International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 7 ǁ July 2022 ǁ PP. 68-71

Thiozole based receptor for the detection of toxic cyanide ion with turn on Fluorescence

Ganesan Punithakumari[1*], A. Kiruthiga[1]
Department of Chemistry, Theivanai Ammal College for Women (A), Villupuram,TN,India
Corresponding author:
**E-mail: gpunithababu@gmail.com (Dr. G. Punithakumari)*

Abstract
The thiozole based receptor was synthesized with 2-hydroxy 5-nitro benzaldehyde with 2-aminobenzothiozole by simple condensation method and the properties were studied under naked eye, UV-Vis and fluorescence studies etc. The synthesized receptor detects cyanide, in 20:80 H_2O: DMSO medium. Furthermore it shows the observable colorimetric response from colorless to yellow for cyanide ion in DMSO medium which were seen under naked eye without the aid of any instruments. Furthermore, the cyanide bound receptor with nucleophillic substitution reaction. The detection limit of receptor with cyanide was found to be 6.63 × 10^{-7} M.
Keywords: *indole-3-carboxaldehyde, Red shift, Turn on-fluorescence.*

Date of Submission: 22-06-2022 Date of acceptance: 04-07-2022

I. Introduction

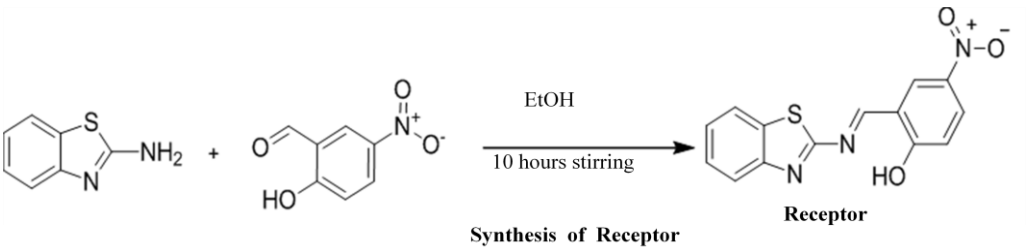
Nowadays, anion sensor plays an important role in the field of chemical sensors. Compared to other ions, cyanide is one of the most toxic and dangerous ions to humans and the environment. Food sources such as potatoes, apple seeds, almonds and cassava contain trace amount of cyanide. [1]. Still the food samples containing CN^- ion may lead to rigorous health problems such as respiratory problems, cardiac arrest, unconsciousness and eventually death [2- 3]. Cyanide ion plays an important role in electroplating, gold mining and polymer processing. For these dangerous ions we need a simple and easy method of detection. Many techniques available for the detection of these ions are ascribed with difficult synthesis, poor sensitivity & selectivity and also interference of other ions like F^-, AcO^-. Chemical sensors have many amazing unique advantages in overcoming these shortcomings, as well as many other advantages such as high sensitivity and selectivity, making it easy to see target ions visually and at a low cost [4]. For cyanide ion detection, M.Chemchem and co-workers reported the receptor for cyanide ion detection in the DMSO / H_2O medium, which detects cyanide ions through a deprotonation and ICT mechanism [5]. Wang and co-workers developed a receptor with coumarin derivative with benzothiazole Schiff base moiety which sense cyanide ion by nucleophilic addition mechanism [6]. Due to their possible therapeutic uses thiozole derivatives displays the ground breaking discovery in the research field. All the above cases, a single receptor detect multiple ion with a single approach. Though benzothiozole derivative known for quite a few years and have been well studied for its biological activities. Herein we report the receptor with thiozole moiety for cyanide ion detection.

II. Materials and instruments

Required chemicals like 2-Hydroxy-5-nitrobenzaldehyde, 2-aminobenzothiozole, ethanol, tetra butyl ammonium salts of AcO^-, F^-, I^-, Cl^-, CN^-, Br^-, $H_2PO_4^-$,HSO_4^-, NO_3^-, OH^- and metal ions such as were purchased from Sigma Aldrich and used without any purification or modification. Using Bruker 500 MHz NMR spectrometer, ^1H and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as an internal standard and DMSO as a solvent. IR-spectra were recorded by the KBr pelletization method using a Thermo Fisher Nicolet FT-IR spectrometer. Shimadzu UV-2600 was used to measure the UV-Vis spectrum. Shimadzu-RF-5301PC spectrofluorometer was used to run the fluorescence spectra. For all UV and PL titrations, $5x10^{-5}$ M solution in ACN medium was taken as a standard. 0equ. - 2.0 equ. of the analyte was used for the incremental addition.

2.1 Receptor synthesis

The receptor was synthesised by using 2-hydroxy 5-nitro benzaldehyde with 2-aminobenzothiozole in the presence of ethanol for 10 hours stirring. The melting point was 145°C. The receptor was characterised by ^1H NMR. ^1H NMR (DMSO, 500 MHz, δ ppm) 13.1 (s, 1H, O-H proton) 9.39 (s,1H, imine proton) 8.52 (s,1H,) 8.52 (d, 2H J=7.5 Hz) 8.03 (d, 2H, J=8 Hz) 7.90 (d,2H,)



Synthesis of Receptor

III. Results and discussion

3.1 Naked eye detection of CN^- ion

The receptor was tested with various anions by naked eye detection in 20:80 H_2O: DMSO medium. On adding cyanide ion to the receptor it changes its colour from colourless to yellow. However there is no visible color change in all other ions (Fig.1). The colour change of the receptor was related with the large red shift of 443 nm in UV-Vis spectra upon the addition of cyanide ion. However, by the addition of 2.0equ.of cyanide ion into the receptor its get saturated. Large bathochromic shift and observed color change are responsible for the strong hydrogen bonding and the deprotonation of the NH protons by the CN^- ions in solution.

Fig.1 Visual changes of receptor (5.0 $x10^{-5}$ M in 20:80 H_2O: DMSO medium) upon adding 200 µL of anions (1.5 $x10^{-3}$ M in DMSO)

3.2 Spectral studies of receptor with all anions

To examine the sensitivity of the receptor, UV-visible studies of the receptor with all ions were carried out in 20:80 H_2O: DMSO medium. Anions like CN^-,Br^-, F^-, I^-, Cl^-,AcO^-, HSO_4^-, $H_2PO_4^-$, and NO_3^- and OH^- are taken in the form of their tetrabutyl ammonium salts. By the addition of all anions into the receptor, only the cyanide ion got a colour change from colourless to yellow with red shift. By adding cyanide ion to the receptor, the new peak was formed at 528 nm and the receptor peak got decreases (Figure 3a). The new peak is due to the ICT band between the receptor (>NH/CN^-) and signalling benzene units. On incremental addition from 0.equ. to 2.0 equ it was saturated. Moreover there is an isosbestic point at 497 nm which indicates the stable complex formation of the receptor-cyanide complex.

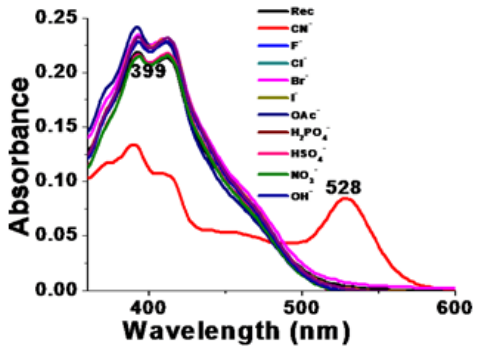


Fig.2 UV-Vis spectral changes of Receptor (5.0 $x10^{-5}$ M in 20:80 H_2O: DMSO medium) upon adding 200 µL of anions (1.5 $x10^{-3}$ M in DMSO)

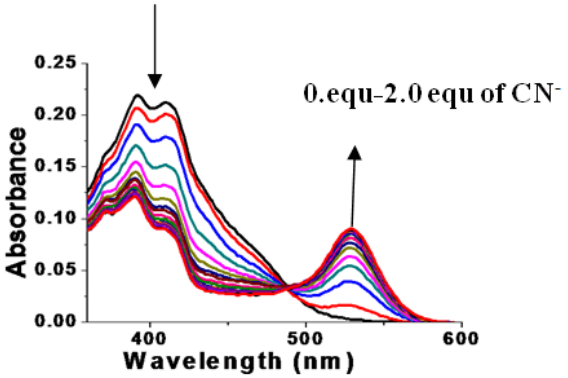


Fig.3 Incremental addition of receptor (5.0 x10^{-5} M in 20:80 H_2O: DMSO medium) upon adding 200 µL of anions (1.5 x10^{-3} M in DMSO)

3.3. Fluorescence studies of all anions with receptor

To find out the emission properties of the receptor with all anions the fluorescence titration was done with the help of spectrofluorometer with slit width as 5nm and the excitation wavelength as 420nm. By the addition of all anions into the receptor, only cyanide ion got a fluorescence enhancement with at 478nm (Fig.5a). By the continuous addition of cyanide ion in to the receptor upto 2.0 equ. its intensity got gradually enhanced which was depicted in (Fig.5b). This is due to the deprotonation take place in the hydroxyl O-H and the NH group in the receptor.

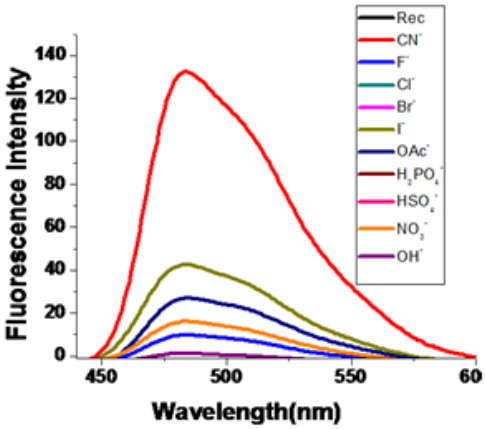


Fig.4 Fluorescence spectral change of receptor (5.0 x10^{-5} M in 20:80 H_2O: DMSO medium) upon adding 200 µL of anions (1.5 x10^{-3} M in DMSO).

3.3 Fluorescence incremental addition of receptor with cyanide ion

For the addition of CN^- ion in to the receptor solution the emission maxima of CN^- ion are 478 nm which gives remarkable fluorescence enhancement this was observed in the figure.4

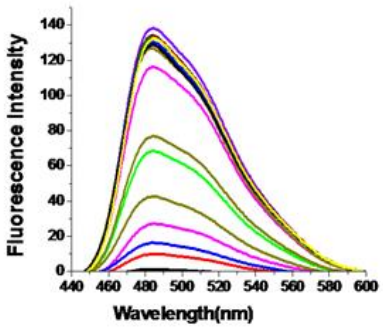


Fig.4 The incremental addition of CN^- ion in receptor (5.0 x10^{-5} M in 20:80 H_2O: DMSO medium) upon adding 200 µL of anions (1.5 x10^{-3} M in DMSO.

2.4. Benesi–Hildebrand plot and limit of detection of CN^- ions

By plotting the straight line using $1/\Delta A$ and $1/[CN^-]$, the Benesi–Hildebrand plot which was shown in figure.5. The binding constant of the receptor with cyanide4 shows $6.2x10^6$ .Similarly the detection limit was calculated using the formula 3* σ/m. The limit of detection of receptor with cyanide ion is $6.63x10^{-7}$ displayed in fig .6.

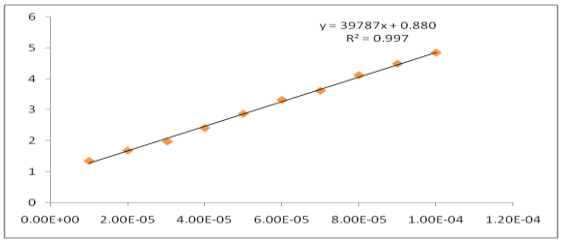


Fig.5 Binding constant of receptor with cyanide

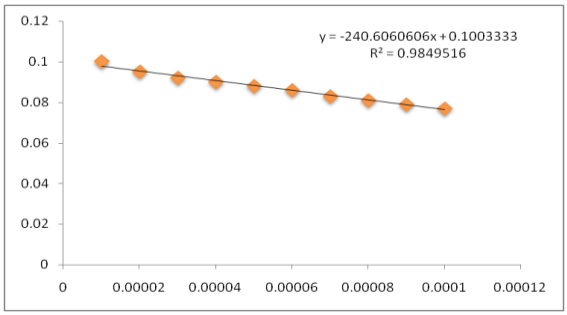


Fig.6 The limit of detection of receptor with cyanide ion

IV. Conclusions

In summary, we have developed the receptor with thiozole moiety which detect cyanide. By the addition of cyanide ion into the receptor it changes its colour into yellow which is due to the deprotanation of NH proton by CN^- ions cause large bathochromic shift in UV-Vis spectra. The limit of detection of cyanide, as 6.23×10^{-7} M which were lower than the permissible level given by World Health Organization (WHO).

Reference

[1]. A.E. Burns, J.H. Bradbury, T.R. Cavagnaro, R.M. Gleadow, Total cyanide content of cassava food products in Australia. J. Food Compos. Anal., 25 (2012), pp. 79-82.

[2]. X. Bin Cheng, H. Li, F. Zheng, Q. Lin, H. Yao, Y.M. Zhang, T.B. Wei, A simple chemosensor for the dual-channel detection of cyanide in water with high selectivity and sensitivity . RSC Adv., 6 (2016), pp. 27130-27135.

[3]. W. Gong, Q. Zhang, L. Shang, B. Gao, G. Ning, A new principle for selective sensing cyanide anions based on 2-hydroxy-naphthaldeazine compound. Sens. Actuators B Chem., 177 (2013), pp. 322-326.

[4]. J. Isaad, A. El, Colorimetric sensing of cyanide anions in aqueous media based on functional surface modification of natural cellulose materials. Tetrahedron., 67 (2011), pp. 4939-4947.

[5]. M.Chemchem, I.Yahaya, A novel and synthetically facile coumarin-thiophene-derived Schiff base for selective fluorescent detection of cyanide anions in aqueous solution: Synthesis, anion interactions, theoretical study and DNA-binding properties,Tetrahedron74, (2018) pp 6897-6906.

[6]. K. Wang,W. Feng, A coumarin derivative with benzothiazole Schiff's base structure as chemosensor for cyanide and copper ions. Inorg. Chem. Comm.,71(2016) pp 102-104.