Analytical Methods

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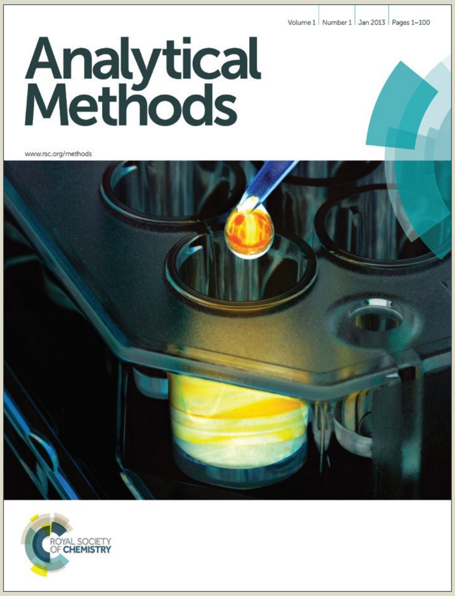

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Novel Chromogenic Selective Sensors for aqueous Cyanide ions under High Water Content and Real Sample Analysis

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Novel chromogenic receptors (**R1**-**R2**) containing anthraquinone as signalling unit and imidazole as binding unit were especially designed for enhancing the sensing action under aqueous medium. **R1** showed an obvious color change from yellow to red for aq. CN^- ions among other anions even under 8:2 H_2O: DMSO medium. **R2** showed good sensitivity with micro molar detection limit for cyanide ion in aqueous medium. The binding stoichiometry of the complexes formed by cyanide ions with receptors was found to be 1:1. Further, ^1H NMR titration, DFT theoretical studies had supported the obtained results. Real sample analysis of cyanide in domestic water samples and cow urine sample were quantitatively obtained.

Introduction

The business of anionic species has been manifested in the environment and biological processes and they might be harmful to human and environmental system if they crossed the tolerance level[1-3]. Cyanide ion is one of the most hazardous anions to human and other living system including plants even at 1.9 μM [4-6]. Beyond the hazardness, because of the wide usage of cyanide by Gold mining (cyanide leaching process), electroplating, refineries (fluid catalytic cracking and coking), printed circuit board manufacturing, steel and chemical industries, cyanide ions can easily be reached the environment[7-9]. A surplus of new reagents for cyanide detection has been developed in recent years[10-13]. But sensing cyanide ions under aqueous medium remains a tough task. In many reported papers for cyanide detection, anions alone were taken in semi aqueous medium or aqueous medium whereas receptors were taken in pure organic medium. In some other cases, receptors had been taken in organic solvents with very little amount (1-10%) of water for increasing the selectivity for cyanide ions among other anions[14-22] (Table 1). To overcome this issue, we planned to design the receptor that can be soluble or solvolisable by water. In general, a molecule is said to be hydrophilic by means of the number of polarisable functional groups present in the molecule, in other words, it depends on the functional groups that can be easily solvated by water molecules. Considering the role of hydrophilic functional groups, herein, we designed the receptor **R1** with two hydroxyl groups and **R2** containing two hydrophobic groups to support the results of **R1**. The former showed strong color change with aq. cyanide ion even at 8:2, v/v H_2O/DMSO medium. As expected, **R2** didn't detect cyanide ion above 20% of water content in DMSO. Herein, we designed novel receptors and demonstrated the multifunctional sensing behavior of **R1**-**R2** that are capable of sensing aq. CN^- ion under semi aqueous medium and quantitative analysis of the same was successfully done.

Experimental

Reagents and Instruments

1,2-Diaminoanthraquinone (DAAQ), 2,4-dihydroxybenzaldehyde and 3,5-di-*t*-butyl-2-hydroxybenzaldehyde were purchased from Sigma Aldrich and utilized without further purification. Tetrabutylammonium (TBA) salts of anions such as CN^-, F^-, Cl^-, Br^-, I^-, OAc^-, $H_2PO_4^-$, HSO_4^- , OH^- and analytical grade solvents were purchased commercially and used as such. NMR spectra were obtained using a Bruker 300 MHz spectrometer using Tetramethylsilane (TMS) as an internal standard. Thermo Fisher FT IR Spectrometer was used to record IR spectra in pellet mode. UV-vis spectroanalysis were done on Shimadzu UV-2600 UV-vis spectrophotometer in quartz cell with 1 cm path length. 1.5×10^{-3} M aq. solutions of the anions with 5×10^{-5} M solutions of **R1** and **R2** in H_2O: DMSO (0-90% of H_2O) medium had been utilized for the studies. UV titrations were carried out by the incremental addition of 0.1 eq. (10 μL) - 2 eq. (200 μL) of guest solutions to 3 mL of receptor solution in the UV cuvette. All the experiments were performed in compliance with the relevant laws and institutional guidelines and the institutional committee has approved the experiments. Informed consent was not obtained from any experimentation with human subjects.

General Procedure for the syntheses of receptors

Substituted benzaldehyde (0.5 mmol) and 1,2-diaminoanthraquinone (0.5 mmol) were taken in dimethyl sulphoxide (DMSO) (1 mL) and heated to 120°C for 6 h. (Scheme 1) The completion of the reaction was monitored by thin layer chromatography (TLC) using hexane: ethylacetate (6:4) as an eluent. After cooling the reaction mixture to room temperature, ethanol (5 mL) was added and stirred for few minutes. The solid obtained was filtered, washed with ethanol (5 mL), dried and triturated with ethanol (5 mL) to yield receptors.

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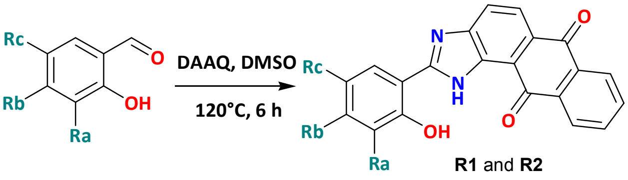
Table 1: A comparison from the recent literature at which sensing of cyanide was done in organic or semi aqueous medium.

Ref.	Receptor	Host	Guest
14.	Coumarin- chalcone derivative	Acetonitrile(ACN)	ACN
15.	Coumarin - benzothiazole derivative	ACN	ACN
16.	Coumarin amide derivative	ACN	ACN
17.	Aurone derivatives	ACN	ACN
18.	Sulfonamide and urea based derivatives	ACN	95:5 ACN:H_2O
19.	pyridinium N-phenolate betaine and merocyanine	ACN	300:1 ACN:H_2O
20.	Dinitrobenzylidine and dinitrostilbene derivatives	Dimethylsulfoxide (DMSO)	DMSO
21.	Dicyanovinyl derivatives	8:2 Tetrahydrofuran(THF)/H_2O	8:2 THF/H_2O
22.	1,9-Pyrazoloanthrone	ACN	ACN
- -	This work	2:8 DMSO/H_2O	H_2O



R1 => Ra, Rc=H, Rb=OH
R2 => Ra, Rc=*t*-Bu, Rb=H

Scheme 1: Syntheses of receptors **R1**-**R2**

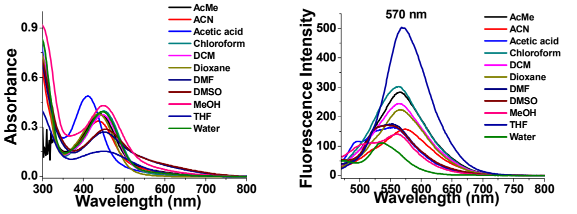


Fig. 1: UV-vis and Fluorescence spectra of **R1** in presence of various solvents at 5x10^{-5} M.

Results and discussion

Effect of Solvents

The photophysical properties of receptors were demonstrated with UV–vis absorption and fluorescence emission study in various solvents (**fig. 1**). The stock solutions of receptors (1.5x10^{-3} M in DMSO) were prepared and diluted with the solvent under consideration. Usually, ACN and rarely DMSO were used for the investigation of sensing behaviour in the many reported works. Even though there isn't much difference among λ_{max} of **R1** in various solvents, the fluorescence intensities of **R1** under different solvents revealed the key role of the polarity of the solvent that drives the interaction with binding sites through hydrogen bonding. In weak polar solvents such as acetone, $CHCl_3$, DCM, dioxane and THF, **R1** showed good fluorescence with red shift whereas other polar solvents showed weak fluorescent. Deliberately, our motive is to investigate the sensing behaviour of **R1** towards the anions in water therefore DMSO might be the good choice due to its higher miscibility with water.

Naked eye Experiments

Initially, 200 μL of anions, CN^-, F^-, Cl^-, Br^-, I^-, OAc^-, $H_2PO_4^-$, HSO_4^-& OH^- (1.5x10^{-3} M in DMSO) were added to 3 mL of **R1** and **R2** (5x10^{-5} M in DMSO) to examine the sensitivity visually. Except Cl^-, Br^- and I^- ions, other ions showed significant color changes. By considering the acidity of the 1-H in imidazole and –OH groups of **R1**, aqueous solutions of anions at same concentration had been used. In case of CN^-, F^- and OAc^- due to their high nucleophilicity compare to other anions, the color changes from yellow to purple color for **R1** and red color for **R2** were observed. During the optimization of the percentage of H_2O in DMSO of **R1**, selective sensing of CN^- ions had been achieved at 20% aqueous medium. Interestingly, **R1** has been selectively sensing CN^- ion under 90% aq. DMSO medium (**fig. 2a-2b**). While increasing the percentage of water content in the organic medium, the color change was diagonally reduced from deep violet color to pale pink color. This phenomenon may be accorded with the fact that under organic medium easy approach of cyanide ions towards the acidic –OH and imidazole –NH of **R1** led to deprotonate all the three binding sites. Under semi aqueous medium, due to the polarising effect of water, the interaction of cyanide ions with –OH protons of **R1** will be reduced and so the intense violet color change was suppressed to pink color thanks to the interaction of –NH of **R1** and cyanide ions.

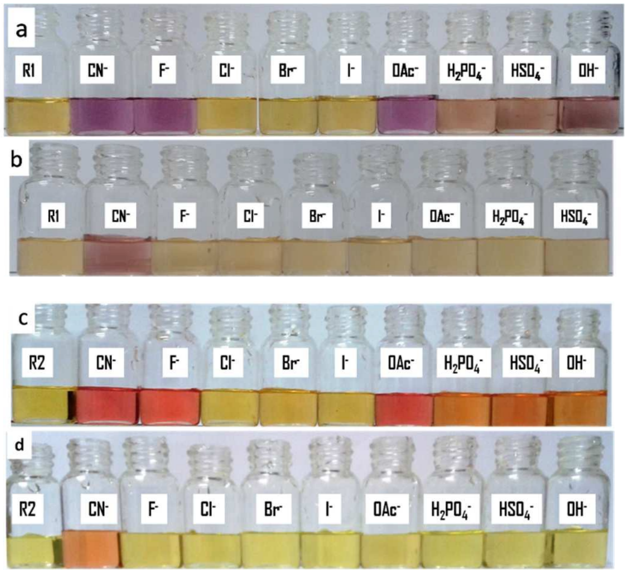


Fig. 2: (a,c) Naked eye experiments of **R1-R2** (5.0 x10^{-5} M in DMSO) with 200 μL of anions (1.5 x10^{-3} M in DMSO) respectively; (b) Visual color changes of **R1** (5.0 x10^{-5} M in 6:4 H_2O:DMSO medium) upon adding 200 μL of anions (1.5 x10^{-3} M in H_2O). (d) Visual color changes of **R2** (5.0 x10^{-5} M in 2:8 H_2O:DMSO medium) upon adding 200 μL of anions (1.5 x10^{-3} M in H_2O).

UV-vis studies

Based on the naked eye tryouts, the UV-vis spectro analytical studies had been carried out to investigate the binding behavior of **R1, R2** with anions in semi aqueous medium. Likely, CN^- ions in **R1** showed significant bathochromic shift of the band at 450 nm to 500 nm whereas other anions didn't perform under 60:40 H_2O/DMSO medium (**fig**. **3a, 3b**). The incremental addition of cyanide ions (0-4.0 eq.) to **R1** showed a gradual decrease in the intensity of the band at 450 nm and a steep increase in the intensity of the new band at 500 nm (**fig**. **3c**). It is inferred from the above observation that the hydrogen bonding between imidazole NH and cyanide ion followed by the deprotonation increases the electron density over the conjugated system of the molecule which in turn the energy gap between the bonding and anti- bonding molecular orbitals has been reduced and so the wavelength absorbed by the species invariably increases that derives the color change. To accomplish the effect of water in the sensing behaviour of **R1**, receptor was taken in the medium of 0-99% water in DMSO. Cyanide ion in DMSO was added to **R1** under 0-99% water in DMSO and recorded UV-vis spectrum (**Fig. 4**). The bathochromic shift for the addition of cyanide to **R1** was observed till >90% water content which concludes the effective sensing behaviour of **R1** towards cyanide ions. In case of **R2**, the shift could not be obtained above 2:8 water/DMSO ratio (**fig. 3d**). It could be inferred that the role of hydrophilic functional groups is important in case of aq. anionic recognition. Sensing action of **R1** and **R2** in THF at which **R1** showed higher fluorescence intensity that did not show any colour change above 20% aq. THF. **R1** is very weakly fluorescent in DMSO and the interaction of cyanide ion leads to the fluorescent quenching. So we couldn't get any support from photoluminescence spectra authentically.

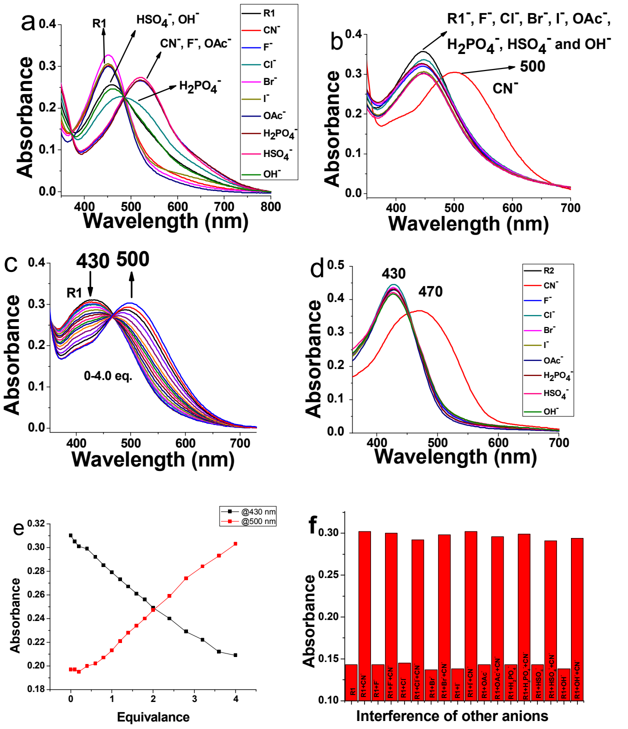


Fig. 3: (a) UV-vis spectroscopic analysis of 200 μL of anions (1.5 x10^{-3} M in DMSO) to **R1** (5.0 x10^{-5} M in DMSO); (b) UV-vis spectroscopic analysis of 200 μL of anions (1.5 x10^{-3} M in H_2O) to **R1** (5.0 x10^{-5} M in 6:4 H_2O:DMSO medium) (c) The incremental addition of CN^- ion (1.5x10^{-3} M in 60% aq. DMSO medium) to **R1** (1.5x10^{-3} M in 60% aq. DMSO medium). (d) UV-vis spectroscopic analysis of 200 μL of anions (1.5 x10^{-3} M in H_2O) to **R2** (5.0 x10^{-5} M in 1:4 H_2O:DMSO medium) (e)The Ratiometric behaviour of **R1** towards cyanide ions (Absorbance at 430 and 500 nm of **R1** towards the addition of CN^- ions). (f) Interference of other anions over the sensing behaviour of **R1** towards cyanide ions with the absorbance at 500 nm.

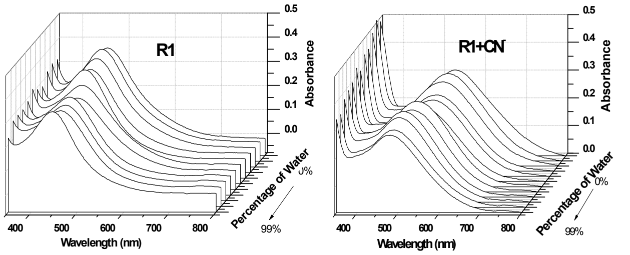


Fig. 4: An optical spectra comparison of R1 and R1-CN^- complex under 0-99% of water in DMSO medium.

Table 2: Binding constants, detection limit, limit of quantification and stoichiometric ratio of cyanide complexes of **R1** and **R2**.

Species	Binding Constant	LOD	LOQ	Stoichio-metric Ratio
R1-CN^-	8600 with RSD 0.6%	5.3x10^{-7} M	1.76x10^{-6} M	1:1
R2-CN^-	6394 with RSD 0.4%	1.18x10^{-5}M	3.92x10^{-5} M	1:1

It could be inferred that the role of hydrophilic functional groups is important in case of aq. anionic recognition. Sensing action of **R1** and **R2** in THF at which **R1** showed higher fluorescence intensity that did not show any colour change above 20% aq. THF. **R1** is very weakly fluorescent in DMSO and the interaction of cyanide ion leads to the fluorescent quenching. So we couldn't get any support from photoluminescence spectra authentically. The ratiometric behaviour of **R1** towards cyanide ions could be helpful to quantitatively analyze the same in the real sample by using Beer-Lambert's law (**fig.3e**). Interference of other anions towards cyanide sensing of **R1** was demonstrated successfully that shows there is no effective interference in the absorbance maxima of **R1**-CN^- complex. (**Fig.3f**) Using Benesi-Hildebrand plot, from the incremental addition of CN^- ions to **R1** and **R2**, Binding constants were calculated (**table 2**). **R1** showed a very good binding constant compared to **R2**. This experiment was repeated for 3 times with the relative standard deviation of 51.31. Micromolar detection limit of the receptors displays the effectiveness of the receptor's sensitivity towards cyanide ions. Job's plot for various mole ratio revealed the 1:1 stoichiometric ratio for the R1-CN^- and R2-CN^- complexes. All the experiments were repeated to ensure the repeatability and permanence of the receptors.

^{1}H NMR titration

The recognition of cyanide by **R1** can further be supported by ^{1}H NMR titration (**fig. 5**). The titration was carried out with $1.2x10^{-2}$ M of **R1** and $2.76x10^{-2}$ M of TBACN in DMSO-d_6 at room temperature. Highly acidic in nature and the ability to interact through hydrogen bonding of the –OH and imidazole NH with cyanide drives the proton to appear at down field. Upon adding 0.25 eq. of cyanide ions, peaks at 12 and 12.6 ppm belonged to -OH protons had been disappeared due to the higher acidity of them compared to –NH of imidazole which was broadened. The addition of 0.5 eq. of cyanide led to fade away the signal at 10.2 ppm and appear a new broad signal at 6.23 ppm. In case of aromatic protons, upfield shifting was observed due to the deprotonation followed by the increase in the electron density over the aromatic system. Addition of 1.0 eq. of cyanide ions ensured the new broad signal at 6.23 ppm signal that corresponds to free HCN. Due to the higher basicity of cyanide in DMSO solution, it might produce the deprotonation of imidazole –NH and –OH groups[23].

Theoretical Calculation Studies

Density Functional Theory (DFT) calculations have been done to understand the behaviour of **R1** with cyanide ions. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for **R1** and its cyanide complexes have been generated from optimized structures of the sensor **R1** and its respective complexes (**fig. 6**). The structural optimization and the computational calculations were carried out using Gaussian09 quantum chemistry package and the results were viewed with GaussView5 GUI. The appropriate choice of model chemistry for the computation of electronic structure property plays a vital role. Density Functional Theory (DFT) supported B3LYP/6-311G (+, d, p) model chemistry was executed for all the structures under vacuum condition. It can be seen that deprotonation of –NH of imidazole in R1 lead to decrease in the energy gap between HOMO and LUMO compared to that of **R1** whereas deprotonation of all the 3 binding sites further decreased the energy gap between HOMO and LUMO. λ_{max} predicted by the theoretical methods is in good agreement with the experimental observations which is red- shifted compared with those of the independent probe. The proposed structures of R1 and CN^- was shown in **fig. 7**.

Real Sample Analysis

Designing a sensor is getting fulfilled only when it will be useful in practical applications. Sensing cyanide in drinking water and tap water was demonstrated with **R1**. Samples were collected from our institute and checked for CN^-. No color change was observed in case of the test samples. As state pollution control board in India set the lethal dose (0.2 ppm or $8x10^{-6}$ M), solution has been prepared and checked for CN^- ion. From the color change observed, it could be concluded that **R1** acts as a highly sensitive and selective chemoreceptor for CN^- ion (**fig. 8a-b**). We demonstrated the analysis of cow urine sample for cyanide ions using **R1**. 200µL of cow urine was directly added to **R1** ($5x10^{-5}$ M in 60:40 DMSO: H_2O), there was no color change or shift in UV-vis spectroscopy was observed. After preparing 1, 2 and 4 eq. of cyanide ions in cow urine sample, the experiment was repeated 3 times with each samples and the results was shown in **table 3**. Almost 90% recovery was obtained in all the cases with the standard deviation <1. This shows the effectiveness of the receptor towards sensing of cyanide ions quantitatively.

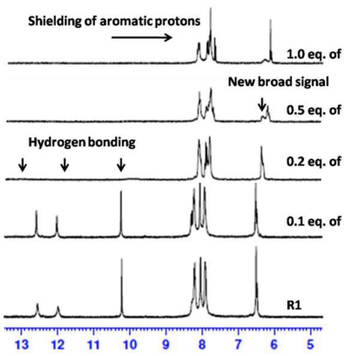


Fig. 5: ^{1}H NMR titration of cyanide ion ($1.2x10^{-2}$ M in DMSO-d_6) with **R1** ($2.76x10^{-2}$ M in DMSO-d_6).

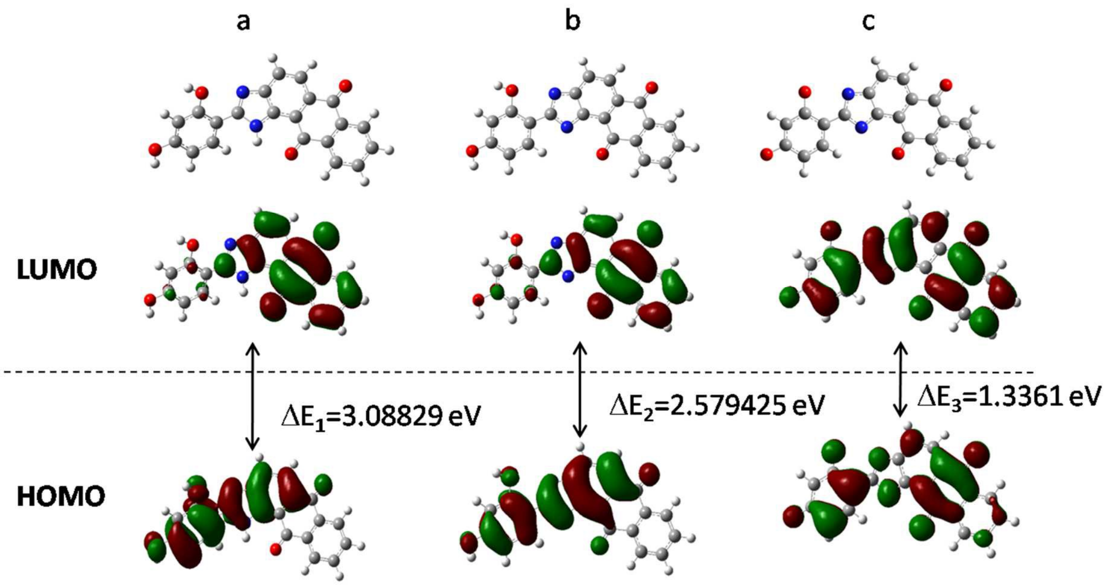


Fig. 6: Optimised structures of **R1 (a)**, **R1$^-$ (b)**and **R1^{3-} (c)**and DFT calculated HOMO and LUMO of **R1**, **R1$^-$**and **R1^{3-}**.

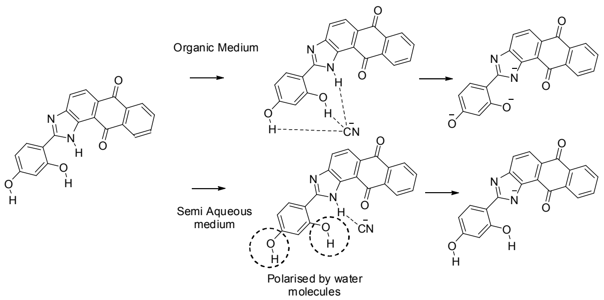


Fig. 7: The possible mechanism for the binding of cyanide ion with **R1**.

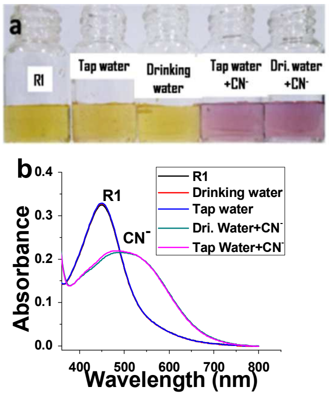


Fig. 8 (a,b) Detection of CN$^-$ ion in tap water and drinking water.

Table 3: Real Sample analysis of cow urine for cyanide ions.

Sample (ppm)	Average Recovery (3 sampling)	% Recovery
0	0	-
15	13.7	91.33
30	28.33	94.43
60	55.7	92.83

2-(2,4-Dihydroxy-phenyl)-1H-anthra[1,2-d]imidazole-6,11-dione (R1): Yield: 81%. M.p. 286-288°C. ^{1}H NMR 300 MHz, DMSO-d$_6$: δ 6.48-6.51 (m, 3H), 7.91-7.92 (m, 2H), 7.93-8.05 (m, 2H), 8.20-8.20 (m, 2H), 10.24 (s, 1H, imidazole NH), 12.01 (s, 1H, -OH), 12.58 (s, 1H, -OH). ^{13}C NMR (75 MHz, DMSO-d$_6$) 182.00, 161.75, 156.79, 134.2, 133.8, 133.0, 132.8, 131.00, 130.43, 126.8, 126.54, 125.99, 123.28, 121.00, 108.31, 105.10, 102.85. FTIR (ν-cm^{-1}) 3427 (N-H str.), 1666 (C=O str.), 1476 (C=N str.), 715 (N-H bending) HRMS: Calcd. for $C_{21}H_{12}N_2O_4$: m/z 356.0797. Found: m/z 357.00 (M+1).

2-(3,5-Di-tert-butyl-2-hydroxy-phenyl)-1H-anthra[1,2-d]imidazole-6,11-dione (R2): Yield: 75%. M.p. 280-284°C. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 1.38-1.41 (m, 18H, *t*-butyl), 7.44 (s, 1H, salicylic ring), 7.89-7.91 (m, 2H, anthraquinone ring), 8.09 (s, 1H, phenyl), 8.12-8.16 (m, 4H, anthraquinone ring), 13.30-13.67 (bs, 2H, OH and NH Protons). ^{13}C NMR (75 MHz, DMSO-d$_6$) 140.25, 134.23, 132.94, 128.38, 126.93, 126.74, 126.12, 31.44, 29.33 FTIR data (ν-cm^{-1}) 3435 (N-H str), 1666 (C=O str), 1474 (C=N str), 1293 (Ar C-N Str), 712 (N-H bending) HRMS: Calcd. for $C_{29}H_{28}N_2O_3$: m/z 452.21. Found: m/z 453.183 (M+1).

Conclusion

Novel benzimidazole based chromogenic receptors synthesized and characterized with various spectroscopic techniques. Due to the presence of two polarisable hydroxyl groups in **R1**, it acts as highly selective cyanide sensor even under higher water content with good binding constant and micromolar detection limit whereas **R2** didn't. From UV-vis spectrometry, ^{1}H-NMR titration and DFT theoretical calculation of **R1** with cyanide, it could be concluded that cyanide ion interacts with the receptor through hydrogen bonding with imidazole N-H followed by deprotonation. The real sample analysis of cyanide in domestic water samples and cow urine samples made the receptor valuable.

Acknowledgements

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Graphical Abstract