ACRYLONITRILE EMBEDED BENZ(IMIDA/THIA)ZOLE BASED CHEMODOSIMETER FOR CYANIDE IONS

A

Thesis submitted

In the partial fulfilment of the requirement for the degree of

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Submitted By

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UNDER THE SUPERVISION OF

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(Associate Professor)

SCHOOL OF CHEMISTRY AND BIOCHEMISTRY,

THAPAR UNIVERSITY,

PATIALA-147004

2017

CERTIFICATE

I hereby declare that the thesis entitled "ACRYLONITRILE EMBEDED BENZ(IMIDA/THIA)ZOLE BASED CHEMODOSIMETER FOR CYANIDE IONS" is an authentic record of my work carried out as requirements for the award of degree of **Master's of Science** in **Chemistry** at, **Thapar University, Patiala** under the supervision of **Dr. Vijay Luxami**, Assistant Professor, School of Chemistry and Biochemistry, Thapar University, Patiala during January, 2017 to July, 2017. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

Nehal Gupta

NEHAL GUPTA

Date: 13/7/2017

It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

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ACKNOWLEDGEMENTS

After an intensive period of six months, today is the day writing this note of thanks is the finishing touch on my dissertation. It has been a period of intense learning for me, not only in the scientific arena but also on a personal level. I would like to reflect on the people who have supported and helped me so much throughout this period.

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Nehal gupta

Nehal Gupta

Abstract

Two novel chemodosimeters(Z)-2-(1H-benzo[d]imidazol-2-yl)-3-(4-(6,11-dioxo-5a,6,11,11a-tetrahydro-1H-anthra[1,2-d]imidazol-2-yl)phenyl)acrylonitrile (Probe **3**) and (2Z,2'Z)-3,3'-(1,4-phenylene)bis(2-(3H-1l4-benzo[d]thiazol-2-yl)acrylonitrile) (Probe **5**) were synthesized for cyanide anion detection *via* colorimetric and fluorometric approaches. Probe **3** displayed red shift in absorption spectrum from 415 to 466 nm and near infrared emission at 610 nm in presence of cyanide anion in aqueous acetonitrile solvent system. The probe **3** displayed colour change from yellow to reddish orange in presence of cyanide anion. The probe **3** showed very low detection limit of 2.2×10^{-9} M. On the other hand, probe **5** exhibited red shift in absorption from 385 to 584 nm and quenching in emission at 490 nm. The presence of cyanide anion changes colour of probe **5** from yellow to purple. The probe **5** shows very low detection limit of 3.5×10^{-7} M. Therefore, both probe **3** and probe **5** shows chromo and fluorogenic response towards cyanide anion in aqueous acetonitrile medium. Both probes contains nitrile-vinyl group as a reorganisation unit and their electron withdrawing properties creating electron deficient site allow nucleophilic attack by cyanide anion revealing intramolecular charge transfer.

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Introduction

Supramolecular chemistry is basically designing of new molecular architecture with the excellence of sensitive and specific reorganisation of various different analytes.[1] These molecular architect contain recognition and signalling moieties as important parts employed with different strategies and mechanisms such as photoinduced electron transfer (PET), intramolecular charge transfer (ICT), Förster resonance energy transfer (FRET), excited state intramolecular proton transfer (ESIPT), aggregation induced emission (AIE), aggregation-caused quenching (ACQ) etc.[2] The molecular architect called the chemosensors which produce the optical signals on binding to analytes (cations, anions etc.) via non-covalent interactions.[3] The signalling unit are chromophore and fluorophore which imparts colour changes and variation in emission spectrum upon excitation. The recognition unit contains hetero atom capable of binding to analytes.[4] The recognition unit is normally abiotic in nature, advantages of high affinity, high specificity, and sensitivity. The analyte attached to binding unit alter the electronic environment of molecular structure as a consequence further changes the absorption and emission signals.[5] The reaction of analytes can be reversible and irreversible in nature. Thus, chemosensors generally convert chemical changes or chemical information into analytically useful signals in presence of matter and energy.[6]

Supramolecular chemistry examines the molecule with weaker interactions while traditional chemistry based on the covalent bonding. Supramolecular chemistry includes molecular self–assembly, folding and recognition of molecules. The neutral and ionic species widely found in physiology, medical diagnostics, catalysis and environmental chemistry.[7] Due to the ever increasing concentrations of industrial chemical and agriculture pesticides, the presence of cations and anions in the environment, chemosensors are thus beginning to find many applications. There are three approaches which have been employed by various groups in pursuing the chemosensor.[8]

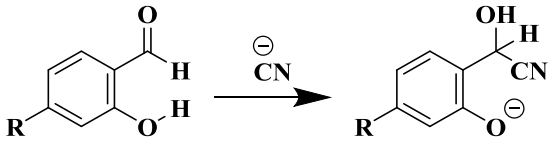
1) Binding site-signalling approach
2) Displacement approach
3) Chemodosimeter approach.

In the “binding site-signalling subunit” approach, the interaction of the analyte with the binding site brings about changes in the electronic properties of the signalling subunit resulting in sensing of the target anion. The displacement approach is based on the formation

of molecular assemblies of binding site signalling subunit, which on the coordination of a particular anion with the binding site results in the release of signalling subunit into the solution with a simultaneous change in their optical properties. In the chemodosimeter approach, a specific anion-induced chemical reaction occur which results in an optical signal. The chemodosimeter was termed as abiotic molecule where analyte recognition took place by an irreversible process of bond breaking and bond forming while the optical response was then measured.[9] Various design approaches of chemodosimetric probes are reported for cyanide ion detection on pure organic molecules:

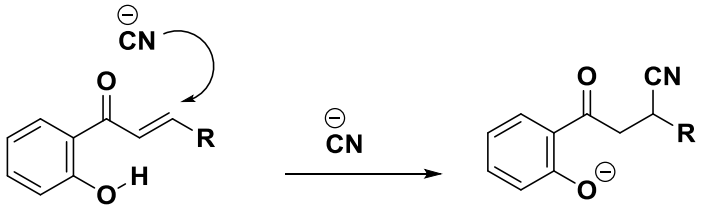
1.1 <u>Addition to carbonyl group:</u>

The C-centre of carbonyl group is known to be electron deficient centre and it is further activated by ortho-substituted hydroxyl group via intramolecular hydrogen bonding. The nucleophilic attack at carbon centre of carbonyl and proton transfer to generate alkoxy group from phenol group facilitate colorimetric changes and fluorescent enhancement. The process supplemented by restricted excited state intramolecular proton transfer phenomenon.[10]



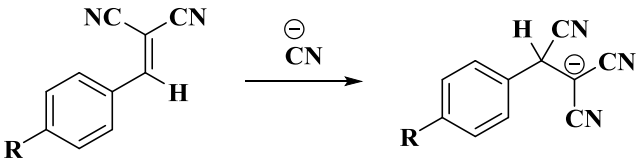
1.2 <u>Michael addition</u>:

The molecular system containing α, β unsaturated carbonyl group, attacked by anion at alkene carbon atoms. 3-amido coumarin-based chemosensor and enone-functionalised benzochromene can detect even micro molar concentration of cyanide ion.[11]



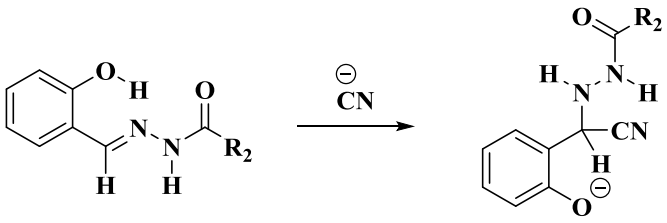
1.3 <u>Addition to the di-cyano vinyl group:</u>

Recent chemodosimeters involve the selective addition of cyanide to 1, 1 dicyano-vinyl group forming stabilised anionic adduct. Change in the colour, as well as fluorescence properties, can be related to disruption in ICT which occurs basically due to restriction between dicyano and vinyl group molecular conjugation after the attack of cyanide ion.[12]



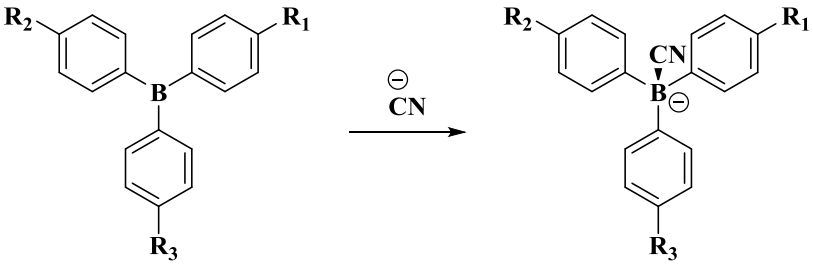
1.4 Addition to the imine group

Schiff base and hydrazone based chemodosimeter are a good example for sensors where the cyanide ion acts as a nucleophile and attacks the imine carbon.[13]



1.5 Addition to boron containing compounds:

The presence of vacant p-orbitals for boron atom makes it a suitable electrophilic site for cyanide to attack. Thus the molecules having a boron molecule acts as chemodosimeter for cyanide ion detection.[14]

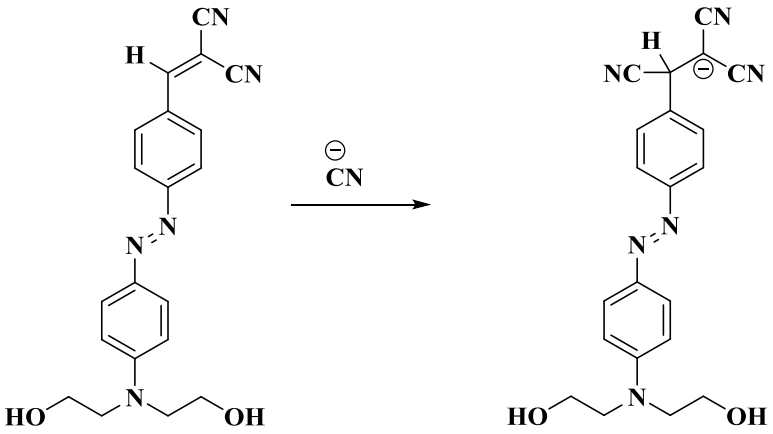


LITERATURE STUDIES

2.1 Literature Review

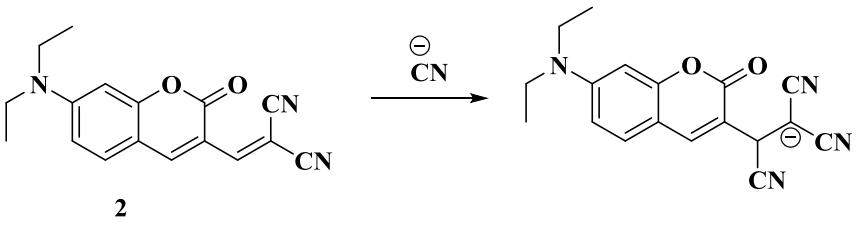
Toxic nature of cyanide makes it poisonous for the physiological system and cause environmental concern because of its extensive exploitation in industries causing a significant development in the cyanide sensing process.[15] Various research methods were employed to detect the cyanide ion like titrimetric, volumetric, potentiometric, etc. which were not only slow but also required sophisticated instrumentation with high detection limit.[16] In the recent years various chromogenic and fluorogenic chemosensors were developed for optical sensing of cyanide ion because of their cheap, fast and simple functioning. Cyanide can enter the human body either through absorption by lungs, exposure to skin or from contaminated food and water. Cyanide selective optical sensors have not been so extensively reviewed and here we will discuss the detection of cyanide ion using the di-cyano vinyl group as the electrophilic centre.[17] Nucleophilic attack by equivalent cyanide anion was expected to occur toward the electrophilic C of the C=C double bond. During the addition reaction, the electron-withdrawing dicyano-vinyl group was expected to be transformed into an anionic electron-rich group due to the destruction of the C=C double bond and the simultaneously emerged negative charge. It was envisaged that replacement of carbonyl group with a more electron deficient di-cyano group can facilitates the attack of nucleophile due to the introduction of the push-pull effect on the reported molecule.[18]

Xiaohong and colleagues reported a ratiometric colorimetric chemodosimeter **1** which showed specific nucleophilicity towards cyanide ion in CH_3CN. Probe **1** showed a ratiometric blue shift in absorption spectrum from 515 to 435 nm with an isosbestic point at 475 nm accompanied by a colour change from deep red to light yellow on the successive addition of CN^-. The chemodosimeter**1** was utilised for paper strip approach to detect CN^- ion and different colour changes at different concentration of CN^- allowed it to serve as a colorimetric sensor. The detection limit was 1.1 µM for CN^- detection.[19]



1

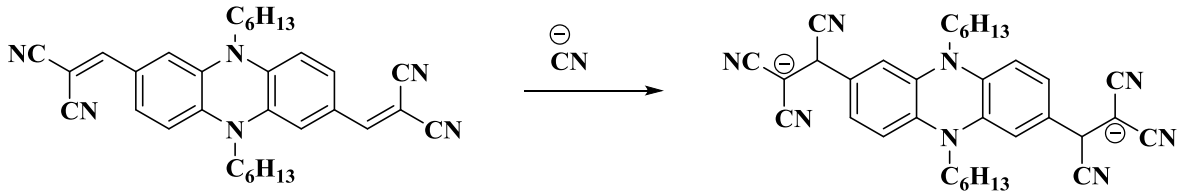
Li *et. al.* designed and synthesised a coumarin-containing ratiometric chemodosimeter **2** having specific and sensitive nucleophilicity towards cyanide ion in THF:H_2O (5:5; V/V). Probe **2** showed a ratiometric blue shift in absorption spectrum from 535 nm to 445 nm. Covalent linkage between two units of donor and acceptor takes place *via* double bond formation and a change in colour from red to yellow upon successive addition of CN^- was observed. Change in excitation wavelength of the spectrum from 520 nm to 415 nm with a change in fluorescent properties from red to green was detected. Probe **2** was used for the detection of CN^- ions in live cells *via* scanning microscopy by penetrating into the cell membrane and tracking the intracellular CN^- ion concentration. Minimum detection limit was 800 nM.[20]



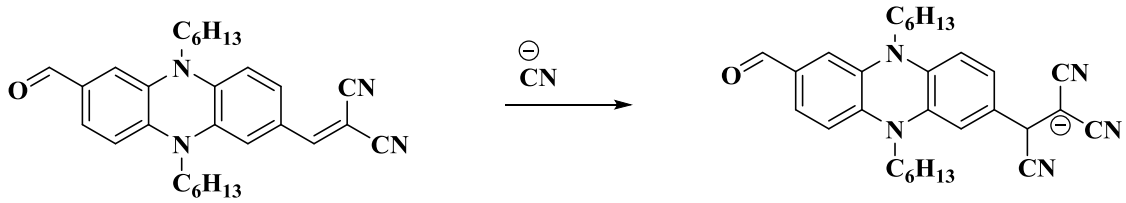
2

Yang and co-workers designed two phenazine based ratiometric near-IR chemodosimeters **3** and **4** for the detection of cyanide ion. Both **3a** and **4a** consisted of mono and dual dicyano group as an electron withdrawing group with probe **3** having an additional formyl group. Both the chemodosimeters showed nucleophilicity towards cyanide ion in CH_3CN to form compounds **3b** and **4b**. Probe **3** exhibited absorption spectrum at 545 and 372 nm, and further addition of CN^- ion shifted the absorption band to 600 nm and 350 nm respectively with hypochromic effects. Gradual addition of CN^- upto 1.0 eq. led to change in colour from purple to blue, while further addition of CN^- ion to 2.5 eq. diminished the colour. Probe **3** gave two different emission bands at 730 nm and 600 nm upon excitation at 540 and 400 nm

respectively. The addition of CN^- further decreases the emission bands. On the other hand, Probe **4** has absorption peaks at 570, 452, 360, and 293 nm respectively. The gradual addition of CN- ion decreases the absorption intensity at 570 and 452 nm. The absorption intensity increases at 293 with an isosbestic point at 316 nm along with red shift with respect to the band at 360 nm. The dosimeter showed a colour change from dark brown to light yellow simplified its demonstration to naked eye detection. The emission band at 720 nm shifted by 10 nm hypsochromically moved to 630 nm with an commission point at 664, accompanied by fluorescence colour change from dark red to orange.[21]



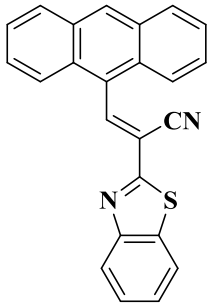
3a **3b**



4a **4b**

Balasubramanian *et. al*. developed different benzothiazole based chemodosimeter **5-7** all of which displayed selectivity towards CN^- ion. Probe **5** comprised of anthracene moiety as fluorophore unit and exhibited multiple absorption peaks at 350, 367, 388 and 471 nm addition of CN^- caused the hypsochromic effect to the band at 417 nm while the hyperchromic effect was observed at 350, 367 and 392 nm. Isosbestic points at 317 and 476 nm with the visible colour change from greenish yellow to light yellow upon addition of CN^- to probe**5** is observed. Blue shift in emission band from 497 to 416 nm after addition of CN^- is attained when excitation wavelength was fixed at 325 nm. Probe **6** comprised of pyrene moiety as fluorophore unit and giving absorption peaks at 269, 313 and 446 nm. The addition of CN^- ion caused a blue shift in absorption spectra from 446 to 357 nm and ~12 nm of shift for a peak at 269 nm with hyperchromic effect besides the isosbestic point at 373 nm. Visible colour changes from orange-yellow to light-yellow and red shift in emission spectra from 350 nm to 529 nm was noticed. Likewise, a yellowish-green coloured chemodosimeter**7** consisted of N,N-dimethyl benzyl group as fluorophore unit which gave absorption bands at 326,343 and 431 nm. The addition of cyanide gave hyperchromic effect for bands at 326 and 343 nm

and hypsochromic effect forth band at 431 nm with an isosbestic point at 368nm in addition to a red shift in emission spectra from 390 and 409 nm to 474 nm was observed. Both the above-mentioned chemodosimeter showed a green fluorescence upon attachment with receptor moiety and are much useful chemosensor for detection of CN^- in living cells because of their strong cell permeability and least toxicity as tested on HeLa cells.[22]



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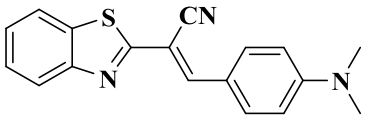

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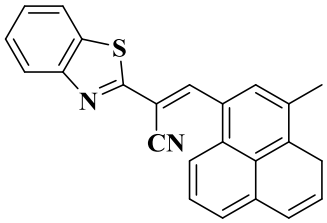
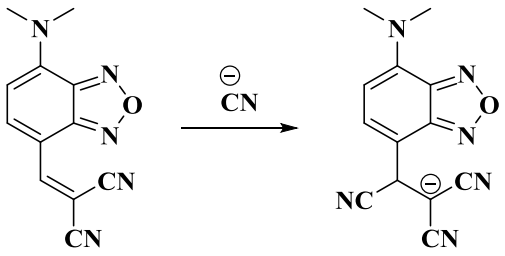


7

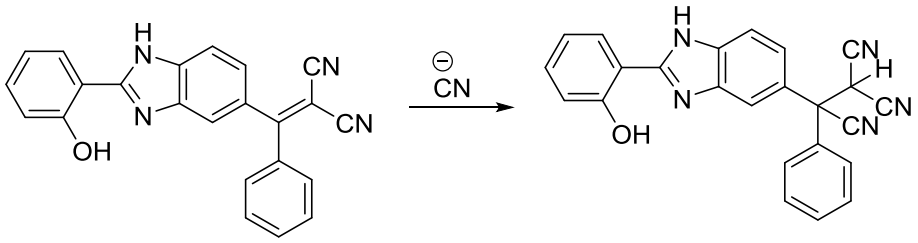
Liu and co-workers designed a ratiometric chemosensor containing dicyanovinyl-substituted benzofuran moiety which was used for the detection of CN^- ion. Chemodosimeter **8** showed a blue shift in the absorption spectrum from 513 to 441 nm with a distinct reduction in intensity upon addition of CN^- ion. The similar hypsochromic shift was observed in the fluorescence spectrum from 581 to 526 nm. All the analyses were performed in a solution of $CH_3CN{-}H_2O$ (95:5 v/v) and a colour change from pink to colourless was observed upon addition of CN^- to ligand.[23]



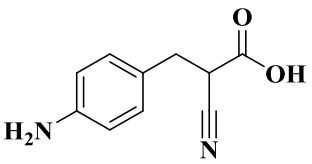
8

Gupta and co-workers synthesized a chemodosimeter **9** comprising of dicyano group substituted with benzimidazole moiety and compared it with one involving a keto group used selectively for the sensing of fluoride and cyanide using the internal charge transfer mechanism. Keto- group containing sensor gave absorption peak at 335 nm and emission band at 540 nm when the excitation wavelength was set to 330 nm. Probe **9** involved more electronegative dicyano group in place of keto group gave absorption band at 370 nm while emission band at 505 nm as a result of ESIPT phenomena. Selective sensing ability in probe

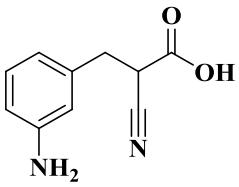
9 was examined using THF; addition of F^-, CN^-, OAc^- gave a red shift by 95 to 465 nm while colour changed from colourless to yellow. Gradual addition of CN^- reduced the intensity of absorption bands at 370 and 285 nm while new band is formed at 465 nm, 315 nm, and 260 nm in addition to an isosbestic point at 405 nm. Emission band in the presence of cyanide was observed at 425 nm while in presence of F^- at 435 nm and 365 nm were observed.[24]



Manivannan and colleagues synthesized two chemodosimeters **10(a)-(b)** based on Michael addition to C-atom when NH_2 was attached to meta or para to the receptor moiety for specific detection of cyanide ion. Intramolecular charge transfer *via* π conjugation from amine N-atom (donor) to 2-cyanoacrylic acid (acceptor) takes place in both the chemosensors. Upon CN^- addition to C=C of acceptor moiety ICT transition no longer takes place and a colour change from yellow to colourless can be observed with naked eyes. For spectral sensing 1:1 (v/v) mixture of DMSO and HEPES buffer (pH 7.4) was used. Absorption band at 387 nm and 377 nm was obtained for **10 (a)** and **(b)** respectively. Since presence of NH_2 group at para position increases the overall electron density of receptor moiety due to better electron donation hence value of absorption maxima was higher. Addition of CN^- shifts absorption spectra of probe **10a** from 387 nm to 336 nm with an isosbestic point at 353 nm. Similar changes were observed for probe **10b.** Fluorescence spectra after addition of cyanide showed strong band at 402 nm.[25]



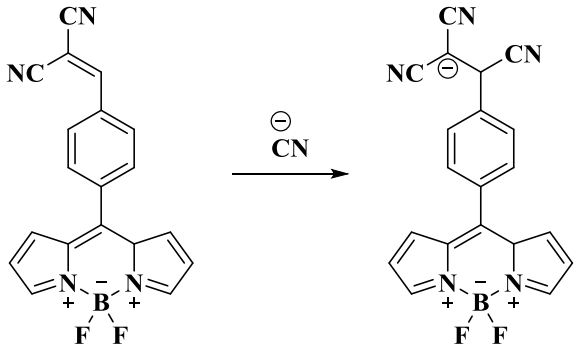
10a



10b

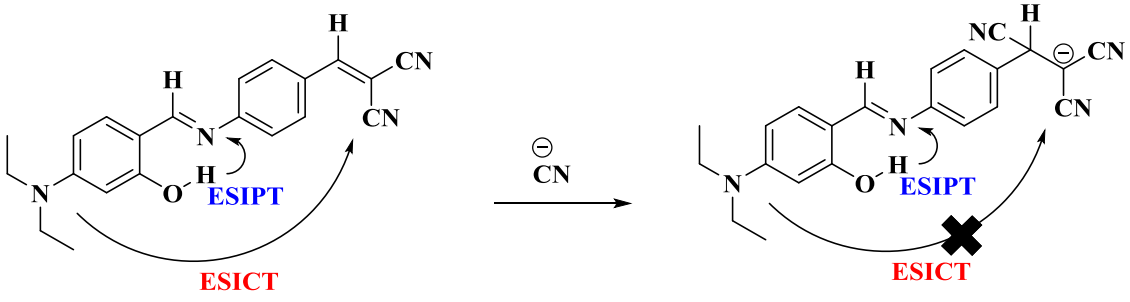
Lee and colleagues synthesized a Boradiazaindacene based chemodosimeter-**11** showing selectivity towards cyanide ion in aqueous medium. Studying the absorption and emission spectra of probe **11** two absorption bands at 325 nm and 500 nm were observed while emission was negligible. Addition of cyanide prevents occurrence of ICT hence decreasing the intensity of band at 325 nm due to disruption of conjugation between phenyl and di-cyano

vinyl moiety while rise in the emission band at 520 nm was observed. Such chemosensors were widely used in ion sensing, as photo sensitizers, artificial light harvesting system etc.[26]



11

Lin and colleagues synthesized a ratiometric chemodosimeter **12** based on ESICT-ESIPT switching phenomena for selective determination of cyanide ion. Probe **12** consisted of a salicylideneaniline based sensor that was used to switch between ESICT-ESIPT system in aqueous medium, where diethylamino act as an electron donating and dicyanovinyl group as electron withdrawing group. Probe **12** gave two absorption peaks at 330 nm (exhibiting the $\pi-\pi^*$ transition) and at 470 nm (exhibits ICT) with all the sensing properties being detected in a THF: H_2O (8:2, V/V) on addition of CN^- diminished and subsequent appearance of new band at 376 nm. Visible colour change from orange to colourless were observed and two isosbestic points at 339 and 418 nm were indicated. Emission spectra did not show any significant change on addition of other anions when addition of cyanide gave a weak band at 523 nm and a strong band at 626 nm.[27]



12

2.2 RESEARCH GAP IN STUDY

Designing anion receptors is challenging because of size difference between anions *w.r.t.* isoelectric cations which have lower charge is to radius ratio. This implies electrostatic binding for a cation is much higher and effective than for an anion due to its small size. Also, anions are sensitive to pH (lose their negative charge at low pH), providing a narrow window of pH for receptors to work on the target anion. Anionic species can occur in a wide range of geometries hence a higher degree of design may be required to make receptors complementary to their anionic guest.

2.3 OBJECTIVE

From literature survey, it has been observed that the introduction of electron withdrawing groups such as di-cyano, nitriles, generate the electron deficient atom adjacently, and further facilitate the attack of nucleophiles due to charge separation pull push effects. Thus, cyanide ions which are known to be better nucleophiles than other anions in fully or partially aqueous solvent medium chemodosimeterically. Thus, we plan to synthesise molecular architect capable of charge transfer and contain electron deficient sites as objective:

1) To synthesize the chromogenic and fluorogenic moieties appended with acrylonitrile moiety
2) To evaluate the sensing ability of synthesised compounds towards various anions.
3) To evaluate the binding behaviour of anion with the synthesized compounds.

EXPERIMENTAL SECTION

3.1 Materials, Methods and Instrumentations

All the chemicals used for synthesis were purchased from Sigma-Aldrich Chemical Ltd., Loba Chemie depending upon availability. All the solvents used were of spectroscopic grade purchased from Spectrochem Ltd. All chemicals and solvents were used without any further purification. The progress of the chemical reaction was monitored by means of thin-layer chromatography (TLC). ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL ECS-400 MHz spectrometer at ambient temperature in $CDCl_3$ or/and DMSO (d_6) with TMS as an internal reference. All chemical shifts were reported in ppm relative to the reference. Mass Spectrum of the synthesised compound was recorded at Water Micromass-Q-T of Micro.

The stock solutions of various anions of concentration 1×10^{-1} $molL^{-1}$ were prepared to form their corresponding salts. The anions were taken as tetra butyl ammonium salts respectively. A stock solution of ligands was prepared at 10^{-3} M (25mL). The diluted solution was used further for photophysical studies in respective solvents.

The absorption spectra were recorded on SHIMADZU-2600 spectrophotometer and quartz cuvettes of 1 cm in path length. The fluorescence spectra were performed on a Varian Carey Eclipse fluorescence spectrophotometer using a slit width (excitation = 20 nm, emission = 20 nm) at stated excitation. The stoichiometry of complexes was determined by Jobs Plot. Stability constants were determined using Benesi-Hildebrand equation. Melting points were recorded by open capillary tube method and were uncorrected.

3.2 Calculation of binding constant and limit of detection

The binding constants of ligands for different analyte were determined using the following Benesi-Hildebrand equation

$$\frac{1}{I - I_0} = \frac{1}{K_a(I_{max} - I_0)[C]^n} + \frac{1}{I_{max} - I_0}$$

Where I_0, I, and I_{max} are the absorption/emission intensities of the ligand in absence of analyte, at an intermediate analyte concentration, and at a concentration of complete interaction with analyte respectively. K_a is the binding constant, C is the concentration of analyte and n is the number of analytes bound per ligand molecule. The detection limit (DL) is determined from the following equation:

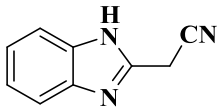
$$DL = \frac{K \times Standard\ deviation\ of\ the\ blank\ solution}{slope\ of\ calibration\ curve}$$

Where K = 2 or 3

3.3 Job's Plot

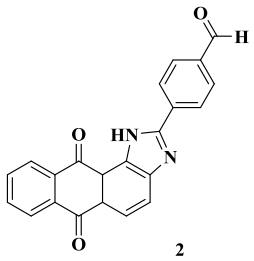
A series of solutions containing ligand and TBACN were prepared such that the sum of the total anion and ligand concentration remained constant. The mole fraction (X) of CN^- was varied from 0.1 to 1.0. The intensity at respective wavelength was plotted against the molar fraction of the CN^- solution.

3.4 Synthetic Experimental Table



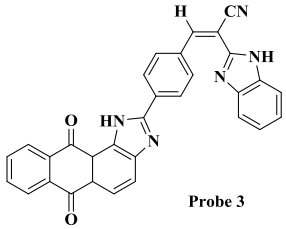
1

Yield = 83%; m.pt. = 120-122 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.78 (s,1H, NH), 7.32-7.22 (m, 4H, ArH), 4.16 (s, 2H, CH_2); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 141.5, 138.9, 123.0, 117.8, 115.2 (ArC), 18.8 (CH_2).



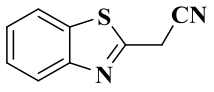
2

Yield = 73 %; m.pt. = 197-199 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.47 (s, 1H, CHO), 10.14 (s,1H, NH), 8.63 (d, *J* = 7.60 Hz, 3H, ArH), 8.28 (d, *J* = 8.40 Hz, 2H, ArH), 8.18 (d, *J* = 8.40 Hz, 1H, ArH), 8.10 (d, *J*=8.80 Hz, 2H, ArH), 7.84-7.80 (m, 2H, ArH);^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 192.9 (CHO), 191.0 (CO), 189.9 (CO), 146.8, 140.5, 138.8, 136.9, 135.2, 133.0, 130.4, 128.0, 127.3, 125.8, 123.6, 123.1, 121.1, 118.6 (ArC).



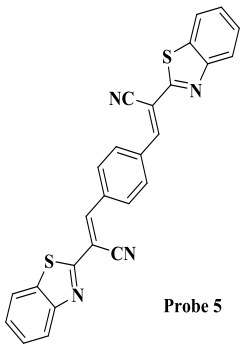
Probe 3

Yield = 69%; m.pt. = 280-283^0C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.62 (d, *J* = 8.80 Hz, 2H, ArH), 8.41 (s, 1H, ArH), 8.27-8.11 (m, 6H, ArH), 7.96-7.92 (m, 2H, ArH), 7.70 (d, *J* = 7.60 Hz, 1H, ArH), 7.57 (d, *J* = 8.00 Hz, 1H, ArH), 7.32-7.23 (m, 2H, ArH); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 182.1 (CO), 153.5, 146.8, 141.5, 138.9, 138.8, 135.2, 133.9, 132.1, 127.4, 126.9, 126.3, 125.3, 123.0, 121.1, 118.8, 118.6, 115.2, 107.7 (ArC); MS (ESI), m/z: 493.5 (M^++1).



4

Yield = 90 %; m.pt. = 100-102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.04 (d, *J* = 8.40 Hz, 1H, ArH), 7.89 (d, *J* = 8.40 Hz, 1H, ArH), 7.53 (t, *J* = 7.60 Hz,1H, ArH), 7.45 (t, *J*= 7.20 Hz, 1H, ArH), 4.25 (s, 2H, CH_2); ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 158.2, 152.8, 135.4, 126.7, 125.9, 123.3, 121.7 (ArC), 23.2 (CH_2).



Probe 5

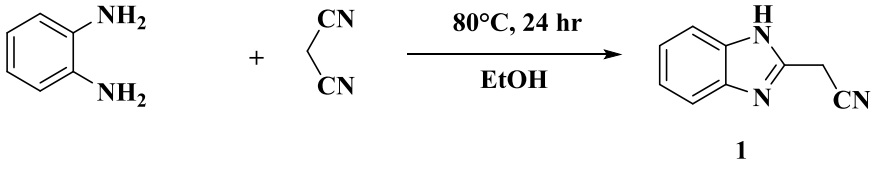
Yield = 85%; m.pt. 280-282^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.30 (s, 1H, ArH), 8.17 (s, 3H, ArH), 8.11 (d, *J* = 8.00 Hz, 1H, ArH), 7.94 (d, *J* = 8.00 Hz, 1H, ArH), 7.57 (t, *J* = 8.20 Hz, 4H, ArH), 7.48 (t, *J* = 8.00 Hz, 4H, ArH) ; ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 160.5, 153.5, 153.4, 136.2, 134.4, 129.0, 125.3, 124.5, 121.6, 118.8, 107.7. MS (ESI), m/z: 446.5 (M^{+}+1).

RESULTS AND DISCUSSION

The functionalities such as nitriles, dicyano groups when present on the fluorescent moieties like benzimidazole or benzothiazole have the property of withdrawing electron density, as a consequence generating electron-deficient site and charge separation. The electron-deficient site show efficient binding towards different anions depending upon their nucleophilicity, basicity and size. Such type of molecules are expected to show colorimetric or/and fluorometric properties. Thus, we have designed the fluorescent molecules containing electron withdrawing group successively generating nucleophilic centres for anion recognition.

4.1 Synthesis of Chemodosimeters

4.1.1 Synthesis of 2-(1H-benzo[d]imidazol-2-yl)acetonitrile (1): Benzene-1,2-diamine (1.08g, 0.01mol) and malononitrile (0.66g, 0.01mol) were mixed in 10 mL ethanol. 1mL of glacial acetic acid was added to above solution. Further, the reaction mixture was refluxed at 85^{0}C for 18 hours. After the completion of reaction (monitored by TLC), the obtained white coloured solid was filtered and washed with ethanol. A fine white coloured powder of compound **1** was obtained by column chromatography ($CHCl_3$: CH_3OH::95:5) as the eluting solvent. (Yield = 83.2%; m.pt. 120-122 ^{0}C); ^{1}H NMR (400 MHz, $CDCl_3$) showed 1H singlet at 9.78 for aromatic N-H, 4H multiplet at 7.32-7.22 for aromatic C-H, 2H singlet at 4.16 for aliphatic CH_2. ^{13}C NMR (100MHz, $CDCl_3$) 141.5 (C between two nitrogens in benzimidazole), 138.9, 123.0, 115.2 117.8 (Aromatic C), 18.8 (aliphatic CH_2).

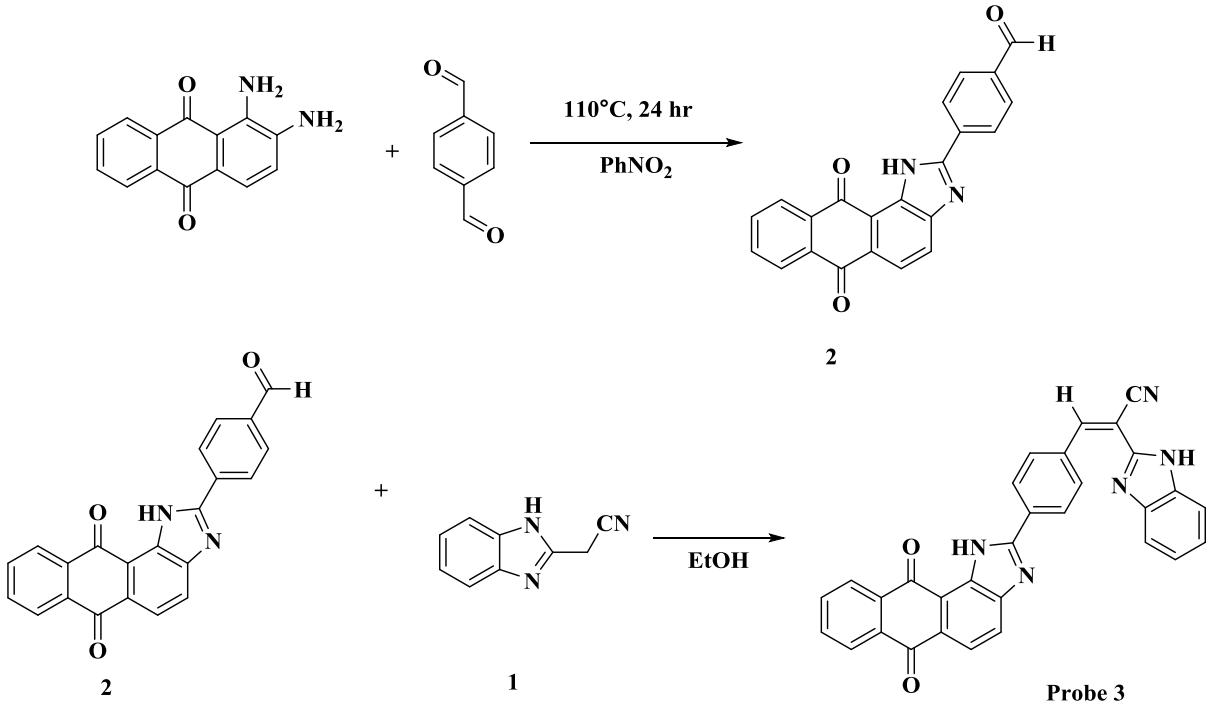


1

4.1.2 Synthesis of 4-(6,11-dioxo-5a,6,11,11a-tetrahydro-1H-anthra[1,2-d]imidazol-2-yl)benzaldehyde (2): A solution of 1,2-diaminoanthraquinone (0.5g, 2.1 mmol) and terephthaldehyde (0.5g, 3.7 mmol) was refluxed at 110 ^{o}C in nitrobenzene for 24 hours. After the completion of reaction (monitored by TLC) brown coloured solid was filtered and washed with diethyl ether. The crude was further purified by column chromatography ($CHCl_3$ as eluting solvent). The fine yellow coloured powder was obtained. (Yield = 73.12 %); m.pt. 197-199 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1H singlet at 11.47 (N-H), 1H singlet at 10.14 for aldehydic-H, 3H doublet at 8.63 (J = 7.6 Hz) for aromatic-H, 2H doublet at 8.28 (J = 8.4Hz) for aromatic-H, 1H doublet at 8.18 (J = 8.4Hz) for aromatic-H, 2H doublet at 8.10

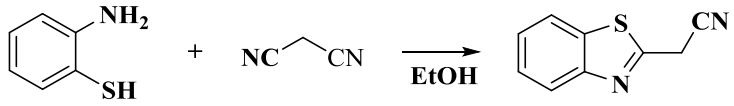
(J = 8.8Hz) for aromatic-H, 2H multiplet at 7.84-7.80 for aromatic-H; ^{13}C (100MHz, $CDCl_3$) NMR signals at δ 192.9 due to aldehydic C, 191.0 for CO, 189.9 for CO, 146.8, 140.5, 138.8, 136.9, 135.2, 133.0, 130.4, 128.0, 127.3, 125.8, 123.6, 123.1, 121.1, 118.6 all for aromatic C.

4.1.3 Synthesis of Probe 3: A solution of compound **1** (350 mg, 0.9 mmol) and compound **2** (150 mg, 0.001 mmol) in EtOH were refluxed in presence of piperidine (catalytic amount). After the completion of reaction (monitored by TLC), a pale yellow coloured solid was observed was filtered and washed with ethanol. The obtained crude was purified by column chromatography ($CHCl_3$:CH_3OH::90:10) to obtain a pale yellow coloured fine powder of probe **3** (Yield=69%); m.pt. = 280-283^{0}C**;** ^{1}H NMR (400 MHz, $CDCl_3$) showed signals at δ (ppm): 2H doublet at 8.62 (J = 8.8 Hz) for aromatic C-H, 1H singlet at 8.41 for aromatic-H, 6H multiplet at 8.27-8.11 due to aromatic H, 2H multiplet at 7.96-7.92 for aromatic-H, 1H doublet at 7.70 (J = 7.6 Hz) for aromatic H, 1H doublet at 7.57 (J = 8 Hz) for aromatic H, 2H multiplet at 7.32-7.23 for aromatic-H. ^{13}C (100MHz, $CDCl_3$) δ(ppm): 182.1 due to CO, 153.5, 146.8, 141.5, 138.9, 138.8, 135.2, 133.9, 132.1, 127.4, 126.9, 126.3, 125.3, 123.0, 121.1, 118.8, 118.6, 115.2, 107.7 are all for aromatic C; Mass spectra showed m/z peak at 493.53, confirming the structure for probe **3**.



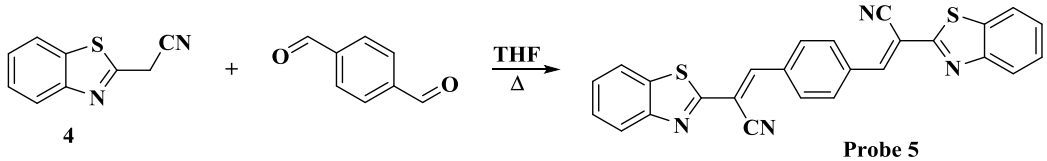
SCHEME 1

4.1.4 Synthesis of 2-(3H-1l4-benzo[d]thiazol-2-yl)acetonitrile (4): 2-aminobenzenethiol (4.2 g, 0.02 mol) and malononitrile (2.2 g, 0.063 mol) were mixed in 10 mL ethanol. 1mL of glacial acetic acid was added to above solution and allowed it to stir at room temp for overnight. After the completion of reaction (monitored by TLC), obtained a white coloured solid that was filtered and washed with ethanol. A fine white coloured powder of compound **4** was obtained (Yield = 90%); m.pt. 100-102 ^{0}C.^{1}H NMR (400 MHz,$CDCl_3$) showed 1H doublet at 8.04 (*J* = 8.40 Hz) for aromatic-H, 1H doublet at 7.89 (*J* = 8.40 Hz) for aromatic-H, 1H triplet at 7.53 (*J* = 7.60 Hz) for aromatic H, 1H triplet at 7.45 (*J* = 7.20 Hz) for aromatic C-H, 2H singlet at 4.25 for aliphatic CH_2. ^{13}C (100MHz, $CDCl_3$) δ: 158.2, 152.8, 135.4, 126.7, 125.9, 123.3, 121.7 for aromatic-H, 23.2 for aliphatic CH_2.



4

4.1.5 Synthesis of Probe 5: A solution of compound **4** (0.36g, 2.06 mmol) and terephthaldehyde (0.14g, 1.04 mmol) was refluxed in ethanol. An orange coloured solid was obtained after the completion of reaction (monitored by TLC). The reaction mixture was filtered and washed with ethanol. The obtained solid was purified by column chromatography ($CHCl_3$:Hexane::7:3), as eluting solvent) to obtain fine dark orange coloured powder of probe **5.** (Yield = 85.2%; m.pt. = 280-282^{0}C)**.** ^{1}H NMR (400 MHz,$CDCl_3$) showed 1H singlet at 8.30 for aromatic-H, 3H singlet at 8.17 for aromatic-H, 1H doublet at 8.11 (*J* = 8.00 Hz) for aromatic H, 1H doublet at 7.94 (*J* = 8.00Hz) for aromatic-H, 4H triplet at 7.57 (*J* = 8.20 Hz) for aromatic H, 4H triplet at 7.48 (*J* = 8.00 Hz) for aliphatic CH_2.^{13}C (100MHz, $CDCl_3$) δ: 160.5, 153.5, 153.4, 136.2, 134.4, 129.0, 125.3, 124.5, 121.6, 118.8, 107.7.



4 **Probe 5**

4.2 Photophysical properties of probe 3 and probe 5

Photophysical properties of Probe **3** and **5** were studied through absorption and emission studies. Probe **3** (20 μM, CH_3CN) exhibited absorption maxima at 415 nm and an emission band at 510 nm whereas probe **5**, showed absorption band at 385 nm and an emission band at 490 nm. The changes in photophysical properties of both probes were studied in presence of

different anions in different solvent systems like pure acetonitrile (CH_3CN), CH_3OH, tetrahydrofuran (THF), as well as their different ratio with water to determine the sensing behaviour. Both the probes showed specific binding toward CN^- ion.

4.2.1 Absorption studies of Probe 3 towards anions

The recognition behaviour of probe **3** toward various anions, *viz*., CN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^-, I^-has been investigated by absorption and emission spectroscopic techniques in CH_3CN: H_2O (9:1) solvent system. Among these anions, the only introduction of CN^- ion showed significant changes in the absorption spectra of the probe **3 (Figure 1a).** On the addition of CN^- ion, the probe **3** showed a red shift in the absorption spectrum of ~ 51 nm from 415 to 466 nm accompanied by colour change form yellow to orange. On gradual addition of CN^- ions to the solution of probe **3**, the absorption peak at 415 nm was decreased with simultaneous formation of a new band at 466 nm with a clear isosbestic point at 443 nm **(Figure 1b).** The decrease in probe's absorption maxima with a simultaneous increase in spectra allowed the probe to serve ratiometric probe for CN^- ion in aqueous acetonitrile solvent. The absorption ratio at 458 and 415 nm vary from 0.13 to 1.06 indicating ~8 fold ratiometric response. The spectral changes attained plateau after addition of 350 µM of cyanide ions. The spectral changes were associated with visible colour changes shown in **Figure 2.** Thus, probe **3** can be used to estimate cyanide ion with a detection limit of 2.2×10^{-7} M in aqueous acetonitrile solvent through ratiometric approach.

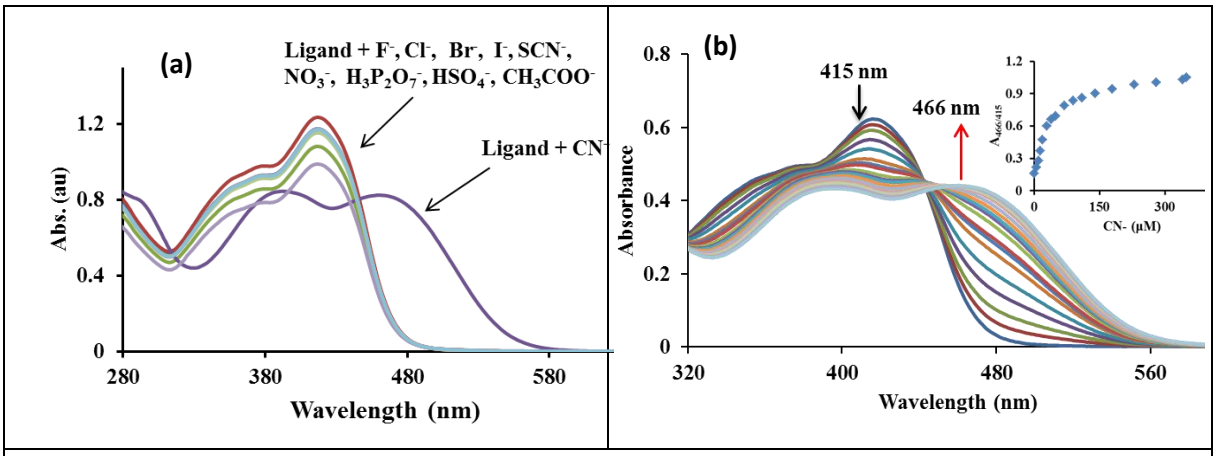


Figure 1: (a) UV–Vis spectra of probe 3 (20 µM in CH_3CN:H_2O::9:1) in the absence and presence of different anions (1000 µM) such as CN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^- and I^- ions (b) Effect of incremental addition of CN^- (0-350 µM) to probe 3 (20 µM, CH_3CN:H_2O:: 9:1) on absorption spectrum. Inset (b) ratiometric response of probe 3 towards CN^- ion.

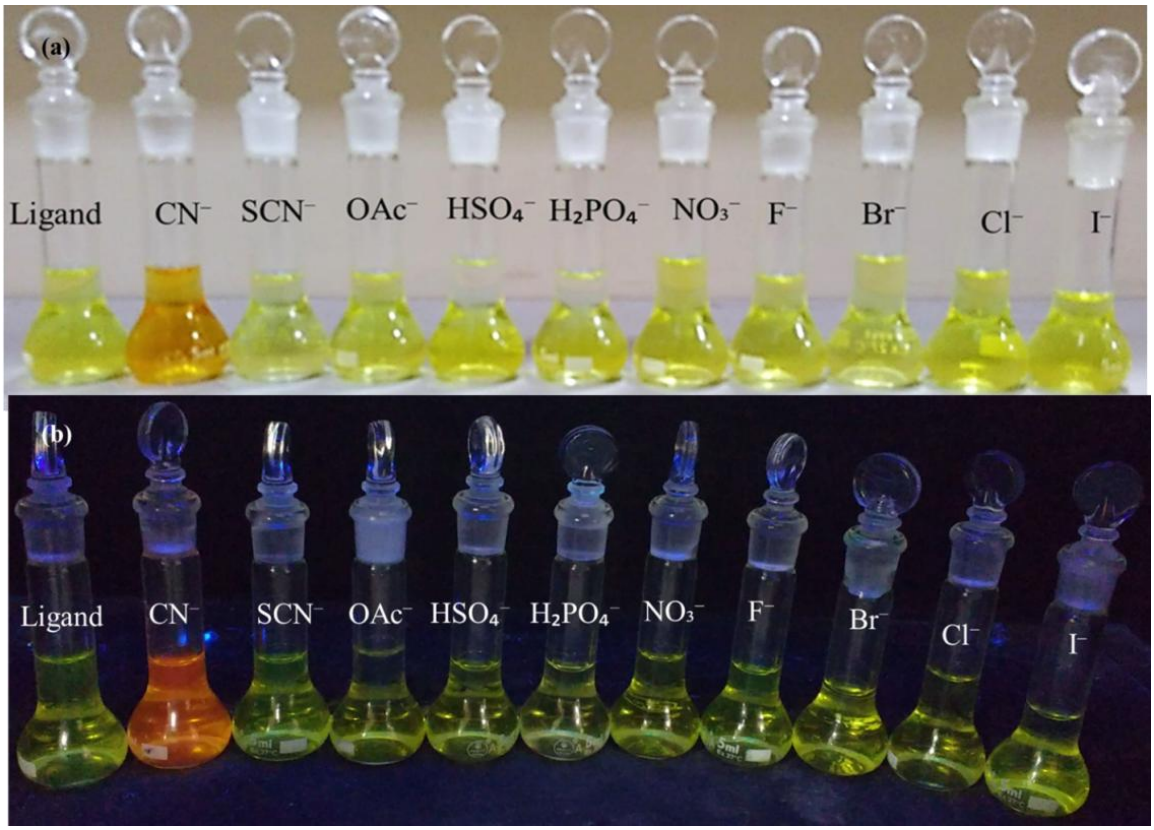


Figure 2: Images of visible colour change for probe 3 (20 µM in $CH_3CN:H_2O$::9:1) on the addition of different anions (1000 µM) in (a) visible light and (b) UV light.

4.2.2 Effect of various anions on emission spectrum of probe 3

Probe **3** (20 µM, CH_3CN: H_2O:: 9:1) on excitation at 415 nm exhibited emission band at 610 nm. On addition of various anions, no significant change was observed except for CN^-ion **(Figure 3a).** On the addition of CN^- ion, the probe **3** showed a red shift in the emission spectrum of ~ 100 nm from 510 to 610 nm. On gradual addition of CN^- ions to the solution of probe **3**, the emission peak at 510 nm was diminished with simultaneous formation of a new band at 610 nm with a clear isosbestic point at 534 nm**(Figure 3b).**The emission ratio at 610 and 510 nm vary from 0.36 to 9.6 indicating ~25 fold ratiometric response. The spectral changes attained plateau after addition of 400 µM of cyanide ions. The spectral changes were associated with red emission changes shown in **Figure 2.** Thus, probe **3** can be used to estimate cyanide ion with a detection limit of 2.2×10^{-9} M in aqueous acetonitrile solvent through ratiometric approach.

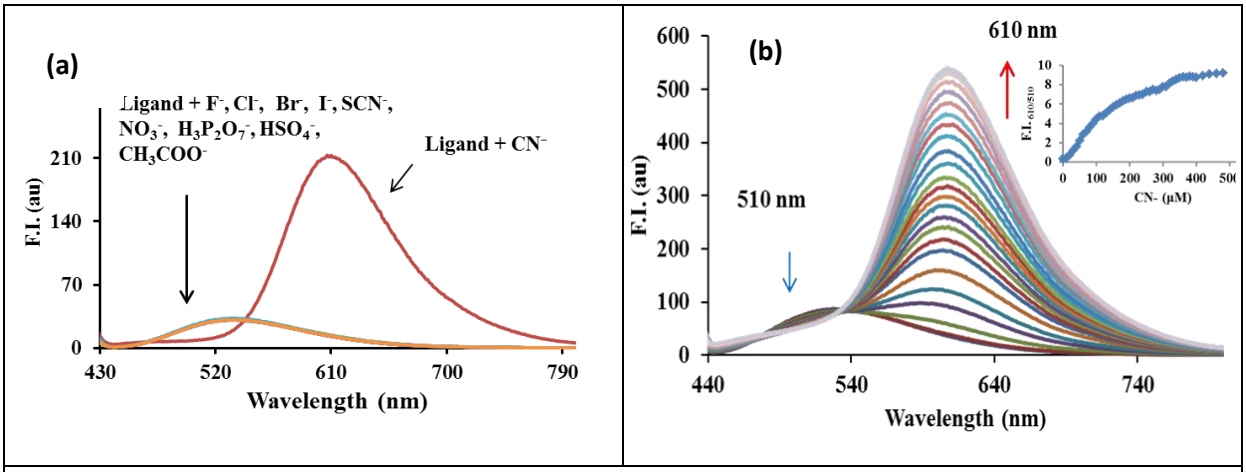


Figure 3: (a) Emission spectra of probe 3 (20 µM in $CH_3CN:H_2O$::9:1) in the absence and presence of different anions (1000 µM) such as CN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^-, I^- (b) Effect of incremental addition of CN^- (0-400 µM) to probe 3 (20 µM, $CH_3CN:H_2O$::9:1) on emission spectrum. Inset (b) ratiometric response of probe 3 towards CN^- ion.

4.2.3 Job's plot analysis of Probe 3 towards CN^-

To determine complexation behaviour of probe **3** towards CN^- ion**,** Job Plot was drawn**.** A stock solution of the same concentration of probe **3** and CN^- was prepared of the order of 2.0 $\times 10^{-5}$ M in $CH_3CN:H_2O$::9:1 solvent system. The emission of each case with different probe-analyte ratio but equal volume was recorded. Job plots were drawn by plotting emission intensity *vs* $X_{analyte}$ (ΔI = change of intensity of the emission spectrum during titration and $X_{analyte}$ is the mole fraction of the analyte in each case, respectively) and found that there exists a 1:1 stoichiometry **(Figure 4)**.

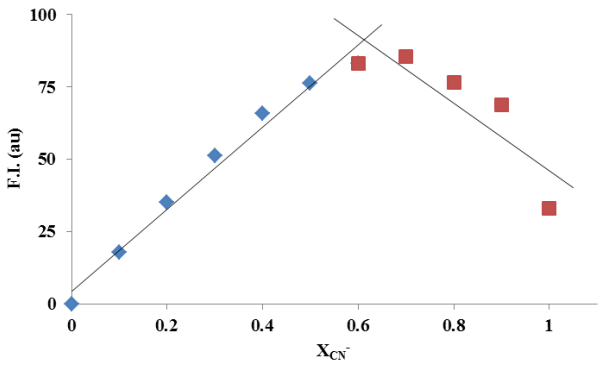


Figure 4: Job plot diagram of probe 3 with cyanide ions in CH_3CN: H_2O:: 9:1.

4.2.4 Effect of CN^- ion on NMR spectrum of probe 3

In order to get a better insight for the interaction of probe **3** towards CN^- anion, NMR titrations were performed. On addition of CN^- ion to probe **3** (5mM, DMSO (d6)), a downfield shift in aromatic protons and a new peak at 4.5 ppm due to hydrogen (**Figure 5**). As cyanide ions act as nucleophilde and therefore would attack at the carbon attacked by CN^- ion. The CN^- ion as a nucleophile could act as chemodosimeter to most electron deficient carbon adjacent to benzimidazole nitrile moiety and resulted in a downfield shift to adjacent protons. Thus, NMR titration results support the chemodosimeter behaviour probe **3** towards CN^- ion.

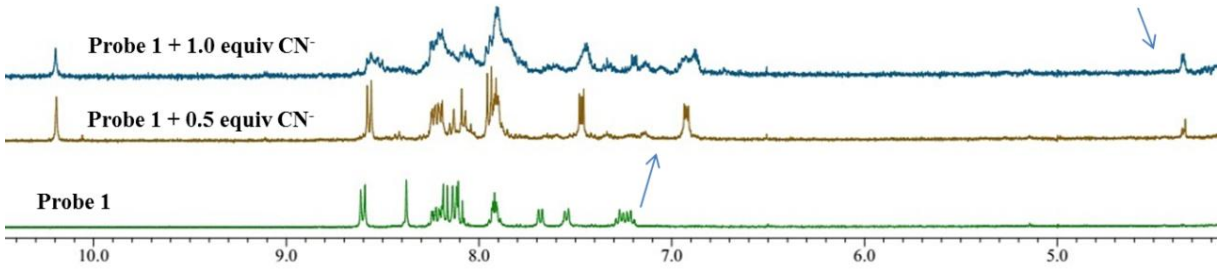
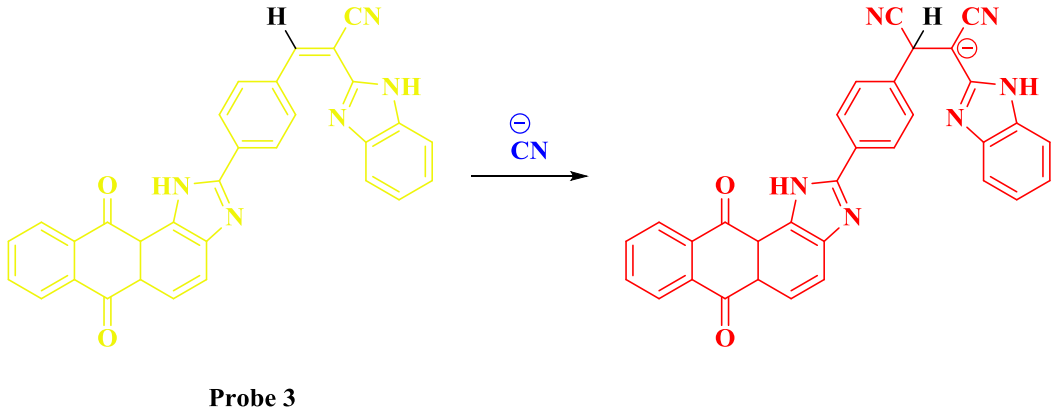


Figure 5: NMR titrations of Probe 3 with TBACN in DMSO-(d6) at 5mM

4.2.5 Proposed mechanism

Job plot analysis revealed the 1:1 stoichiometry of probe **3** toward CN^- ion. On the other hand, NMR titration showed a shift in proton signal along with anew peak at 4.5 ppm, clearly depict the nucleophilic attack of CN^- ion over probe **3**. Pictorial presentation was shown in **figure 6**.



Probe 3

Figure 6: Proposed mechanism for nucleophilic attack of CN^- over probe 3.

4.2.6 Practical Applicability of probe 3

To evaluate the probable interference of other anions in CN^- detection, we measured the fluorescence responses of probe **3** to CN^- was measured in the presence of another anion such as CN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^-, I^-in $CH_3CN:H_2O$::9:1 solvent system. All the examined anions showed negligible interfere with the detection of CN^- (**Figure 7**). Therefore, turn-on fluorescence signal of probe **3** is a good indication for the prime presence of CN^-. Further, the probe **3** was used in paper strip test for different anions. The paper was spotted with a solution of probe **3** (20 μM, $CH_3CN:H2O$::9:1), and dried in air. The different anions (500 μM) were imparted on spots of probe **3**. There was no noteworthy colour change in case of anions except CN^- ion. We have observed the distinct colour change in case of CN^- ion only. The spot (probe **3** + CN^-) gave colour change from yellow to blue under visible light and yellow-greenish to pink colour change was observed UV light **(Figure 8).**

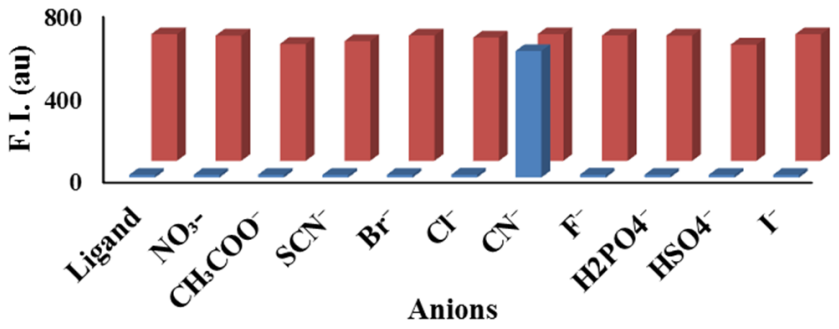


Figure 7: Relative emission intensity of probe 3 (20 μM) in $CH_3CN:H_2O$::9:1 (λ_{ex} = 415 nm) with different competing anions (1000 μM) in the absence and presence of CN^- (1000 μM), at λ = 610 nm, where blue bar represents the emission intensity change of probe 3 with different anions and red bars represents probe 3 with CN^- plus different relevant competing anions.

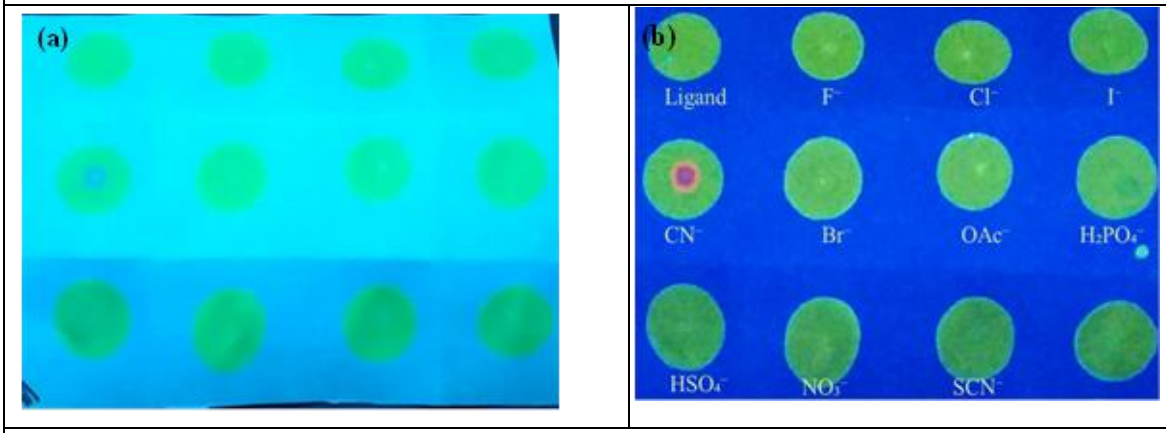


Figure 8: Images of colour change on paper for probe 3 and different anions under (a) visible and (b) UV light.

4.2.7 Absorption studies of probe 5 towards anions

The recognition behaviour of probe **5** toward various anions *viz*., CN^-, F^-, Cl^-, Br^-, I^-, CH_3COO^-, HSO_4^-, $H_2PO_4^-$, NO_3^-has been investigated by absorption and emission spectroscopic techniques in CH_3CN:H_2O (98:2) solvent system. Among these anions, the only introduction of CN^- ion showed significant changes in the absorption spectra of the probe **5 (Figure 9a).** On the addition of CN^- ion, the probe **5** exhibited shift in absorption spectrum from 385 to 584 nm. On gradual addition of CN^- ions to the solution of probe **5**, the absorption peak at 385 nm was decreased with simultaneous formation of two new bands at 350 and 584 nm with clear isosbestic points at 462 and 352 nm (Figure 9(b)). The decrease in probe's absorption maxima with a simultaneous increase in spectra allowed the probe to serve ratiometric probe for CN^- ion in aqueous acetonitrile solvent giving a visible colour change from yellow to purple. The absorption ratio varied from 0.002 to 1.187 at 584/385nm indicating ~593 fold ratiometric response. The spectral changes attained plateau after addition of 40 µM of cyanide ions. The spectral changes were associated with visible colour changes shown in **Figure 9b.** Thus, probe **5** can be used to estimate cyanide ion with detection limit of 3.5×10^{-7} M in aqueous acetonitrile solvent through ratiometric approach.

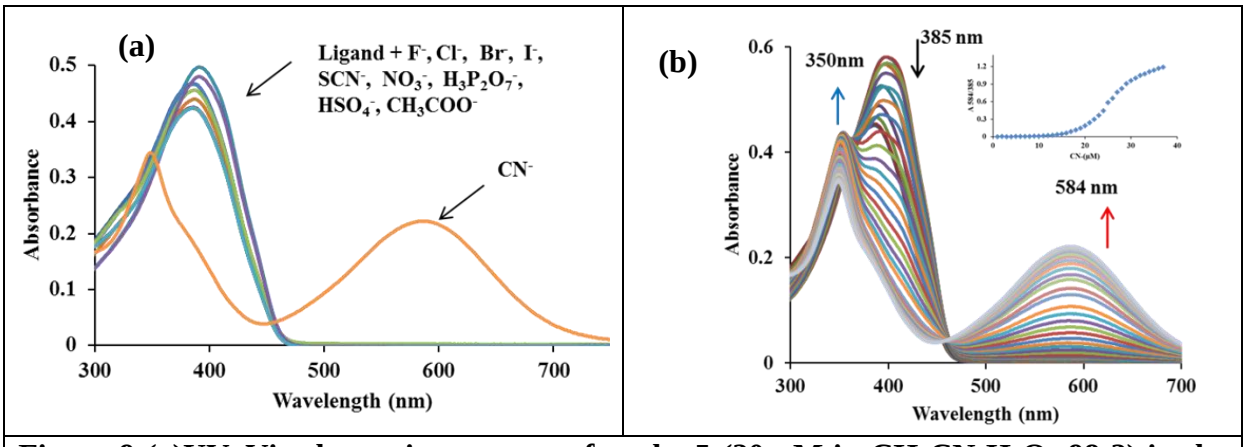


Figure 9:(a)UV–Vis absorption spectra of probe 5 (20 µM in CH_3CN:H_2O::98:2) in the absence and presence of different anions (1000 µM) such as CN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^-, I^- (b) Effect of incremental addition of CN^- (0-400 µM) to probe 5 (20 µM, CH_3CN:H_2O::98:2) on absorption spectrum. Inset (b) ratiometric response of probe 5 towards CN^- ion .

Figure 10: Images of visible colour change for probe 5 (20 µM in $CH_3CN:H_2O$::98:2) on the addition of different metal ions (1000 µM) in (a) visiblelight and (b) UV light.

4.2.8 Effect of various anions on emission spectrum of probe 5

Probe **5** (20 µM, CH_3CN: H_2O:: 98:2) on excitation at 385 nm exhibited emission band at 490 nm. On addition of various anions, no significant change was observed except for CN^- ion **(Figure 11)**. On the addition of CN^- ion, the probe **5** exhibited quenching in the emission spectrum. On gradual addition of CN^- ions to the solution of probe **5**, initially caused increase in the intensity of emission band until 8 µM of cyanide had been added **(Figure 12a)**, further addition of cyanide cause the intensity to decrease and completely quench at about 30 µM **(Figure 12b)**. Consequently, probe **5** can be used to estimate a wide range of cyanide ions between 0-30µM.

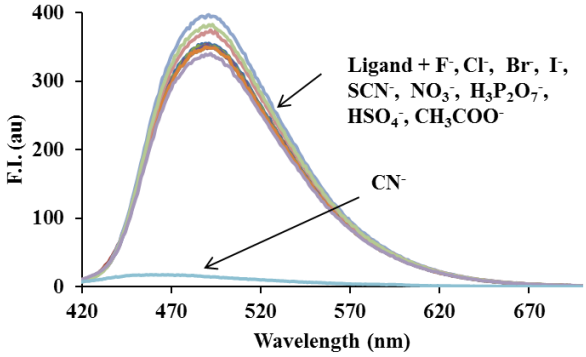
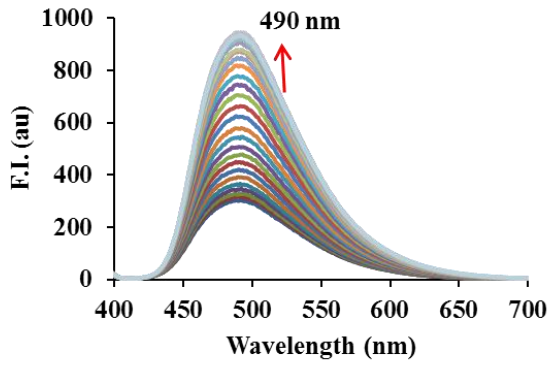


Figure 11: Effect of addition of various anions on emission spectrum of probe 5 (20 µM, acetonitrile: H_2O:: 98:2).



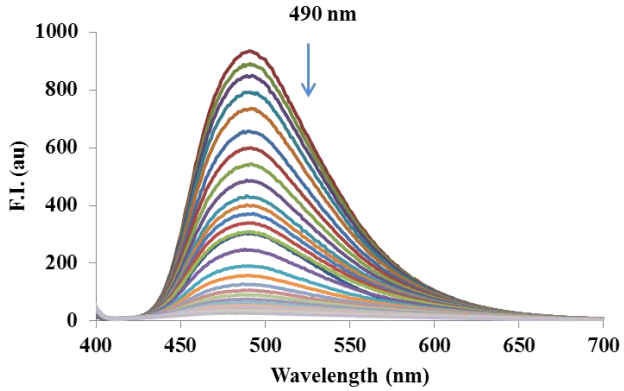


Figure 12: (a) the effect of incremental addition of CN^- (0-8µM) to probe 5 (20 µM, $CH_3CN:H_2O$::98:2) on emission spectrum. (b)Effect of incremental addition of CN^- (8-30µM) to probe 5 (20 µM, CH_3CN: H_2O :: 98 :2) on emission spectrum.

4.2.9 Job's plot analysis of Probe 5 towards CN^-

The complexation behaviour of probe **5** towards CN^- ion, was studied with similar protocol followed for probe **3**. A stock solution of the same concentration of probe **5** and CN^- was prepared in $CH_3CN:H_2O$::98 : 2 solvent system. Job plot was drawn by plotting absorption intensity *vs* $X_{analyte}$ and found that there exists as 1:2 stoichiometry **(Figure13).**

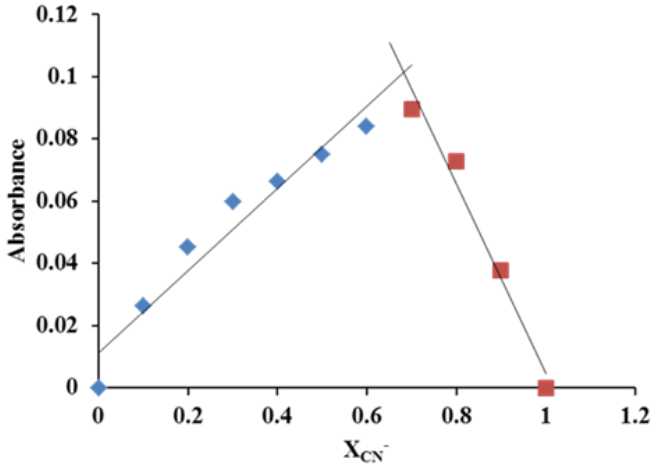


Figure 13: Job plot diagram of probe 5 with cyanide ions in CH_3CN: H_2O:: 98:2.

4.2.10 Proposed mechanism

Job plot analysis revealed the 1:2 stoichiometry of probe **5** toward CN^- ion. Pictorial presentation was shown in **figure 14**.

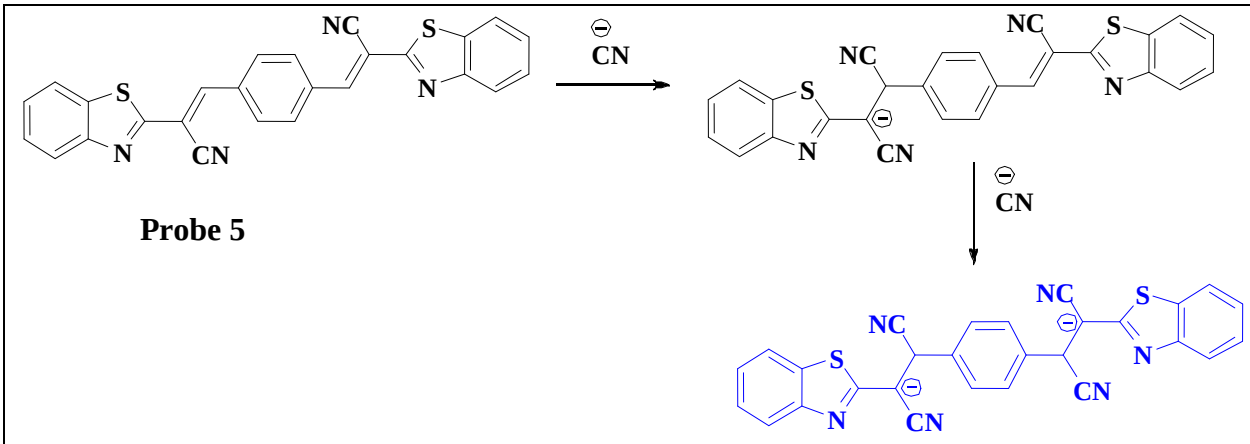


Figure 14: Proposed mechanism for nucleophilic attack of CN^- over probe 5.

4.2.11 Practical Applicability of probe 5

To evaluate the probable interference of other anions in CN^- detection, we measured the fluorescence responses of probe **5** and CN^-ion in the presence of another anion such asCN^-, SCN^-, OAc^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, F^-, Br^-, Cl^-, I^- in CH_3CN:H_2O::98:2 solvent system. All the examined anions showed negligible interfere with the detection of CN^- (**Figure 15**). Therefore, turn-on fluorescence signal of probe **5** is a good indication for the prime presence of CN^-.

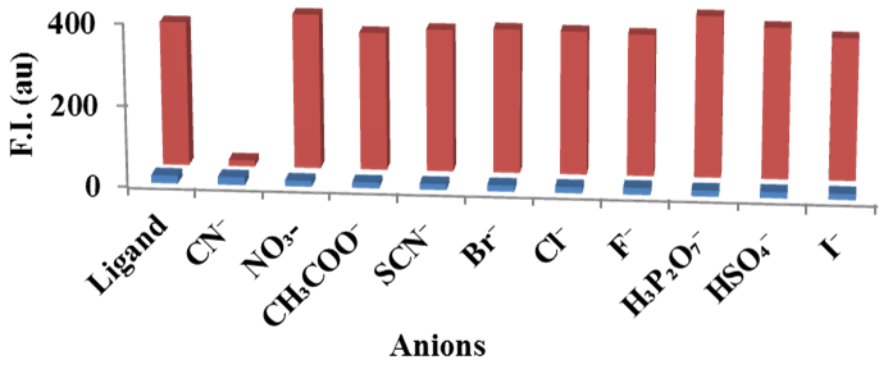


Figure 15: Relative emission intensity of probe 5 (20 µM) in $CH_3CN:H_2O$::98:2 (λ_{ex} = 495 nm) with different competing anions (1000 µM) in the absence and presence of CN^- (1000 µM), where red bar represents the emission intensity change of probe 5 with different anions and blue bars represents probe 5 with CN^- plus different relevant competing anions.

4.2.12 Stability constant:

Stability constants were calculated by using Benesi-Hilderband equation summarized in table.

Table. Stability constants of various anions through UV-Vis and Fluorescence

PROBE	Anion	Stability Constant (Per mole)	Lowest detection limit
3	CN^-	4.33×10^5	2.2×10^{-7}M
5	CN^-	1.95×10^5	3.5×10^{-7}M

CONCLUSION

Two colorimetric chemodosimeters Probe **3** and Probe **5** were synthesised containing benzimidazole and benzthiazole moiety respectively showing selective nucleophilicity for cyanide ion at the α-position to vinylic group. Probe **3** on addition of cyanide showed a red-shift in absorption spectrum while enhancement in fluorescent spectrum with change in colour from yellow to red. The probe **3** was utilised for paper strip test of cyanide anion in aqueous-acetonitrile system. On the other hand, Probe **5** showed a blue shift in absorption spectrum while quenching in fluorescent spectrum with a colour change from yellow to purple. Thus, both chemodosimeters obtained exhibited fluorescent and visible responses on addition of cyanide ion over the other anions.

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