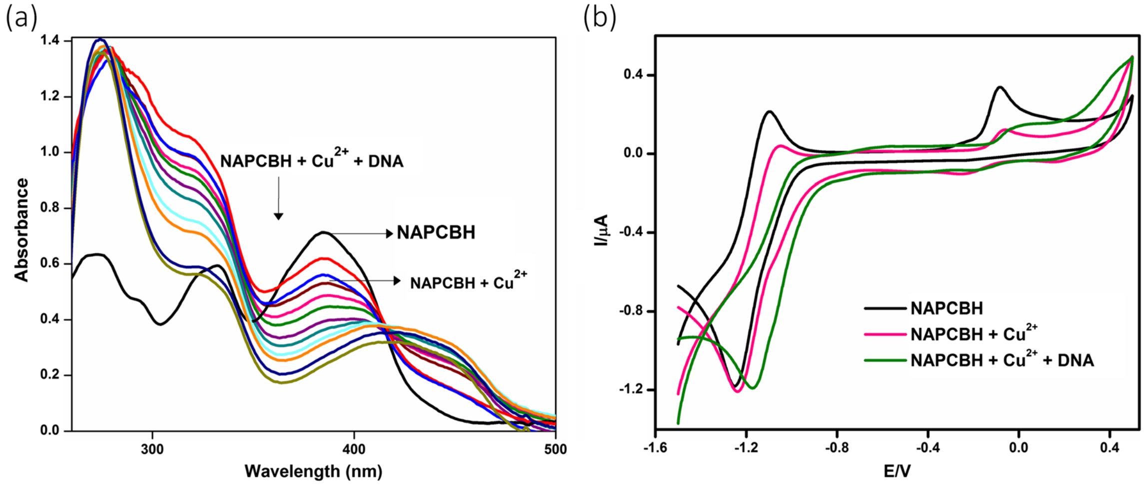


Fig. 5 **a** Absorption spectra for DNA tracking of NAPCBH-Cu^{2+} (**b**) Cyclic voltammetry spectra for DNA tracking of NAPCBH-Cu^{2+}

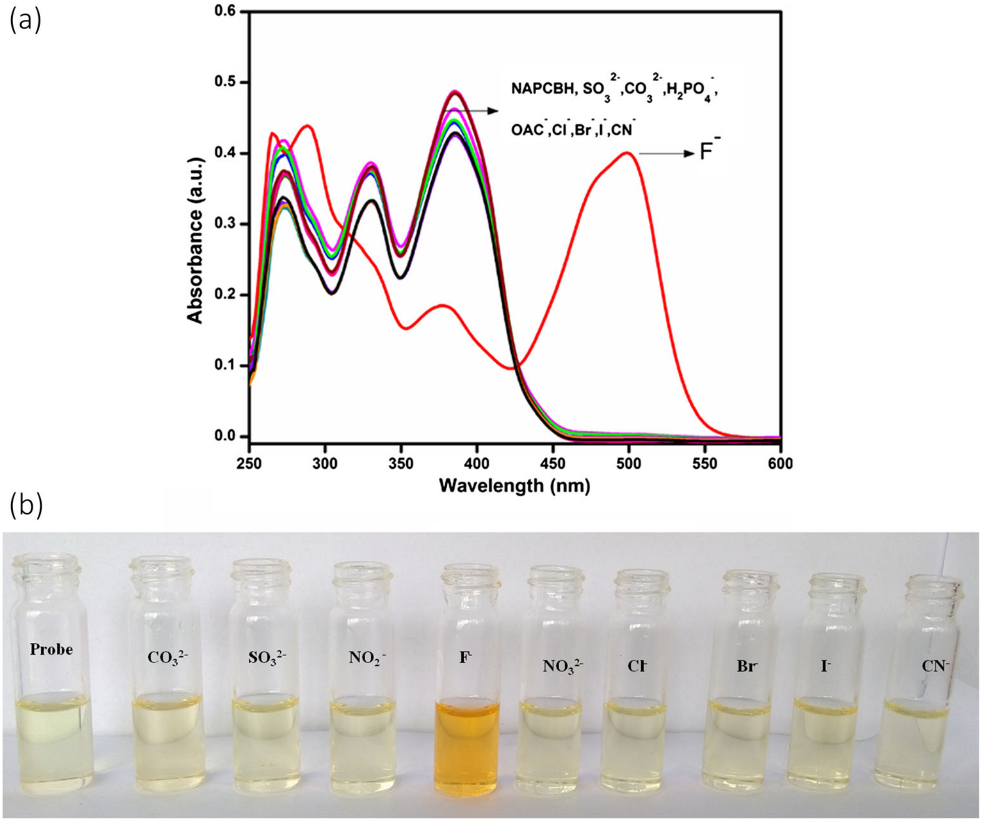


Fig. 6 **a** UV-Vis spectra of NAPCBH (15 μM) in the presence of various anions in DMSO and (**b**) The color changes of NAPCBH (15 μM) upon addition of various anions in DMSO

The binding constant was calculated from the absorbance data using Benesi-Hinderbrand equation,

$$1/(A_0 - A) = 1/k\,\{(A_{max} - A_0)\ (C)\} + 1/(A_{max} - A_0),$$

where A_0 is the absorbance of the probe in the absence of cation/anion, A is the absorbance recorded in the presence of cation/anion and A_{max} is the absorbance maximum recorded in the presence of cation/anion and K is the association constant could be determined from the slope of the straight line of the plot of $1/A_0$-A against 1/C.

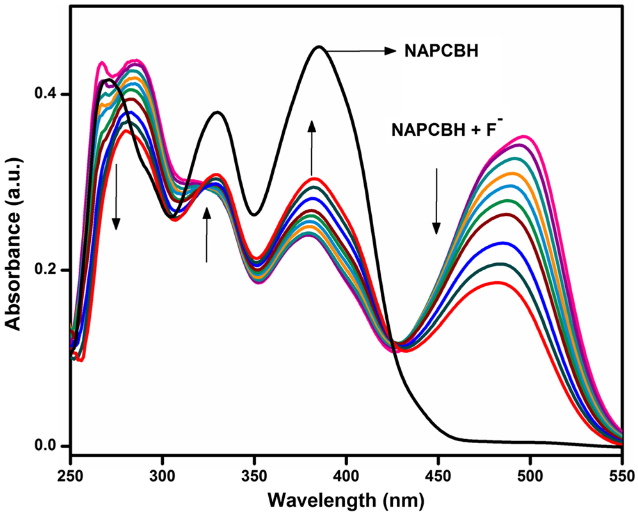


Fig. 7 UV-Vis spectral changes of NAPCBH (15 μM) upon addition of F^- ion in DMSO

Job's Plot Measurement for NAPCBH with Cu^{2+} and F^- Ions

Job's plot measurements for NAPCBH with Cu^{2+} and F^- ions were prepared in double distilled water and DMSO respectively in the concentration of 10^{-4} M. The probe and Cu^{2+}/F^- ratio of 2:2, 1.8:2, 1.6:4, 1.2:8, 1:1, 8:1.2,6:1.4, 4:1.6, 2:1.8 and 0:2 were prepared in an appropriate procedure and the color changes were monitored using UV-Vis spectrophotometer at room temperature.

^{1}H NMR Titration Studies of Cu^{2+} and F^- Ions

Five NMR tubes consisting of NAPCBH dissolved in DMSO-d^6 were prepared and five different equivalents (0, 0.25, 0.50, 0.75, 1.0) of respective copper and fluoride salts were dissolved in DMSO-d^6 were added to NAPCBH separately. After shaking them for a minute, ^{1}H NMR spectrum was performed.

Computational Calculations

DFT calculations based on the hybrid exchange correlation functional B3LYP were performed using Gaussian 09

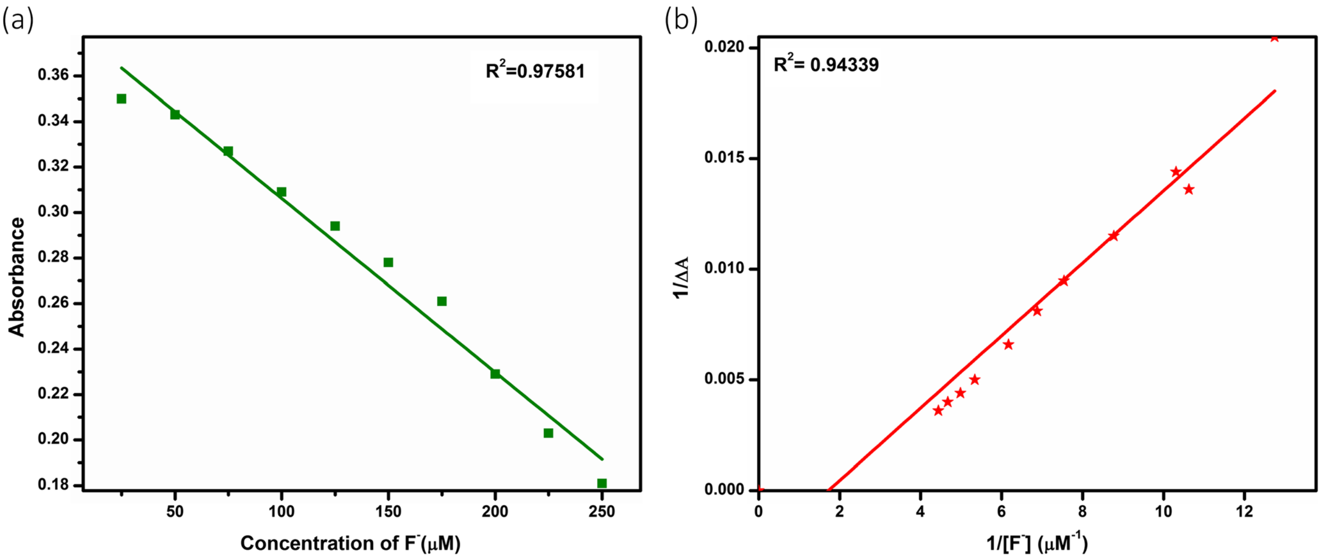


Fig. 8 **a** Linear fit and (**b**) Benesi-Hilderbrand plot obtained from the UV-Vis titration of F⁻ ions

programme. The 6-31G basis set was used for the probe NAPCBH, and the LANL2DZ was the basis set employed for copper and fluoride ions.

Results and Discussion

Synthesis and Characterization of Precursor and Probe

The precursor CBH was prepared by a known synthetic procedure. The probe NAPCBH was synthesized by the condensation reaction of 2-hydroxy-1-naphthaldehyde with the precursor in methanol (Scheme 1). The structure of CBH and the probe was confirmed by ^{1}H and ^{13}C-NMR and HR-MS spectroscopic techniques.

UV-Vis Spectral and Colorimetric Response of NAPCBH Towards Cu^{2+}

The colorimetric selective sensing capabilities of NAPCBH with diverse metal ions in DMSO were monitored using UV-Vis electronic spectra. Upon addition of Cu^{2+}, the probe caused distinguishable spectral changes while other metal ions showed either no or small spectral changes (Fig. 1a and b). This phenomenon was seen from the UV-Vis electronic spectrum changes and on other hand the color changes was also monitored by naked eye while adding Cu^{2+} solution to the

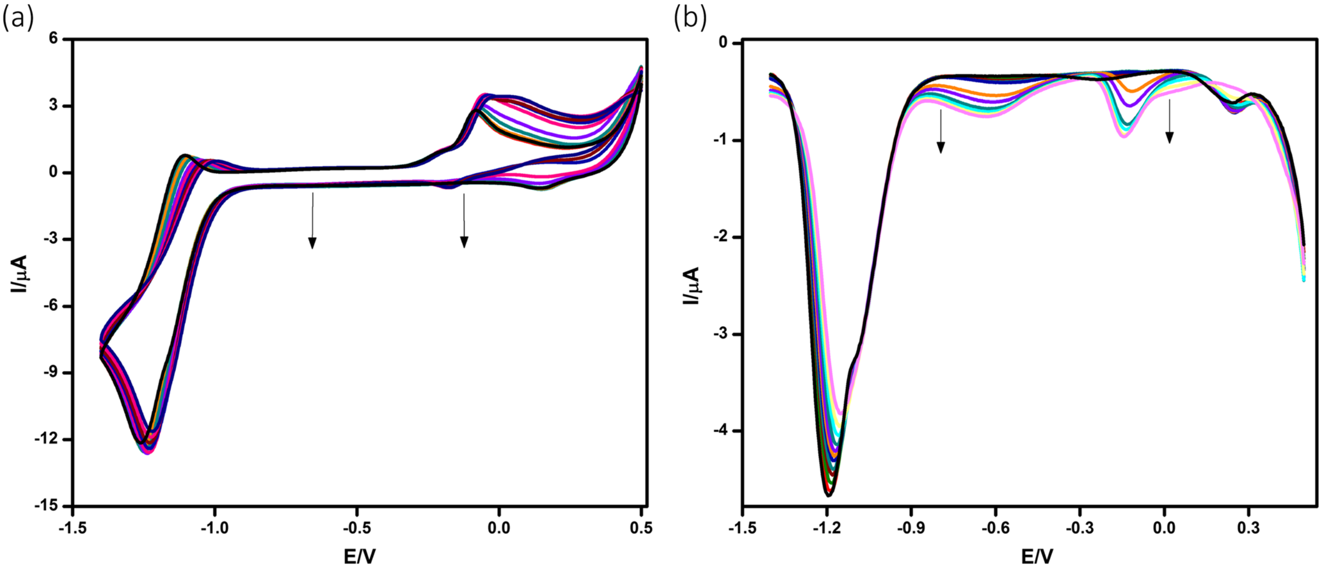


Fig. 9 **a** Cyclic voltammetry titration of NAPCBH with F⁻ ions and (**b**) Differential pulse voltammetry titration of NAPCBH with F⁻ ions

Fig. 10 ^{1}H NMR titration studies of F^- in d^6 DMSO

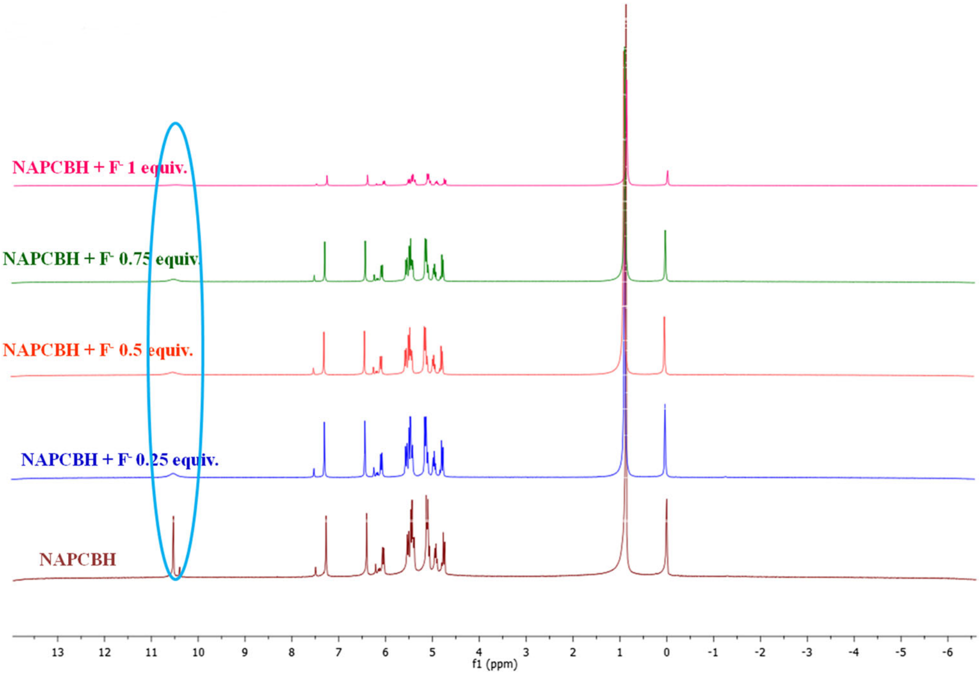
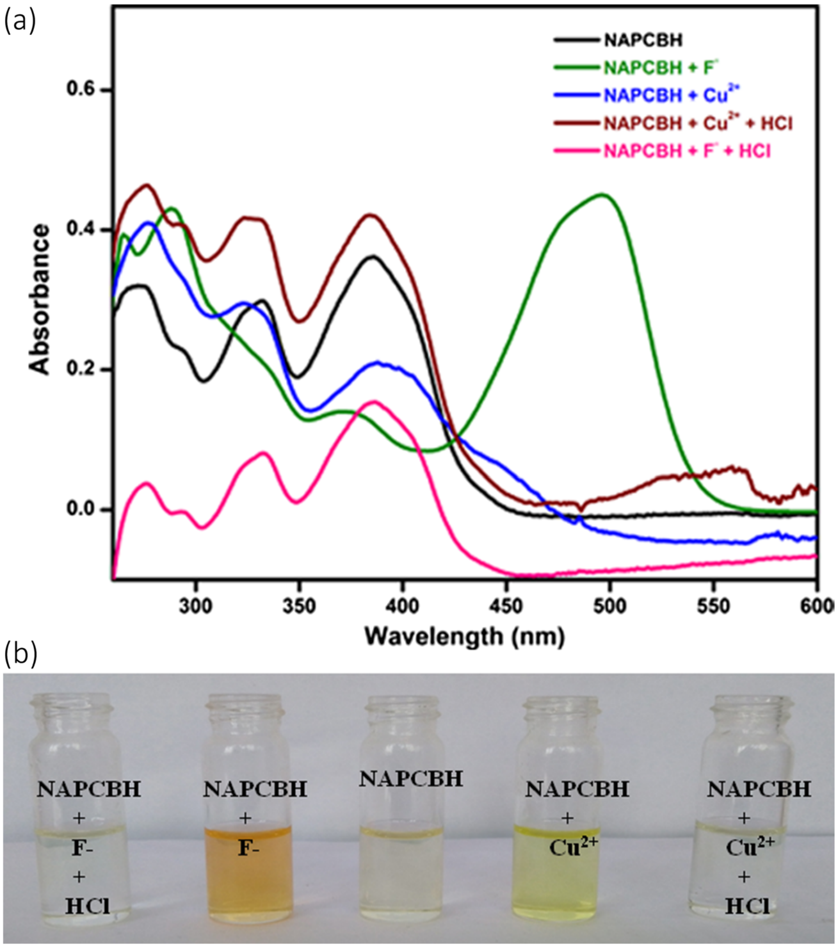


Fig. 11 **a** UV-Vis spectra of reversibility and regeneration of NAPCBH; **b** color changes of NAPCH upon addition of copper, fluoride and HCl



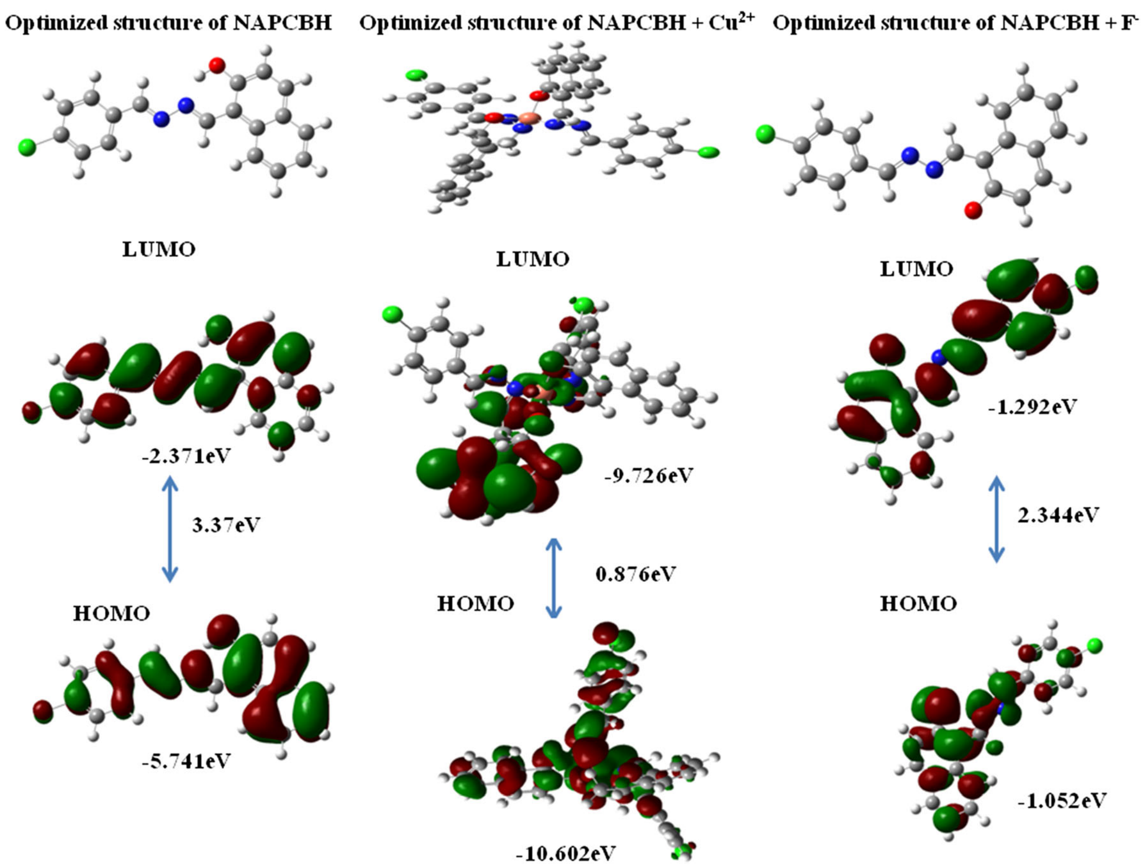


Fig. 12 Optimized structure, LUMO, HOMO of the NAPCBH with Cu^{2+}, F^{-} ions

probe from pale yellow to yellowish green indicating that the probe, NAPCBH can efficiently behave for a "naked-eye" chemosensor of Cu^{2+} (Fig. S7).

In order to investigate the binding ability of NAPCBH with Cu^{2+} ion, UV-Vis titration experiments were performed at room temperature. The absorption spectrum of NAPCBH shows three bands at 271, 331 and 384 nm. Upon addition of Cu^{2+} to a solution of NAPCBH, the intensities of absorbance bands at 271 and 331 nm were significantly increased and altogether fashioned a single band at 290 nm by exhibiting a new band at 447 nm, observable ratiometric changes were also seen [55–57]. From these spectral measurements, three isobestic points were located at 366, 416 and 473 nm which imply that only one product was generated from NAPCBH upon binding with Cu^{2+} (Fig. 2). The sensing mechanism of NAPCBH with Cu^{2+} might be explained by

Table 1 Determination of Cu^{2+} ions in water samples

Water sample	Cu^{2+} estimated (μL)	Cu^{2+} found (μL)	Recovery (%)
Thamirabarani River water collected from Tirunelveli	0	0	–
	10	13	130
	20	22	110
	30	32	106
RO processed drinking water from Author department	0	0	–
	10	15	150
	20	26	130
	30	31	103
tap water collected from Madurai corporation	0	0	–
	10	15	150
	20	22	110
	30	35	116

Table 2 Determination of F⁻ ions in water samples

Water sample	F⁻ estimated (μL)	F⁻ found (μL)	Recovery (%)
Thamirabarani River water collected from Tirunelveli	0	0	–
	10	11	110
	20	22	110
	30	31	103
RO processed drinking water from Author department	0	0	–
	10	14	140
	20	29	145
	30	33	110
tap water collected from Madurai corporation	0	0	–
	10	12	120
	20	23	115
	30	32	106

ICT and LMCT mechanisms due to the red shift of about 20 nm and decreases band at 384 nm which indicates ICT mechanism and the appearance of new band at 447 nm upon the addition of Cu^{2+} ion showing the operation of LMCT mechanism [58]. (Scheme. S1).

The stoichiometry between the NAPCBH with Cu^{2+} ion was determined by the Job's plot method. From the job's plot results (Fig.S9), the stoichiometric ratio was identified as 2:1 which is further substantiated from ^{1}H NMR titration and theoretical calculations. From these evidences, the binding structure between NAPCBH and Cu^{2+} ion was proposed as 2:1. The binding constant was calculated by using Benesi-Hilderbrand equation k value to be 1.2 x 10^4M. (Fig. 3a and b) The detection limit was calculated from the formula DL = 3σ/k where σ is the relative standard deviation from the blank titration, k is the slope of the calibration curve and it is to be 5.8 μM which is far below to the recommended value 31.5 μM in drinking water [59, 60].

To investigate further the binding ability of NAPCBH with Cu^{2+}, competitive measurements were performed in the presence of diverse metal cations. The observed experimental data indicate that there are no significant changes for other metal ions except Cu^{2+} ion (Figs. S8 (a) and (b)).

Table 3 Determination of F⁻ ions in tooth paste samples

Tooth paste	F⁻ estimated (μL)	F⁻ found (μL)	Recovery (%)
A concentration	0	0	–
	10	16	160
	20	24	120
	30	35	116
B concentration	0	0	–
	10	14	140
	20	25	125
	30	34	113

Electrochemical Measurements of NAPCBH Towards Cu^{2+} Ion

The electrochemical response of NAPCBH was investigated using cyclic voltammetry and differential-pulse voltammetry techniques at the concentration of 10^{-4} M. The measurement was performed at room temperature using the glassy carbon, Ag/AgCl electrode and platinum electrode were used as working, reference and counter electrode respectively. Tetrabutyl ammonium perchlorate was used as supporting electrolyte.

The electrochemical selective response of NAPCBH with the diverse metal ions in DMSO was tested using cyclic voltammetry in the potential window of 0 V to −1.4 V, scan rate at 50 mV/s. Upon addition of Cu^{2+} ion, the appearance of new cathodic peak at −0.21 V and − 0.65 V was observed which indicates that a quasi-reversible reduction due to the interaction with Cu^{2+} ions whilst the other cations were showed no considerable changes (Fig.S10). This observation is strongly substantiating the detection copper ion [61, 62]. Titration experiments for Cu^{2+} ion were also conducted in cyclic voltammetry and differential pulse voltammetry which showed substantial decrease in the new cathodic peaks. It is signifying the interaction of NAPCBH with Cu^{2+} ions [63] (Fig. 4a and b).

DNA Tracking Towards NAPCBH-Cu^{2+} Ion

Copper is the essential metal and have attracted tremendous interest due to their capability of interacting with DNA/nuclear protein. The strong affinity of the DNA with many fluorescent probes with metal ions was reported so far using fluorescence techniques. In this investigation, we deliberate to undertake a similar study to demonstrate DNA tracking ability of NAPCBH-Cu^{2+} which is the colorimetric probe. Therefore the titration experiments were performed using absorption spectra using a fixed concentration of NAPCBH-Cu^{2+}

(50 μL in 2 ml dmso) to which increasing amounts of DNA (10^{-4} M in CT-DNA in 5 mM Tris HCl/50 mM NaCl buffer, pH 7.2) were gradually added. The binding of the DNA with NAPCBH-Cu^{2+} which led to decrease in the absorption with slight red shift. This output indicating that the binding affinity of the NAPCBH-Cu^{2+} to the DNA is efficaciously. Further to substantiate the effective mode of binding the cyclic voltammery have been achieved. The electrochemical result indicates on addition of DNA (10^{-4} M in buffer) to the NAPCBH-Cu^{2+}(100 μL in 10 ml dmso) decrease with slight shift at −0.12 V and 0.13 V was observed. It is also indicating the effective binding of DNA with NAPCBH-$Cu^{2+.}$ This enables the probe, NAPCBH-Cu^{2+} can be used as an efficient DNA tracker [64].

UV-Vis Spectral and Colorimetric Response of NAPCBH Towards F^-

The colorimetric selective sensing capabilities of NAPCBH with diverse anions in DMSO were performed using UV-Vis electronic spectra. The addition of fluoride ion only showed a significant color change from pale yellow to yellowish brown when compared with other anions and the observed results are shown in Fig. 5a–b and Fig. S11.

To explore the interaction between NAPCBH with F^- ion, absorption spectral changes of NAPCBH was monitored by the titration method. Absorption spectra showed a clear ratiometric response with a slight red shift and the appearance of new band at 482 nm (Fig. 6). This indicates the negative charge on the phenolate oxygen might be a probable reason suggesting the operation of ICT mechanism (Scheme. S2). The stoichiometric ratio was found to be 1:1 from the Job's plot (Fig. S13) which is further supported by ^{1}H NMR titration, DFT calculations. The binding constant was calculated by using Benesi-Hilderbrand equation k value to be 1.7 × 10^4 M. The detection limit was calculated from the formula DL = 3σ/k where σ is the relative standard deviation from the blank titration, k is the slope of the calibration curve and it is to be 0.025 μM which is very low to the permissible value [65–68] (Fig. 7a and b).

In addition to the binding ability of NAPCBH with F^- ions, competitive measurements were also studied with a series of anions shown in Fig. 5. The experimental data indicate that there are no significant changes with other anions than for F^- ion (Fig. S12a-b) (Fig. 8).

Electrochemical Measurements of NAPCBH Towards F^- Ion

The electrochemical response of NAPCBH was investigated using cyclic voltammetry and differential-pulse voltammetry techniques at the concentration of 10^{-4} M. The electrochemical selective responses of NAPCBH with the diverse anions in DMSO were tested using cyclic voltammetry in the potential window of 0.5 V to −1.4 V at scan rate 50 mV/s. Upon the addition of F^- ion, the appearance of new cathodic peak at 0.11 V and − 0.62 V was noticed which indicates that a quasi-reversible reduction due to the formation of fluoride complex whilst the other anions showed no considerable changes [69, 70] (Fig. S14). Further, the titration experiment for F^- ion was performed in cyclic voltammetry and differential pulse voltammetry which shows a steady decrease in the new cathodic peaks. This observation is strongly supporting the detection of fluoride ion. Furthermore, differential pulse voltammetry measurements have also been executed for the additional confirmation of the formation of fluoride complex (Figs. 9a-b and 10).

^{1}H NMR Titration Studies of Cu^{2+} and F^- Ions

^{1}H NMR titration studies was performed to confirm the 2:1 stoichiometric between NAPCBH with Cu^{2+} in DMSO-d^6.

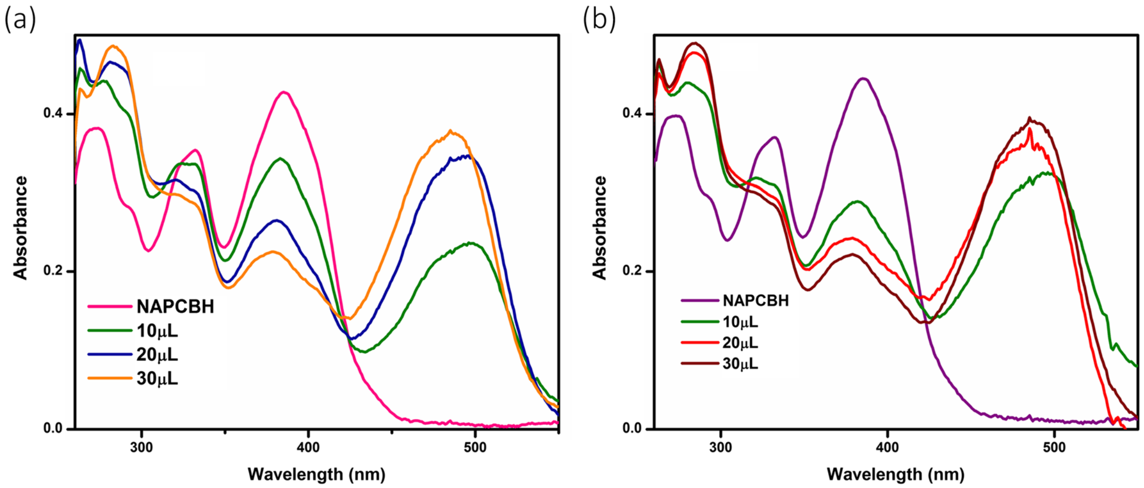


Fig. 13 Absorption spectra of NAPCBH in tooth paste samples for the determination of F^- ions

Upon addition of Cu^{2+} (0.25 equivalent) to a solution of NAPCBH, the phenolic OH peak, imine peak notably decreased due to the interaction with the NAPCBH. Further additions of Cu^{2+} led to a complete disappearance of OH peak and decreased imine peak additionally confirming the participation of these groups in the interaction. Moreover, it is noteworthy to indicate that a well resolved ^1H NMR spectrum for NAPCBH-Cu^{2+} couldn't be acquired because of the paramagnetic character of the Cu^{2+} ions (Fig.S15). The ^1H NMR titration experiments were also conducted for NAPCBH with F^- ions to confirm the 1:1 stoichiometric between NAPCBH with F^- ions in DMSO-d^6. The addition of F^- ions to a solution of NAPCBH showed a decrease in the phenolic OH peak intensity and further increasing the additions, the O-H peak became disappeared due to the hydrogen bonding which disclosed the interaction of F^- with NAPCBH [71, 72] (Fig. 9).

Reversibility and Regeneration of NAPCBH

A realistic sensor probe may be significant beneficial if a probe may be readily recovered and subsequently reusable for sensing ions. In order to study the reversibility and regeneration of NAPCBH, an absorption spectrum of the recovered probe was measured. The spectral results and color changes clearly demonstrated that NAPCBH can be readily regenerated by utilizing an appropriate reagent like HCl at a concentration of 15 μM. The absorption spectrum is almost reversible after the addition of HCl with copper and fluoride consisting NAPCBH (Fig. 11a, b). Such reversibility and regeneration are significant for the fabrication of chemosensors to sense Cu^{2+} and F^- ions as an environmental solution [73] (Fig. 11a-b).

Computational Calculations

Density Functional Theory has played a significant role in understanding sensing mechanism theoretically. In order to confirm and rationalize the spectroscopic results, DFT calculations studies were performed, as shown in Fig. 12, the geometry of NAPCBH was optimized using DFT-B3LYP 6-31G basis set, the HOMO-LUMO energy gap is decreased when compared with the free NAPCBH. These results were also confirmed and well correlation with the proposed binding mode, and mechanism [74–77].

Practical Performance of Cu^{2+} and F^- Ions

In order to examine the practical applicability of NAPCBH, real sample analyses have been performed to determine the Cu^{2+} and F^- ions. Three distinct water samples had been collected from thamirbarani, Tirunelveli, drinking water in the author department and tap water from Madurai residential area were used for the analysis. The water samples have been spiked with the standard Cu^{2+} and F^- ions and determined by a well known addition approach with the NAPCBH in UV-Vis spectra. A satisfactory recovery of the spiked samples was acquired. The result suggested that the NAPCBH efficiently quantifies the amount of Cu^{2+} and F^- ions in the environmental samples [78]. (Tables 1 and 2) and (Fig. S 16 & 17).

In addition, the realistic application of NAPCBH for detection of F^- ions in oral care item has also been tried. Commercially available toothpaste used in the water sample. The toothpaste have been weighed and extracted with two specific amounts of water (A and B). The combinations had been centrifuged and filtered to get clean extracts. A certain quantity of every extract added into the NAPCBH solution one after the other and response of the sensor become monitored. The estimated fluoride ion concentration was calculated in line with the fluoride content material listed in the aspect label of toothpaste and the dilutions. The observed fluoride ion concentrations were received in line with absorbance ratio response. It is located that the decided fluoride concentrations had been steady with the anticipated information as given in Table 3 and Fig. 13 which displaying that the NAPCBH can quantitatively determine the fluoride ions from toothpaste samples [79].

Conclusions

In the present work, a new dual responsive colorimetric, ratiometric chemosensor was developed with a probe bearing hydrazone moiety for the detection of copper and fluoride ions. These detections were possible with very high selectivity and sensitivity due to facile color changes from pale yellow to yellowish green for copper ions and pale yellow to yellowish brown for fluoride ions. The detection limits for Cu^{2+} (5.8 μM) and for F^- (0.025 μM) was observed and these values are far below than the value recommended by WHO. The colorimetric recognition was confirmed by various techniques like NMR, HR-MS, UV-Vis, cyclic voltammetry, differential pulse voltammetry. The DNA tracking ability of the NAPCBH-Cu^{2+} was investigated by absorption and cyclic voltammetry techniques which shown efficient affinity towards DNA. Hence, it can be used as a DNA tracking agent. The sensing mechanism was proposed from these results and color changes. The stoichiometric ratio of NAPCBH with Cu^{2+}, F^- ions were confirmed to be 2:1 and 1:1 complex, respectively as evidenced from the Job's plot and ^1H NMR titration studies. All the spectroscopic results were significantly substantiated by the theoretical calculations. The NAPCBH was readily regenerated with HCl, thus showing its feasibility to be utilized as a reusable sensor for the convenient detection of Cu^{2+} and F^- ions. The UV-Vis experiments confirmed the NAPCBH feasibility and quantitatively determine the Copper and fluoride ions in environmental and toothpaste samples. Thus, the present results may become highly useful for the development of commercial dual responsive colorimetric recognition for copper and fluoride ions.

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