

Electron Deficient π -hole Assisted Colorimetric Probe for Selective Cyanide Recognition.

Kumaresan Murugesan, Vanthana Jeyasingh, Sudha Lakshminarayanan, Selvapalam Narayanan, Lakshminarayanan Piramuthu

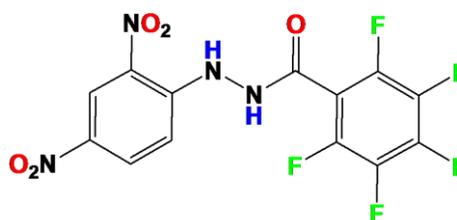
Abstract: Here in, simple and novel electron deficient π -hole assisted amide based colorimetric receptor synthesized for cyanide recognition which produce yellow to brownish red color change upon the addition of cyanide in acetonitrile medium. Cyanide has selectively recognized successfully with 1:1 stoichiometric ratio and 1.5523×10^4 M⁻¹ association constant. Cyanide recognition study was carried out with UV-Vis absorption and FTIR-Analysis and association constant and stoichiometric ratio were calculated by Benesi-Hildebrand plot and job's continues variation method respectively.

Keywords : Anion sensor, colorimetric sensor, cyanide.

I. INTRODUCTION

In recent years design and synthesis of anion receptors getting great attention among various division of supramolecular chemistry [1]-[6]. Anions are participating significant roles in biological systems and many anions are highly toxic such as CN⁻ [8]-[16]. So such hazardous anions has significant attention in molecular recognition chemistry. Cyanide is a highly hazardous anion which was used in many chemical industrial processes like gold mining, Fertilizers manufacturing, metallurgy, electroplating and catalysis [17]. Excess cyanide can lead to immediate death by cyanide replacing oxygen in our blood oxygen carriers. Probably many reports showing a multi anion receptors were designed with strong chromophoric signaling units such as nitro, olefin, imine based moieties and traditional hydrogen bond donor sites. Among the chromophore family nitro group is highly

preferred for designing anion receptors which electron withdrawing chromophore nature makes active acidic H-Bonding donor sites. Another key property of nitro based receptors most desirable tool for Intramolecular charge transfer between electron rich binding site to electron deficient nitro part produce highly active naked eye detection and spectral plays with anion. Most of the nitro based receptors sensing multi anions, but failed to selective sensing by providing same signal for many anions. In that way we designed nitro based receptors for anions which recognizing different dimensional anions such as spherical (F⁻), Linear (CN⁻), Trigonal (AcO⁻) with no selectivity. Many reported receptors are recognizing both fluoride and cyanide ions, so F⁻ and CN⁻ most competitive each other by its strong base nature. To overcome the selectivity issue, in the current work binding sites and geometrical shapes of receptors tuned from hydrazone part to amide which specially designed with modern Supramolecular tool(π -hole) Pentafluorophenyl. π -holes are modern tool in anion recognition chemistry known via many recent reports. Our recent report with nitro signaling unit and hydrazone binding site designed with pentafluorophenyl moiety and met selectivity issue [18]. In addition present work designed with binding site tuning with π -hole assistance gives interesting results in selectivity of CN⁻. Another advantage of nitro based receptors is calorimetrically active which provide color change with naked eye detection. Naked eye detection is simple and low cost than other known spectroscopic detection methods.



Scheme 1 : Chemical structure of 1

II. MATERIALS AND METHODS

A. Materials and methods

2, 4-Dinitrophenylhydrazine and 2,3,4,5,6-pentafluorobenzoylchloride are purchased from Sigma Aldrich. Acetone and acetonitrile were purchased from SRL chemicals India. TBA anion salts were purchased from Sigma Aldrich.

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SHIMADZU-1800 UV-Vis

spectrophotometer was used to study absorption properties and IR-Tracker-100 SHIMADZU used for FT-IR analysis.

B. Synthesis of L :

1mmol of 2,4-Dinitrophenylhydrazine and 2,3,4,5,6-pentafluorobenzoylchloride taken in 50 ml of dichloromethane medium with 8hrs stirrer. Orange color precipitation obtained as 76% yield.

III. RESULT AND DISCUSSION

Absorption properties of Receptor L and their sensing ability were studied with various biologically important toxic anions via both colorimetric and spectroscopic investigations. Acetonitrile medium is used to prepare testing solutions and stock solutions of anions and receptor L. Among various geometrical anions receptor L provides color change from yellow to brownish red with cyanide spectral change with CN^- while no dramatic changes observed in spectrum for all other anions(Fig.1).

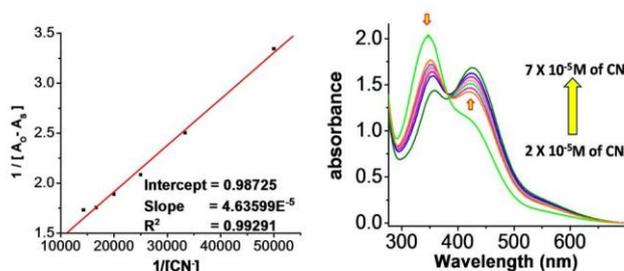


Fig.1. Absorption spectra of L with various anions.

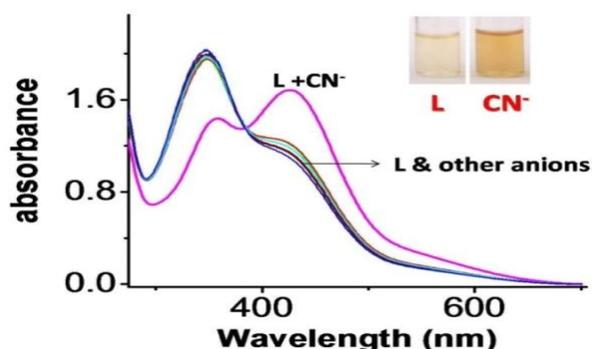


Fig.2. Benesi-Hildebrand method absorption band and plot for L+CN- complex.

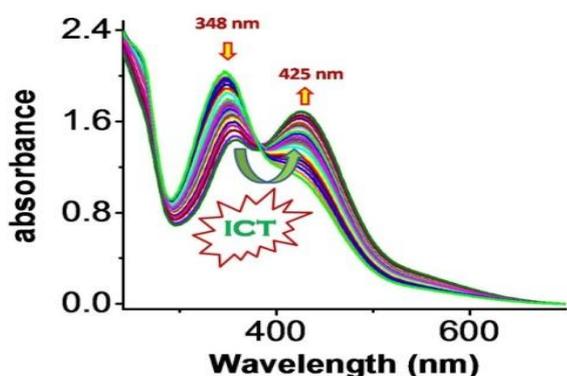


Fig.3. Absorption spectra of L with increasing conc. of CN^- .

These results exploring the selectivity of cyanide over all

other competing anions, and additionally to ensure selectivity colorimetric studies were carried out for all competing anions and successfully observed color change for cyanide (fig.3). Stoichiometric ratio and association constant of $[L+CN^-]$ complex was studied by job plot and Benasi-Hildebrand method respectively.

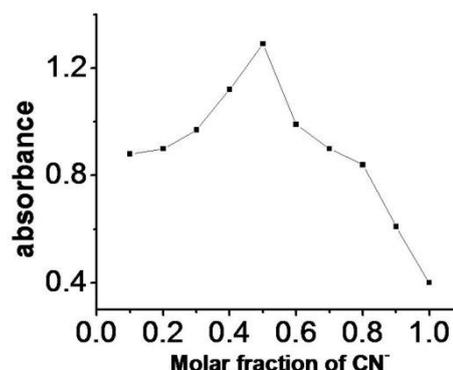


Fig.4. Job plot of L+ CN^- complex. Maximum absorbance observed at 0.5 molar fraction of CN^- ensures 1:1 stoichiometry.

Additionally spectroscopic titration carried for receptor L with following anions (F^- , CN^- , Br^- , Cl^- , I^- , SCN^- , ACO^- , FHF^- , $H_2PO_4^-$, N_3^- and NO_3^-) and obtained ICT (Intramolecular Charge Transfer) absorption formation ensures new complex formation.

A. Cyanide recognition

Cyanide recognition was studied by absorption spectroscopic titration with new absorption at 425nm as spectroscopic signal. Testing solutions were prepared in acetonitrile medium at $1 \times 10^{-5}M$. Receptor L was taken with various anions and recorded absorbance and maximum absorbance of receptor L(348nm) decreased and born new absorbance at 425nm upon addition of cyanide when no such changes caused by other anions. Isosbestic point at 385nm was observed upon addition of increasing concentration of cyanide ensures stable $[L+CN^-]$ complex formation. Observed isosbestic point was beautifully concocted by decreasing ($\pi-\pi^*$) transition with increasing ($n-\pi^*$) transition which known as Intramolecular charge transfer from receptor part to Nitro moiety (fig.3).

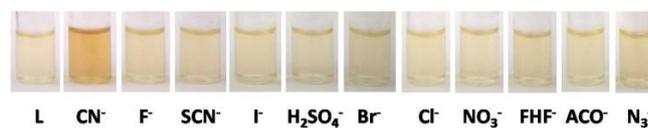


Fig.5. Colorimetric study of L with various anions at $5 \times 10^{-5}M$ in acetonitrile medium.

Electron withdrawing nature of nitro part and pentafluorophenyl part increasing the acidic nature of binding site(NH) which makes ease to interact cyanide and pentafluorophenyl part being as +ve charged π -hole encourage stability of complexation and geometrical nature of receptor L gives selectivity towards cyanide. Cyanide and NH interaction induces ICT by moving electron density from receptor part to electron deficient dinitrophenyl moiety.

B. Titrations

Stoichiometric ratio between receptor L and CN^- were studied by job plot continues variation method and again ensured by Benesi-Hildebrand method.

Binding stoichiometry and binding constant were verified and calculated with the method of Benesi-Hildebrand expression.

$$\frac{1}{A_S - A_0} = \frac{1}{A_S - A_0} - \frac{1}{A_S - A_0} K [\text{Host}]$$

Here,

A_S = maximum absorption of receptor (host) with Anion (guest)

A_0 = maximum absorption of receptor (host) Without anion (guest).

Stoichiometric ratio of L+ CN^- were studied by continues variation method which known as job's method. In this method L and cyanide were taken for absorption study in continues variation concentration from 0 to 1 (as 0.1, 0.2, 0.3, 0.4....0.9, 1) and 1 to 0. Absorbance was high for 0.5 molar ratio of L+ CN^- which ensure 1:1 complex formation(fig4).

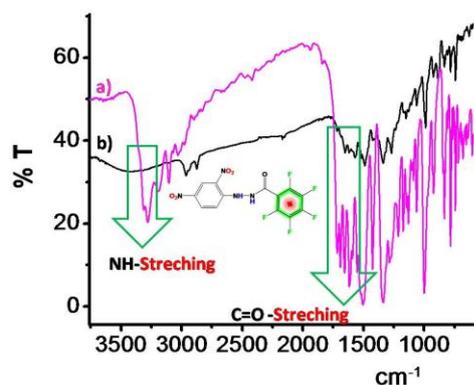


Fig.6. FT-IR analysis of (a) L and (b) L+ CN^- .

Stoichiometric ratio and association constant were calculated again with Benesi-Hildebrand method. Receptor L+ CN^- complex has $1.5523 \times 10^4 \text{ M}^{-1}$ association constant and again ensured 1:1 stoichiometry as calculated with Benesi-Hildebrand method(fig.2). In colorimetric study, receptor and anions were taken in acetonitrile medium at $5 \times 10^{-5} \text{ M}$ and color change was observed from yellow to Brownish red with cyanide and no notable changes were observed with other anions in above mentioned concentration but mild and unconsiderable color changes for F^- , N_3^- , AcO^- and FHF^- by very weak uncomfortable interactions. (fig.5). Reason behind the observed strong color change is hydrogen bonding and π -hole interaction between cyanide and L as theoretically expected which confirmed with FT-IR analysis(fig.6). In FT-IR analysis (NH and C=O) stretching bands were broadening and shifted from 3281 cm^{-1} to 3452 cm^{-1} and 1658 cm^{-1} to 1652 cm^{-1} respectively upon the addition of cyanide.

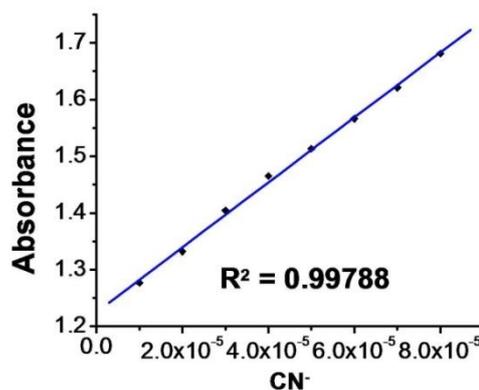


Fig 7: Linear analysis spectra of Receptor L with CN^- .

To ensure the hydrogen bonding interaction water drops were added with L+ CN^- complex solution and color change was not retained and solution back to yellow color which own color of L and here the color disappearance occurred by the hydrogen bond interaction of L+ CN^- broken by water molecules(fig.9). Linear relationship of L+ CN^- complex was studied with increasing concentration of cyanide addition from $1 \times 10^{-5} \text{ M}$ to $7 \times 10^{-5} \text{ M}$ and plotted linear regression line with $R^2 = 0.99788$ correlation coefficient value(fig.7).

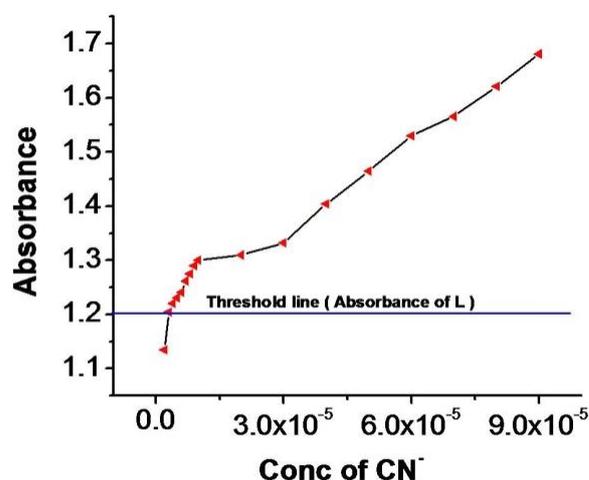


Fig.8. LOD determination of cyanide by receptor L.

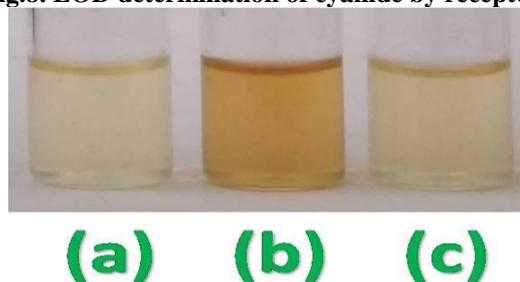


Fig.9. Colorimetric study with water addition (a) L, (b) L+ CN^- , (c) L+ CN^- + H_2O .

Additionally LOD of cyanide $9 \times 10^{-6} \text{ M}$ was calculated by single wavelength absorption method with decreasing concentration of cyanide where wavelength fixed at 421nm which maximum absorption of new band produced by L+ CN^- complex(fig.8).

IV. CONCLUSION

Finally cyanide recognized selectively by novel colorimetric receptor L with color change from yellow to brownish red in acetonitrile medium. 1:1 binding mode and association constant were clearly investigated by absorption analysis with Benesi-Hildebrand plot and job's continues variation method respectively. Hydrogen bonding interactions ensured with FTIR analysis.

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