



REGULAR ARTICLE

Cyanide selective chemodosimeter in aqueous medium, on test strips and its application in real sample analysis

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Abstract. In this paper, synthesis, characterization and detection of CN^- by the compound (N'1E,N'2E)-N'1,N'2-bis((2-hydroxynaphthalen-1-yl)methylene)oxalohydrazide (**1**) have been reported. Compound **1** is synthesized by the reaction of oxalyl dihydrazide and 2-hydroxy-1-naphthaldehyde and characterized by FTIR, ^1H NMR and ESI-Mass spectroscopy. UV-Visible spectral band of **1** is observed to be broadened and shifted to longer wavelength upon addition of CN^- ion selectively in H_2O -DMSO (8:2 v/v) medium. Based on the UV-Visible spectral data, the detection limit of cyanide ion for **1** is found to be 30.2 μM . Colourless solution of **1** changes to yellow in the presence of cyanide ion selectively. The same colour change is also observed on Whatman filter paper test strip. Fluorescence intensity of **1** is quenched due to the nucleophilic addition reaction of cyanide with one of the two imine carbons. ^1H NMR titration of **1** with CN^- ion corroborates the reaction of the latter with one of the two imine carbons of the former, leading to the appearance of cyanomethyl proton signal at 6.15 ppm and consequently, its behaviour as chemodosimeter. The above mentioned chemodosimeter nature of **1** is also validated by ESI-Mass spectroscopy data. Compound **1** is capable for the detection of CN^- in water for real samples with concomitant colour change.

Keywords. Cyanide selective chemodosimeter; oxalic acid hydrazide; 2-hydroxy-1-naphthaldehyde; addition reaction of cyanide as a nucleophile; real water sample analysis.

1. Introduction

Recently, there has been an upsurge in the field of synthetic receptors capable for the selective recognition of anion due to their immense applications in the area of environmental chemistry and mineral exploration.¹⁻⁵ Among different anions, cyanide (CN^-) ion plays a severe detrimental role in living biological systems. The strong binding affinity of cyanide with the active site of cytochrome a3 disrupts mitochondrial electron transport chain, leading to decreased oxidative metabolism in the living cell and finally to cell death.⁶⁻¹³ Cyanide, entered through the gastrointestinal tract, lungs, skin etc., is responsible for convulsion, vomiting and loss of consciousness in human body.¹⁴⁻¹⁶ Despite such drastic toxicity, cyanide is

utilized in the synthesis process of several industrial products such as nylon, fertilizers as well as electroplating industry.¹⁷⁻²⁰ Indiscriminate discharge of cyanide through industrial effluent is the most important concern for the environmentalists and scientists. According to the World Health Organization, water with cyanide concentration lower than 1.9 μM is suitable for drinking purpose.²¹

With reference to the above-mentioned circumstances, it is absolutely necessary that CN^- is detected efficiently and selectively under a real-time situation. Conventional analytical techniques like titrimetric, potentiometric, electrochemical methods, ion chromatography etc., have been used earlier days for the detection of CN^- .²²⁻²⁵ However, these techniques experienced a series of major inadequacies like

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complicated procedure, prolonged analysis time, lack of selectivity which rendered them inappropriate and restricted their scope for real-time analysis. To prevail over these constraints, molecules those are competent for the detection of CN^- by change in colour or fluorescence in the aqueous or predominately aqueous medium have been investigated and reported by different research groups.^{26–40} Colorimetric and fluorometric detection of CN^- have been proven to be the most convenient techniques owing to their high sensitivity, easy-to-measure signal, quick detection time and inexpensive nature.

Chemodosimeters are abiotic molecules which are capable of undergoing reaction selectively with the target analyte *viz.*, anion, cation or neutral molecule, leading to considerable chemical conversion engaging both breaking and forming of covalent bonds.^{41–48} Recently, Kumar and co-workers reported anthracene containing 1-(4'-nitrophenyl) benzimidazolium chemodosimeter for the selective detection of cyanide ion in HEPES buffer-DMSO (95:5 v/v) and in the presence of blood serum, utilizing ratiometric approach through dual UV-Vis and fluorescence channels.⁴⁹ Hae-Jo Kim and co-worker described an α , β -unsaturated nitro group bearing coumarin chemodosimeter which displayed both colorimetric and fluorometric change for the selective detection of cyanide ion, using nucleophilic aromatic substitution reaction.⁵⁰ Cheal Kim and co-workers synthesized triazol group bearing naphthol derivative which was capable for selective sensing of cyanide ion by chemodosimeter approach via nucleophilic addition reaction, with a change in colour and fluorescence.⁵¹ Wei and co-workers synthesized and explored a benzimidazole containing naphthol derivative that behaves as colorimetric and fluorimetric turn-on chemodosimeter for selective detection of CN^- ion in 0.01 M HEPES-DMSO (1:4 v/v, pH 7.26) medium.⁵²

In continuation to our previous endeavour for selective detection of cyanide,^{53–55} we have synthesized compound **1** by the reaction of oxalyldihydrazide and 2-hydroxy-1-naphthaldehyde and characterized it by FTIR, ^1H NMR and ESI-Mass spectroscopy. Compound **1** exhibits red-shift of its absorption band to 410 nm and generation of yellow colour in H_2O -DMSO (8:2 v/v) solution and on Whatman filter paper test strip, whereas its fluorescence band at 530 nm is quenched upon addition of CN^- ion selectively. ^1H NMR titration as well as ESI-Mass spectroscopy data confirm the detection of cyanide ion by compound **1**, utilizing chemodosimeter approach where one of the two imine carbons of **1** is attacked by

cyanide. Compound **1** is found to detect CN^- in water for real samples by changing its colour.

2. Experimental

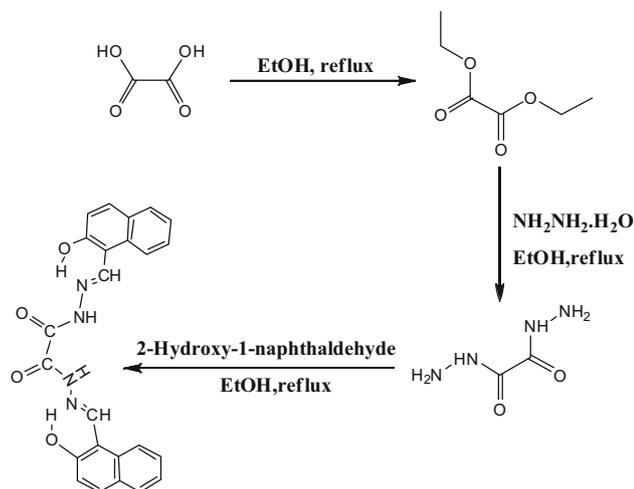
2.1 Instruments, materials and methods

FTIR Spectrum 2 (Perkin Elmer) spectrometer was used for the recording of Infrared spectra where spectrum was recorded by dispersing the solid sample as KBr pellet. Xevo G2-S Q-ToF (Waters, USA) instrument was used for Electrospray ionization mass spectrometry (ESI-Mass) measurements. Bruker Avance II 400 MHz NMR spectrometer was employed for ^1H NMR spectra, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as an internal standard. Shimadzu UV-2450 spectrophotometer (slit width = 2 nm) was utilized for UV-visible spectra by using a pair of quartz cuvettes (path length = 1 cm). Steady-state fluorescence spectra were recorded in a quartz cell (path length = 1 cm) using an Agilent Technology Cary Eclipse Fluorescence Spectrophotometer for solutions having low absorbance at the wavelength of excitation (λ_{ex}), with excitation and emission slit of 5 nm each. Unless otherwise specified, all the experiments were carried out at 298 ± 1 K.

All reagents for synthesis were obtained commercially and used without further purification. DMSO and water, both HPLC grade, were procured from Merck. All anions, in the form of tetrabutylammonium (TBA) salts, were purchased from Aldrich Chemical Co. (USA), stored in a desiccator under vacuum containing self-indicating silica and used for titration without any further purification. Compound **1** (4.6 mg) was dissolved in DMSO to prepare 10 mL solution and a certain volume of this solution is added to 2.5 mL of H_2O -DMSO (8:2 v/v) mixture to prepare the solution for absorption and fluorescence titration. The test kit of **1** was prepared by immersing Whatman filter paper strips into its solution and dried them at 50°C . The test strips prepared by above method were dipped in an aqueous solution of different anions F^- , Cl^- , Br^- , I^- , CN^- , CH_3COO^- , HSO_4^- , H_2PO_4^- , ClO_4^- and $\text{C}_6\text{H}_5\text{COO}^-$ (all as TBA salt) and dried in the same manner as stated above. Compound **1** was dissolved in DMSO-d_6 , taken in an NMR tube and then, concentrated TBACN solution in DMSO-d_6 (in small quantities) was added to the above solution to perform the ^1H NMR titration.

2.2 Synthesis of (*N'*1*E,N'*2*E*)-*N'*1, *N'*2-bis ((2-hydroxynaphthalen-1-yl) methylene) oxalohydrazide (**1**)

Compound **1** is prepared by three steps reaction procedure (Scheme 1).^{56–58} In the first step, oxalic acid (2 g, 22 mmol) is dissolved in ethanol (15 mL) and refluxed for 3–4 h in presence of 4–5 drops of concentrated sulphuric acid. Ethanol is almost completely evaporated in vacuum and the



Scheme 1. Synthesis procedure of **1**.

remaining viscous liquid is extracted 3–4 times by CHCl_3 – H_2O mixture. CHCl_3 phase is collected and then dried by anhydrous Na_2SO_4 and evaporated by rotary evaporator to generate diethyl oxalate (2.57 g, 17.6 mmol). In the second step, diethyl oxalate (0.5 g, 3.42 mmol) is reacted with excess hydrazine hydrate (0.256 mL, 8 mmol) in ethanol (20 mL) under reflux condition for 3–4 h and progress of the reaction is assessed by thin-layer chromatography (TLC). The reaction mixture is cooled to room temperature and filtered. Oxalyldihydrazide (0.34 g, 2.87 mmol) is obtained as white solid. In the final step, oxalyldihydrazide (0.34 g, 2.87 mmol) and 2-hydroxy-1-naphthaldehyde (0.99 g, 5.74 mmol) dissolved in EtOH (50 mL) and heated under reflux for 2 h. The reaction mixture is cooled and the yellow product is separated through filtration and washed with ethanol to afford **1** in 81% yield (0.99 g, 2.32 mmol). FTIR (KBr pellet, cm^{-1}): OH (3624), NH (3250), CO (1630), C=N (1536), (Figure S1, Supplementary Information). ^1H NMR (DMSO-d_6 , 400 MHz, TMS) δ /ppm: 7.24 (dd, 2H, $J = 8.8$ Hz), 7.4 (t, 2H, $J = 7.4$ Hz), 7.59–7.65 (m, 2H), 7.90 (t, 2H, $J = 9$ Hz), 7.98 (d, 1H, $J = 9.2$ Hz), 8.13 (d, 1H, $J = 9.2$ Hz), 8.22 (d, 1H, $J = 8.4$ Hz), 8.93 (d, 1H, $J = 8.4$ Hz), 9.73 (s, 2H), 10.81 (s, 2H), 12.59 (s, 2H) (Figure S2, Supplementary Information). ESI-Mass (m/z): 427.2769 $[\text{M}+\text{H}]^+$ (Figure S3, Supplementary Information).

3. Results and Discussion

3.1 Synthesis of **1**

Compound **1** is synthesized using three-step reaction (scheme 1), as reported elsewhere.^{56–58} First, oxalic acid is converted to diethyl oxalate by the reaction of the former with ethanol in the presence of catalytic amount of concentrated H_2SO_4 . Then, the ester (diethyl oxalate) is reacted with hydrazine hydrate to form

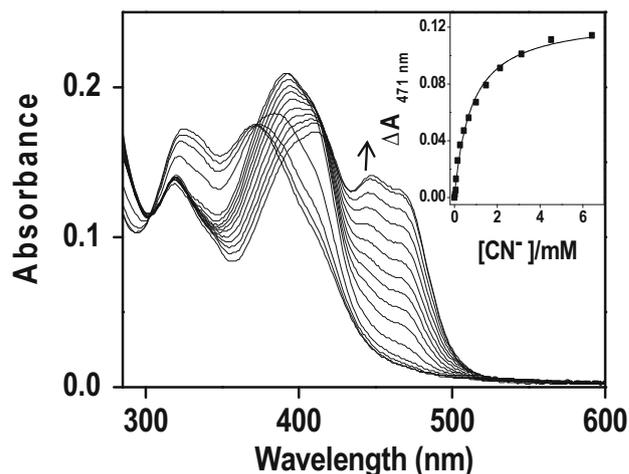
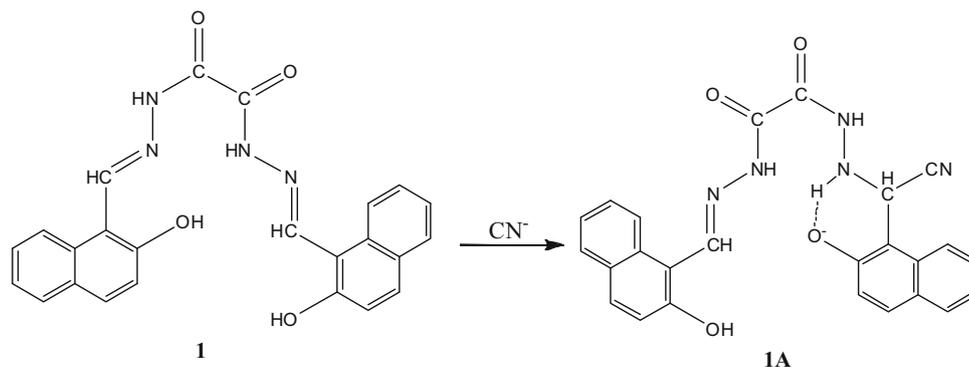


Figure 1. UV–Visible spectral change observed for **1** upon addition of CN^- in H_2O – DMSO (8:2 v/v) at 298 K. $[\mathbf{1}] = 1.05 \times 10^{-5}$ M, $[\text{CN}^-] = 0$ – 6.42×10^{-3} M. Inset shows scatter plot of the experimental data (ΔA for **1** at 471 nm vs $[\text{CN}^-]$).

oxalyldihydrazide which is heated under reflux with 2-hydroxy-1-naphthaldehyde in ethanol to produce **1** in an 81% yield. Compound **1** is well characterized by FTIR, ^1H NMR and ESI-Mass spectroscopy. Stretching of NH and OH groups of **1** is observed at 3250 cm^{-1} and 3624 cm^{-1} , respectively and that for CO is found at 1630 cm^{-1} . ^1H NMR signal for OH and NH appears as singlet at 12.59 and 10.81 ppm, respectively. ESI-Mass of **1** gives a peak at 427.2769 which corresponds to $[\text{M}+\text{H}]^+$ fragment. Singh and co-worker reported selective fluorescence sensing of Al^{3+} ion by **1** in EtOH – H_2O (2:3 v/v) mixture.⁵⁷ However, sensing/detection of CN^- by **1** has not been explored by the above research group.

3.2 Absorption titration study

UV–Visible spectrum of **1** displays two bands at 325 nm and 370 nm in an aqueous medium, i.e., 80% H_2O –20% DMSO (v/v) mixed solvent, as shown in Figure 1. Upon gradual addition of CN^- ion, band at 325 nm decreases continuously. The other absorption band, originally at 370 nm, is shifted to longer wavelength to 410 nm. On the other hand, a new band is generated at a higher wavelength at 470 nm with a continuous increase in absorbance during titration as shown in Figure 1. Nucleophilic addition reaction of CN^- to one of the two imine carbons causes shifting of negative charge on nitrogen which, being a strong base, instantly abstracts proton by intramolecular mechanism from naphthol OH, leading to the formation of naphthoxide ion (**1A** in Scheme 2) and might be responsible for the generation of the band at 470 nm.



Scheme 2. Proposed reaction mechanism of **1** with cyanide ion.

The reaction of CN^- with **1** follows 1:1 stoichiometry which is confirmed by Job's plot analysis (Figure S4, Supplementary Information). The equilibrium constant for the reaction of CN^- with **1** is calculated by eq 1 (Supplementary Information) which is found to be $1.26 \times 10^3 \text{ M}^{-1}$.^{59,60} Compound **1** acts as chemodosimeter during its reaction with CN^- with the deepening of yellow colour. However, the colour intensity reverts to that of **1** upon addition of trace amount of aqueous trifluoroacetic acid solution. This indicates that the reaction of CN^- with **1** is reversible in the presence of H^+ . Based on the UV-Visible spectral change, the detection limit of cyanide ion for **1** is found to be $30.2 \mu\text{M}$.

3.3 Study on the selectivity of **1** with CN^- and interfering effect

Compound **1** reacts with CN^- ion selectively. Figure 2 shows a change in the absorption spectrum of **1** on the

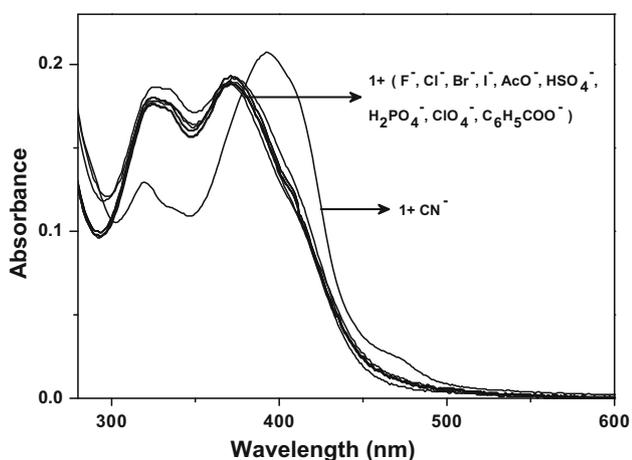


Figure 2. UV-Visible spectrum of **1** ($1.34 \times 10^{-5} \text{ M}$) upon addition of different anions (50 equiv) in H_2O -DMSO (8:2 v/v).

addition of different anions (F^- , Cl^- , Br^- , I^- , CN^- , CH_3COO^- , HSO_4^- , H_2PO_4^- , ClO_4^- and $\text{C}_6\text{H}_5\text{COO}^-$). The UV-Visible spectrum of **1** is changed substantially only with CN^- which confirms the selective detection of the latter by the former. Interfering effect of different anions is checked by adding them in a solution containing **1** and CN^- . Different anions like F^- , Cl^- , Br^- , I^- , CH_3COO^- , ClO_4^- and $\text{C}_6\text{H}_5\text{COO}^-$ show no interfering effect to the solution of **1** containing CN^- , as shown in Figure S5 (Supplementary Information). However, the other two anions HSO_4^- and H_2PO_4^- show a drastic change in the spectrum of **1** containing CN^- . This might be due to the reverse reaction of **1A** with H^+ which is generated from the ionisation of the above two anions.

3.4 Change in colour of **1** in solution and on test strips

Detection of CN^- by compound **1** is also demonstrated by colour change of the latter upon addition of the former, as shown in Figure 3. Upon addition of 100 equivalents of different anions (F^- , Cl^- , Br^- , I^- , CN^- , CH_3COO^- , HSO_4^- , H_2PO_4^- , ClO_4^- and $\text{C}_6\text{H}_5\text{COO}^-$), colourless solution of **1** turns to yellow with CN^- only. No change in colour is observed for **1** in presence F^- , Cl^- , Br^- , I^- , CH_3COO^- , HSO_4^- , H_2PO_4^- , ClO_4^- and $\text{C}_6\text{H}_5\text{COO}^-$. Colour of Whatman filter paper test strip containing **1** is changed to yellow in the presence of CN^- ion selectively in a similar manner, as shown in Figure 3.

3.5 Fluorescence titration study

Compound **1** is weakly fluorescent and its fluorescence quantum yield (ϕ_f) is found to be 0.056 in H_2O -DMSO (8:2 v/v), using fluorescein ($\phi_f = 0.95$ in 0.1 N NaOH)

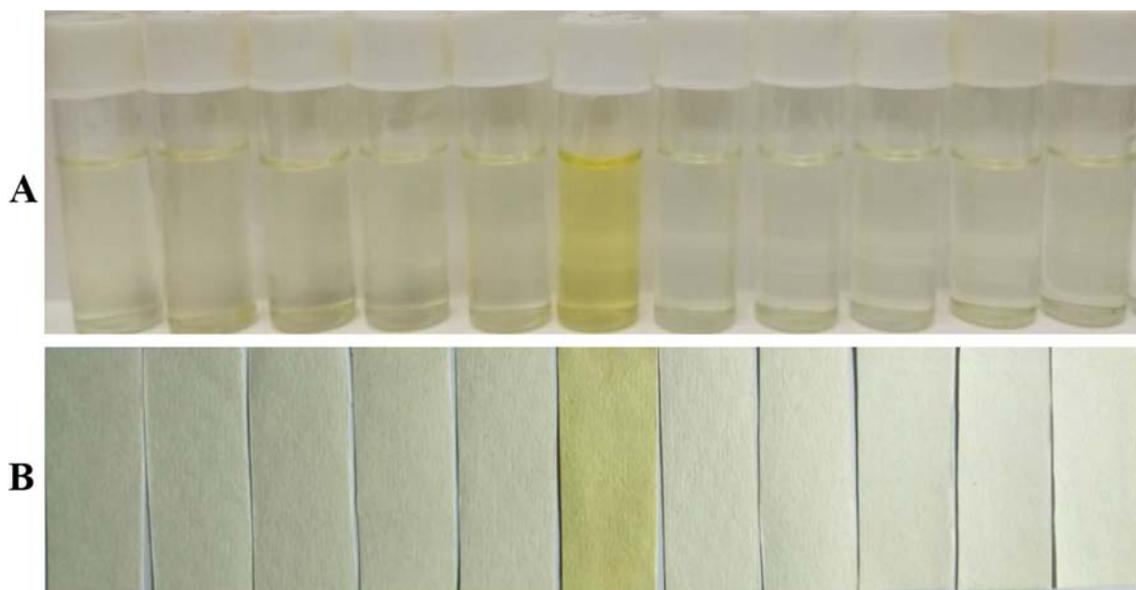


Figure 3. (A) Colour change observed for **1** (2.02×10^{-5} M) in H₂O-DMSO (8:2 v/v) upon addition of 100 equivalents of different anions as TBA salts. From left to right: **1**, F⁻, Cl⁻, Br⁻, I⁻, CN⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, ClO₄⁻, C₆H₅COO⁻. (B) Colour change observed for **1** on Whatman filter paper test strip upon dipping in the aqueous solution of different anions as TBA salts. From left to right: **1**, F⁻, Cl⁻, Br⁻, I⁻, CN⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, ClO₄⁻, C₆H₅COO⁻.

as standard.⁶¹ Fluorescence spectrum of **1** shows a broad band at 530 nm with a shoulder at 490 nm which is shown in Figure 4. Nucleophilic addition reaction of cyanide to one of the imine carbons and simultaneous abstraction of naphthol OH proton leads to the formation of **1A** and, as a result, the non-radiative pathway is dominated, causing to the quenching of fluorescence of **1**. Scatter plot of fluorescence intensity with CN⁻ concentration is fitted in eq 2 (Supplementary Information) which generates equilibrium constant value of 1.27×10^3 M⁻¹.^{59,60} Only

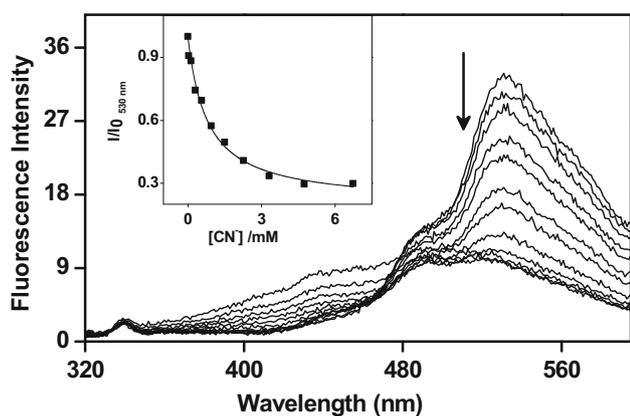


Figure 4. Fluorescence spectral changes observed for **1** upon addition of CN⁻ in H₂O-DMSO (8:2 v/v) at 298 K. [**1**] = 1.36×10^{-5} M, [CN⁻] = (0 – 6.73×10^{-3} M), λ_{exc} = 304 nm. Inset shows fitting (solid line) of the experimental data (fluorescent intensity ratio with and without addition of CN⁻ at 530 nm (I/I₀) vs [CN⁻]).

one of the two naphthol OH groups is deprotonated by CN⁻ which is corroborated by the fact that there is still substantial emission intensity left at 530 nm for the last spectrum of the titration.

3.6 ¹H NMR titration study

To investigate the mechanism of the reaction of **1** with CN⁻, ¹H NMR titration of the former with the latter is performed which is illustrated in Figure 5. CN⁻ ion attacks one of the two imine carbons, leading to the formation of negatively charged nitrogen which abstracts a proton from naphthol OH immediately. The cyanomethyl CH proton generated after an attack on the imine carbon by CN⁻ shows the formation of a singlet initially at 6.44 ppm which finally appears at 6.15 ppm at the end of the titration. Our above observation is similar to that reported by Kim and co-workers where the appearance of cyanomethyl CH proton at 6.1 ppm was detected upon nucleophilic addition reaction of CN⁻ to the imine carbon of 2-hydroxy-1-naphthyl derivative.⁵¹ Attack of CN⁻ to only one of the two imine carbons is substantiated by the fact that singlet at 9.73, corresponding to two imine CH protons, is shifted upfield to 9.35 ppm and not disappeared till the end of the titration. On addition of CN⁻, all naphthyl CH proton signals, except one doublet, are shielded and shifted to upfield region due to negative charge of naphthoxide ion. The aforesaid naphthyl CH doublet is influenced by diamagnetic

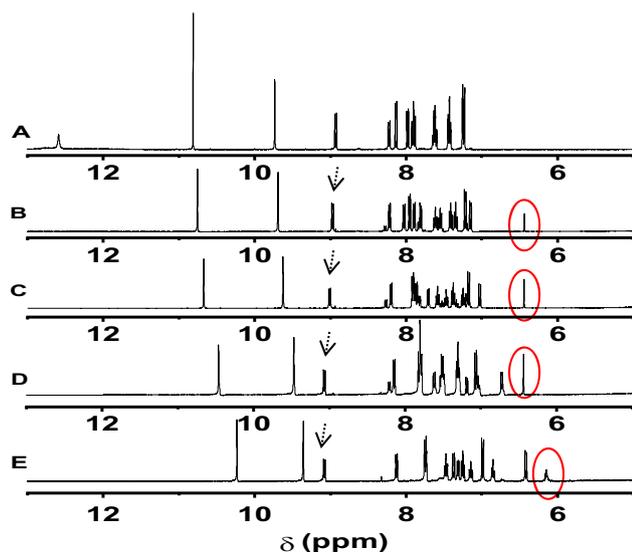


Figure 5. ^1H NMR titration of **1** with TBACN in $\text{DMSO-}d_6$. $[\mathbf{1}] = 2.4 \times 10^{-2}$ M; $[\mathbf{1}]:[\text{CN}^-]$ in these traces are (A) 1:0, (B) 1:0.25, (C) 1:0.5, (D) 1:1 and (E) 1:2. Black dash arrow indicates the shifting of deshielded naphthyl proton doublet to high δ value and the red circle indicates the generation and shifting of cyanomethyl (CH) proton from 6.44 ppm to 6.15 ppm.

anisotropy effect of nitrile group and consequently, shifted to high δ value (down-field) during titration.^{53,62} It is noteworthy to mention that CH protons of two naphthyl rings appear at different positions at the end of the titration. This indirectly confirms that

only one of the two imine carbons is attacked by CN^- , causing a non-symmetric environment for the two naphthyl rings.

3.7 ESI-Mass of **1** in presence of CN^-

The above mechanism is also substantiated by adding CN^- ion to **1**, followed by recording ESI-Mass spectrum data which is displayed in Figure 6. Mass peak is detected at $m/z = 511.7545$ which corresponds to $[\mathbf{1} + \text{CN}^- + \text{CH}_3\text{CN} + \text{H}_2\text{O}]^+$ fragment. This observation unambiguously validates the fact that compound **1** has undergone reaction with CN^- ion, leading to the former's performance as chemodosimeter.

3.8 Real sample analysis

To demonstrate the practical application of the compound **1** for selective detection of CN^- ion, we have utilized three different sources of water such as tap water, de-ionized water and drinking water for the preparation of three different CN^- solutions of same concentration and added an equal volume of these solutions to the H_2O -DMSO (8:2 v/v) solution of **1**. The yellow colour of equal intensity is generated with all the three samples of cyanide (Figure 7). This clearly indicates that **1** is competent for the detection

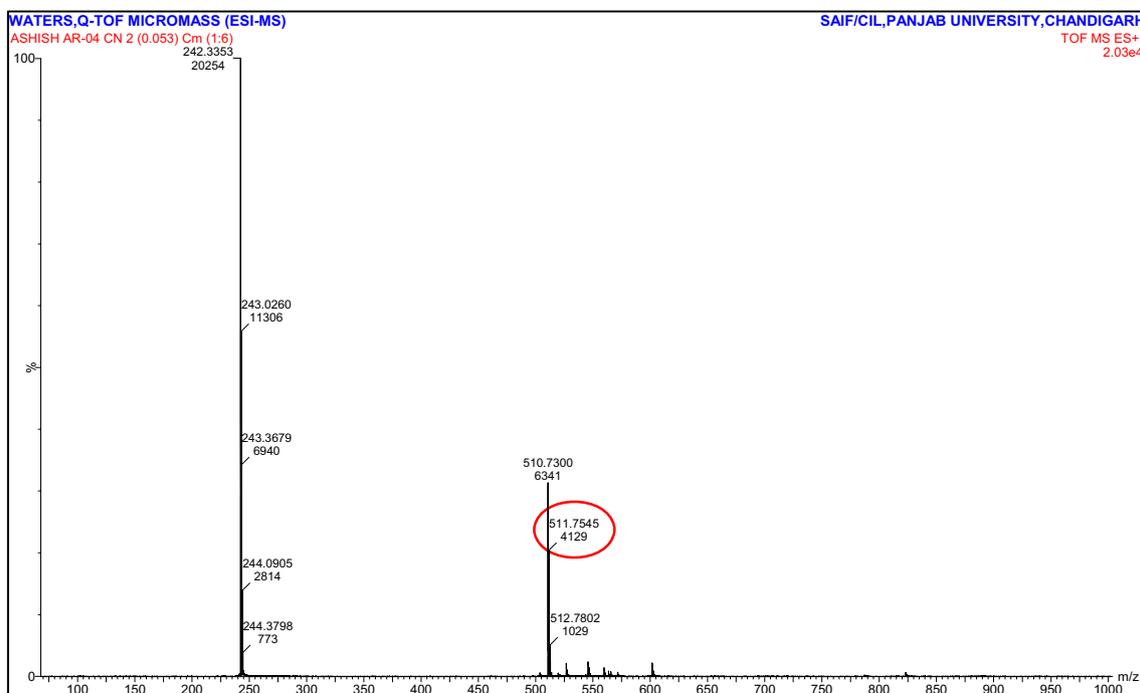


Figure 6. ESI-Mass spectrum of **1** after addition of CN^- ion. Peak at $m/z = 511.7545$ corresponds to $[\mathbf{1} + \text{CN}^- + \text{CH}_3\text{CN} + \text{H}_2\text{O}]^+$ fragment.

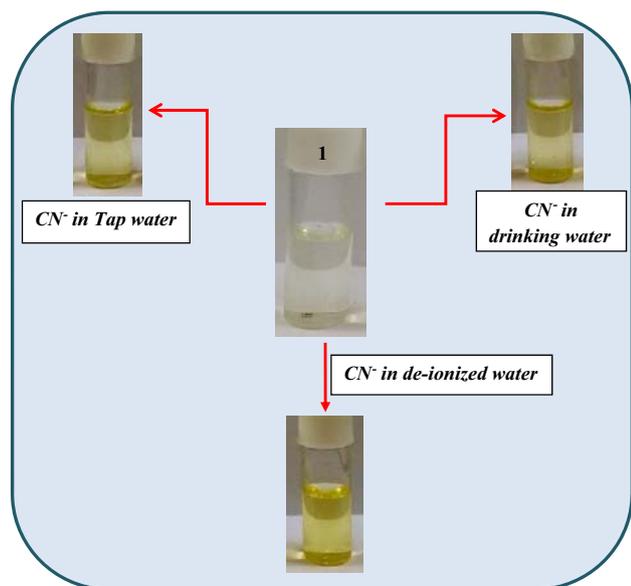


Figure 7. Real sample analysis using **1** (2.02×10^{-5} M) for detection of CN^- in water sample obtained from different sources.

of hazardous cyanide in real-time monitoring of water sample from different sources and can be effectively applied for environmental sample analysis.

4. Conclusions

As concluding remarks for the above work, we have synthesized compound **1** by simple 3-step reaction and characterized it by FTIR, ^1H NMR and Mass spectroscopy. Compound **1** behaves as selective colorimetric and fluorimetric chemodosimeter for cyanide with a concomitant change in its UV-Visible and fluorescence spectrum in a predominately aqueous medium (H_2O -DMSO, 8:2 v/v). Both colourless solution and Whatman filter paper test strip of **1** turn to yellow in the presence of CN^- ion. ^1H NMR titration and ESI-Mass data corroborate that the nucleophilic addition reaction of cyanide with **1** utilizes chemodosimeter approach where one of the two imine carbons of the latter is attacked by the former. Compound **1** can be used for the detection of CN^- in water for real samples.

Supplementary Information (SI)

Supplementary information related to this article can be found at www.ias.ac.in/chemsci.

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