Chromogenic hydrazide Schiff base reagent: Spectrophotometric determination of CN- ion



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$\label{eq:chromogenic} Chromogenic hydrazide \ Schiff \ base \ reagent: spectrophotometric \ determination \ of \ CN^- \ ion$

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Abstract: A Schiff base reagent, Picolinohydrazide-naphthol (HL), is used for trace level detection of toxic CN⁻ selectively in presence of eighteen other anions (SCN⁻, OCN⁻, S₂O₃²⁻, HPO₄²⁻, H₂PO₄⁻, Γ , ClO₄⁻, HSO₄⁻, SO₄²⁻, AsO₄³⁻, NO₂⁻, AsO₂⁻, CΓ, F⁻, HF₂⁻, NO₃⁻, Br⁻, N₃⁻) by visual colour change, colorless to yellow, in DMSO/H₂O (9:1, v/v) at pH, 7.2 (HEPES buffer) medium. The sensitivity of the probe shows that the limit of detection (LOD) is 7.08 μ M. The probable mechanism for the sensing behavior involves the deprotonation of naphthol-OH by CN⁻ that has been authenticated by ¹H NMR titration and Mass spectra. The composition (1:1 mole ratio) is supported by Job's plot and binding constant (K_a, 1.5 × 10⁴ M⁻¹) is reported by Benesi-Hildebrand plot. Furthermore, a simple paper strip device is fabricated for the determination of CN⁻ ion in water. DFT computation is carried out to explain the electronic spectral feature of the sensor.

Keywords: Hydrazide based fluorescent probe, naphthyl, cyanide, colorimetric ion sensor.

1. Introduction

Cyanide (CN⁻) is well known toxic anion and has been released from manufacturing gas plants as by-product; extremely used in crimes; extensively included in the production of plastics, dyes, pigments, nylon, pharmaceuticals, insecticides, road salts, extraction of gold and silver ore and metal degreasing. Besides, tobacco smokers generate CN⁻/HCN in their blood. Thus there is enough scope of entry of CN⁻ in food chain and environment. Selective sensing of anions has incessantly received significant attention due to their wide variety of roles in environmental, chemical, clinical and biological applications [1-3]. Because of severe toxicity of cvanide (CN⁻) to living organisms and easy binding with heme-proteins, the blockage of cytochrome C oxidase functions hampers the mitochondrial electron transfer chain process [4]. Toxic cyanide (HCN) can be inhaled or absorbed via skin; entered through unclean food and contaminated drinking water into human body [5]. In the last few years, a number of experimental methods for detection of cyanide ion have been adopted, for example, electrochemical, chromatographic technique and also flow injection analysis [6-8]. However, spectrophotometric methods have advantageous over the others because of easy to operation, time-saving and low cost technique [9-12]. Therefore, it is important to develop a colorimetric probe with simple structure and high selectivity towards specific anion. A colorimetric sensor generally possess two main parts, one is signaling unit and the other one is binding site; the color change occurs when the binding site interacts with the corresponding ions in the recognition route [13]. There is upsurge in the design of sensors for CN⁻ detection [14-16]. The chemosensors like carbazole-based molecules [17], imidazolyl-naphthoquinone [18], anthraquinone derivatives [19], pyromellitic diimides [20], Rhodamine-B derivatives [21] etc. have been used for trace level determination of Cyanide ion. Most interesting, certainly in public domain, is the use of visual detection of the anion. Azo-

azomethine (-N=N----C=N-) chemosensor has been used as chromogenic reagent for naked-eye determination of CN⁻ [13]. Sensitivity to CN⁻ is largely dependent on the nature of binding site with various functional groups like fluoroactophenone [22], benzyl [23], hydrazone [24], indolium [25-29], boronic acid [4, 30-33], dicyanovinyl [34-40], aldehyde [41-43], amide, pyrrole, indole, phenols, hydrazine based salicyladehyde derivatives [44-50]. In this work, we have designed a simple probe. (E)-N'-((2-hydroxynaphthalen-1very vl)methylene)picolinohydrazide from picolinohydrazide (HL), obtained 2-hydroxy-1and naphthaldehyde which is selective colorimetric sensor for CN⁻ in semi-aqueous solution. Detail of probe characterization, sensing of CN⁻ in presence of large number of anions is reported in this work along with theoretical computation.

2. Experimental Section

2.1. Materials and methods

2-Picolinic acid bought from High-Media and used without further purification. All other chemicals were purchased from Merck. The aqueous solutions were prepared by using Milli-Q (Millipore) water. Elemental analyses (C, H, and N) were done by Perkin-Elmer CHN analyzer (2400 Series-II), USA elemental analyzer. Perkin Elmer Lambda 25 spectrophotometer was used to get UV-Vis spectra. FT-IR spectra obtained from a Perkin Elmer LX-1 FTIR spectrophotometer with KBr disk (4000–400 cm⁻¹). The ¹H and ¹³C NMR spectra were acquired from Bruker (AC) 500 MHz FT-NMR spectrometer with TMS as an internal standard. ESI mass spectra were obtained from a Water HRMS model of XEVO-G2QTOF#YCA351 spectrometer.

2.2. Synthesis of HL

Picolinohydrazide was prepared starting from 2-Picolinic acid [51]. Dry MeOH (10 ml) solution of Picolinohydrazide (137 mg, 1.0 mmol) was added to methanol solution (10 ml) of 2hydroxy-1-naphthaldehyde (172 mg, 1.0 mmol) and was stirred for 6 h and a greenish-yellow solution was obtained. Then this solution was allowed to evaporate slowly keeping in air. After few days solid yellow mass of (E)-N'-((2-hydroxynaphthalen-1-yl)methylene)picolinohydrazide (HL) were obtained (Yield, 87%), M.P., 186°C (Scheme 1). Microanalytical data: C₁₇H₁₃N₃O₂ calcd (found): C, 70.09 (69.55); H, 4.50 (4.54); N, 14.42 (13.85) %. ¹H NMR (500 MHz, DMSO-d₆) (δ, ppm): 12.73 (s, 1H, -OH), 12.387 (s, 1H, -NH), 9.628 (s, 1H, imine-H), 8.573-8.582 (d, 1H), 7.976-8.010 (t, 2H), 7.899-7.917 (dd, 1H), 7.740-7.758 (d, 1H,), 7.699-7.715 (d, 1H), 7.507-7.531 (dd, 1H), 7.404-7.434 (t, 1H), 7.205-7.234 (t, 1H), 7.034-7.052 (d, 1H) (Fig. **S1**); 13 C NMR (in DMSO-d₆) (δ , ppm): 160.49, 158.63, 149.41, 149.15, 149.04, 138.65, 133.34, 132.33, 129.45, 128.27, 128.24, 127,49, 124.06, 123.30, 120.99, 119.43, 108.99 (Fig. S2); ESI-MS peak for HL at 292.1084 (calculated mass, 291.1086) corresponds to $[M+H^+]$ and base peak at 314.0985 for [M+Na⁺], (Fig. S3); FTIR for HL: v 3482 cm⁻¹ (OH), v 3191 cm⁻¹ (NH), v 1661 $cm^{-1}(C=O)$, v 1620 $cm^{-1}(C=N)$ (Fig. S4).



HL

Scheme 1. Synthetic scheme of the probe, HL.

2.3. Analytical Experiments

For UV–Vis measurements stock solution of HL was prepared by dissolving the probe which required producing 1.0×10^{-3} M solution. All the required anion of 1.0×10^{-3} M solution was prepared in deionized water. In this case sodium, potassium, ammonium or tetra ethyl ammonium salts of different anions (NH₄SCN, NaOCN, Na₂S₂O₃.5H₂O, K₂HPO₄, KH₂PO₄, KI, NaClO₄, NaHSO₄, Na₂SO₄, (C₂H₅)₄N(CN), Na₂HAsO₄.7H₂O, NaNO₂, NaAsO₂, NaCl, NH₄F, NH₄HF₂, NaNO₃, KBr, NaN₃) are used. For checking sensitivity, selectivity and all the UV–Vis spectral measurements towards anions, 50 µM main solution in 9:1 DMSO/water (v/v) (HEPES buffer, pH 7.2) were prepared and to this solution 1.00 equivalent anion salts were added.

The limit of detection (LOD) was calculated from the UV-Vis titration measurements. For the determination of standard deviation the absorbance of HL without any analyte was measured. The limit of detection of HL for CN^- ion sensing were determined by following equation: $LOD = 3 \sigma$ and $\sigma = (Sb_1)/(S)$; $Sb_1 =$ standard deviation of the blank solution; S = slope of the calibration curve.

The binding constant value of cyanide with **HL** was determined from the absorbance data and using Benesi–Hildebrand equation, $1/\Delta A = 1/\Delta A_{max} + (1/K[C])(1/\Delta A_{max})$. Here $\Delta A = A - A_{min}$ and $\Delta A_{max} = A_{max} - A_{min}$, where A_{min} , A, and A_{max} are the absorbance values of **HL** measured in the absence of anion, at an intermediate anion concentration, and at a concentration of complete saturation where K is the binding constant and [C] is the anion concentration respectively. In this report of work we represent A_{min} as A_0 . From the plot of $(A_{max} - A_0)/(A - A_0)$ against [C]⁻¹ for anions, the value of K has been determined from the slope.

2.4. Theoretical Computation

For the optimisation of ligand and ligand with CN⁻, DFT/B3LYP method by Gaussian 09 software was used with basis set 6-311G [52]. For approval the optimized geometries, Vibrational frequency calculations were performed which represents the local minima and positive eigenvalues. The absorption energies are theoretically examined by time-dependent DFT (TDDFT) by considering DMSO as a solvent through the conductor-like polarizable continuum model (CPCM) approach [53-55], The fraction of influences of various groups in each of the molecular orbitals were calculated by using GAUSSSUM [56].

3. Result and Discussion

3.1. Synthesis and Formulation of Probe

The structure of (E)-N'-((2-hydroxynaphthalen-1-yl)methylene)picolinohydrazide (HL) is supported by ¹H NMR spectrum in DMSO-d₆ which shows prominent peaks at 12.73 (s, 1H) for NH, 12.38 (s, 1H) for OH, 9.62 (s, 1H) for imine-H (**Fig. S1**). ESI-MS spectrum also shows ion peak at 292.1084 which is characteristic formation of [**HL**+H]⁺ and base peak at 314.0985 for [**HL**+Na⁺] (**Fig. S3**). The IR spectrum confirms the presence of functional groups like C=N (1620 cm⁻¹), C=O (1661 cm⁻¹), N-H (3191 cm⁻¹) and phenolic-OH (3482 cm⁻¹) (**Fig. S4**) and supports the structure of the probe.

3.2. Colorimetric Detection of CN⁻

Use of spectrophotometric method for the detection of CN⁻/HCN is well known in literature [57]. Herein experiment is performed on adding equimolar concentration of anions viz. SCN^- , OCN^- , $S_2O_3^{2-}$, HPO_4^{2-} , $H_2PO_4^{-}$, Γ , CIO_4^- , HSO_4^- , SO_4^{2-} , CN^- , AsO_4^{3-} , NO_2^- , AsO_2^- , $C\Gamma$, F^- , HF_2^- , NO_3^- , Br^- , N_3^- to the 50 μ M ligand solution in 9:1 DMSO-H₂O (v/v) (HEPES buffer,

pH 7.2). Out of this large number of anions, a rapid color change has been observed from colorless to yellow for CN^- only (**Fig. 1**). Furthermore, the selectivity and sensitivity of CN^- is also confirmed by UV-Vis spectroscopic measurements (**Fig. 2**). AsO₄³⁻ and AsO₂⁻ are responding weakly in the absorption spectra and do not affect the CN^- determination.



Fig. 1. Visualization test of the probe, HL (A) with the anions (left to right) $SCN^{-}(B)$, $OCN^{-}(C)$, $S_2O_3^{2-}(D)$, $HPO_4^{2-}(E)$, $H_2PO_4^{-}(F)$, Γ (G), $CIO_4^{-}(H)$, $HSO_4^{-}(I)$, $SO_4^{2-}(J)$, $CN^{-}(K)$, $AsO_4^{3-}(L)$, $NO_2^{-}(M)$, $AsO_2^{-}(N)$, $C\Gamma$ (O), $F^{-}(P)$, $HF_2^{-}(Q)$, $NO_3^{-}(R)$, $Br^{-}(S)$, $N_3^{-}(T)$ under normal light.



Fig. 2. Change in absorption spectrum of HL (50 μ M) upon addition of different anions (50 μ M each) in 9:1 DMSO/H₂O (v/v) (HEPES buffer, pH 7.2), inset: vial image of HL and HL+CN⁻.

The sensitivity of the probe, with CN^- ion has been examined with gradual addition of CN^- ion followed by recording of UV-Vis spectral changes. The probe shows four absorption maxima at 314, 328, 365 and 380 nm, on adding CN^- , the absorption maxima are decreased with generation of a new characteristic band at 460 nm forming an isobestic point at 400 nm (**Fig. 3**). The absorption spectral intensity has changed linearly at 460 nm on adding CN^- (0-50 μ M) to HL in DMSO-H₂O medium (**Fig. 3** inset). The limit of detection (LOD) determined from UV–Vis titration is 7.08 μ M (3 σ /m method, **Fig. S5**) and is comparable with some published data (**Table S1**) [46, 58-61]. The binding constant of the probe, HL with CN^- ion is 1.5×10^4 M⁻¹ (**Fig. S6**). From Job's plot, 1:1 stoichiometry between the probe, HL and CN^- ion has further been validated a 1:1 complex formation (**Fig. S7**).



Fig. 3. Change in absorption spectrum of HL (50 μ M) upon incremental addition of CN⁻ (0-50 μ M) in 9:1 DMSO/H₂O (v/v) (HEPES buffer, pH 7.2).

The mechanism of binding of HL with CN⁻ has been established by the ¹H NMR titration experiment (**Fig. 4**). The spectra show the deprotonation of hydroxyl (-OH) group and the peak δ (OH) of the probe at 12.73 ppm is vanished while -NH proton peak at 12.38 ppm is retained and broadened. The widening of –NH proton signal may be due to the formation of –CN---H–N type hydrogen bonding. Upon addition of excess CN⁻ ion the broad peak of -NH persists which has proposed that CN⁻ ion cannot deprotonate the -NH proton. Therefore, the sensing of CN⁻ ion could be recognized by the probe *via* deprotonation of –OH and hydrogen bonding with –NH and proposed anion complex may be [HCN---L]⁻ (**Scheme 2**). The mass spectrum shows a peak at m/z = 290.1808 (**Fig. S8**), which has agreed with the expected mass of one -H deprotonated mass peak of HL (i.e. L, m/z 290.2961) and has confirmed the 1:1 complexation.



Fig. 4. ¹H NMR spectra of **HL** on gradual addition of CN^{-1} ion in DMSO-d₆.

3.3 Theoretical Studies

The interaction of CN^{-} ion with the HL has been verified by theoretical studies using density functional theory (DFT) calculations. The optimized structure of the probe, HL and HL+ CN^{-} ion was gained in the gas phase by using the Gaussian 09 computational package with

B3LYP functions and 6-311G basis sets (**Fig. 5**). In HOMO of the probe the electron density is localized over the naphthalene moiety whereas in the LUMO, the electron density is spreading over the picolinyl hydrazide unit and the HOMO-LUMO band gap was 3.43 eV. By deprotonating agent CN⁻, the electron density in HOMO-LUMO of probe HL was effected and the band gap decreased to 1.84 eV (**Fig. 6**). The CN⁻, a weak base, assists deprotonation of phenolic-OH and hence effects the electron density of the probe, HL and the energy of MOs (**Table S2-S3, Fig. S9-10**).



Scheme 2. Proposed interaction of CN^{-1} ion with HL.



Fig. 5. The DFT optimized structure of the probe HL and probe HL with CN⁻ ion.



Fig. 6. The energy band gap between probe HL and probe HL with CN^{-} ion.

3.4. Paper Strip Detection Kit

The probe shows no impressive color in DMSO but the addition of CN^- changes to high intense yellow color. For public use, a low cost paper strip transportable detection kit for sensing CN^- is fabricated. A filter paper (Whatman 41) paper strip is coated with HL by dipping into the solution of probe (10 µM) in DMSO and is dried in air. Later, the HL impregnated paper strip is soaked in 20 µM solution of CN^- , immediately white paper strip turns to yellow. It is dried in air, and then images are taken under normal light (**Fig. 7**). This technique could be conveniently used

to detect CN⁻ ion without instrumental analysis, which is valuable practical application of cyanide sensor.



Fig. 7. Normal light image of test strips of probe HL and HL with CN⁻.

4. Conclusion

The probe HL is characterized by different spectroscopic techniques and shows high selectivity and sensitivity to the toxic CN^- in presence of other biologically permissible anions. It acts as a naked eye detection of CN^- ion with detection limit 7.08 μ M. The probable binding mode of the probe, HL with cyanide was established by ESI-MS and NMR titration. This probe is also useful in handy detection of CN^- ion by using simple test paper strips.

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outral control

Chromogenic hydrazide Schiff base reagent: spectrophotometric determination

of CN⁻ ion

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Highlights

- A simple hydrazide Schiff base has been developed using condensation method. •
- CN⁻ ion can be determined from the reflected spectrophotometric response and the ٠ proposed method seems to be very simple, fast, sensitive and selective for CN⁻.
- This cost-effective, useful technique has been successfully applied as a sensor by simple • test paper strip.