Recognition of Cyanide by Urea-Based Bipodal Probe

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

Abstract: ***Two urea based colorimetric receptors were developed. The receptor L showed a exclusive selectivity of cyanide over the other anions in acetonitrile solution and exhibited Intramolecular charge Transfer (ICT). It was studied by UV-vis spectroscopy and their binding ability was explored by using Job's plot and Benesi-Hildbrand routes. From that the receptor L, it recognize CN^- anions and it indicates 1:1 stoichiometric ratio and the receptor L^1(monofluoro substituted) does not recognize any anions. Finally the (difluoro substituted) receptor L shows good sensitivity, selectivity towards cyanide.***

Keywords : Anion recognition, colorimetric sensors, cyanide sensing, urea receptor.

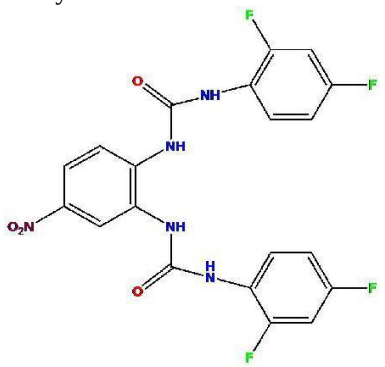
I. INTRODUCTION

Anions play a fundamental role in many industrial, biological and chemical processes [1]-[4]. Thus, the design and alliance for the receptors that can selectively sense the particular anions are always of extensive interest. The colorimetric sensors using anion recognition are an essential role and it cannot require over priced instruments. The colorimetric sensors are preferably used as the signalling unit, because that can be revealed by unaided eye itself.

Cyanide is an important ion and it is more toxic to the living organisms, which can leads to death rapidly It is a basic material for the fabrication of polymers such as acrylic plastics and nylon and it is more important for gold extraction process [5].Cyanide is quite different and hazardous material and it is kept in a few foods and plants and it has been produced in excess volume in different chemical and industrial processes which has involved in gold mining and metallurgy. Mans revealed cyanides through dietary, environmental and other sources. According to world health Organisation, the concentration of cyanide in drinking water is 2 μM[6].

Recently, major emphasis has been placed on strategies encourage colorimetric sensors. From this inference, certain Synthetic receptors, including urea, [7]-[11], thio-urea [3],[12]-[16], amides [17], Imidazolium phenylhydrazone [18],and phenol [19], with units of correlation analysis with negatively charged ionic species.

In this paper we have designed and synthesized highly electron deficient nitro phenyl substituted urea receptors. These synthesized two receptors (L and L^1) are only varied by fluoro substitution, which induce acidity of urea part and plays major role as chromophore unit to produce colour change to expend either hydrogen-bonding or a combination of hydrogen-bonding and electrostatic interactions. Further the urea group confirm to be an good hydrogen bonding donor perform in design and synthesis of anion sensors[20]-[22]. This sensor can selectively detect cyanide via colorimetric assay. Further studies have been detected for the receptor L and their properties of anionic species are observed the change by using UV–visible absorption spectroscopy and FT-IR respectively.



Scheme 1 structure of receptor L^1.

II. MATERIALS AND METHODS

A. Materials

4-Nitro orthophenylenediamine are purchased from SigmaAldrich. 4- Fluorophenyl isocyanate, 2, 4-Difluorophenyl isocyanate and acetone were procured from Spectrochem Ltd., India. Acetonitrile (MeCN) is confirmed without water before using and all the sodium salts were purchased from Merck.

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B. Instruments

FT-IR characterization carried by IR-Tracker-100 SHIMADZU. The absorption spectra were recorded on UV-1800(SHIMADZU). UV/Vis Spectrometer with a quartz cuvette (path length: 1 cm)

C. Synthesis of L & L[1]

4-Nitro ortho-phenylenediamine 0.153g (1mmol) was added to a stirring solution of 0.155g of difluoro substituted phenylisocyanate in acetone and the mixture was stirred at room temperature for 12 hours. The resulting yellowish orange precipitate was filtered. The resulting residue was dried under vaccum to give orange solid product (80%). FT-IR : NH (3282 cm^{-1}) C=O(1641cm^{-1}). The same procedure was continued with the receptor L^1, 4-Nitro ortho-phenylenediamine and 4-Fluorophenyl isocyanate and obtained (76%) yield. FT-IR: NH (3284cm^{-1}) C=O (1610)cm^{-1}).

III. RESULTS AND DISCUSSION

The receptor L were studied by UV-Vis spectra in the presence of tetrabutylammonium salts of various anions such as F^-, CN^-, Br^-, NO_3^-, I^-, FHF^-,$H_2PO_4^-$, AcO^-, Cl^-, N_3^-, SCN^-) to study their binding ability.

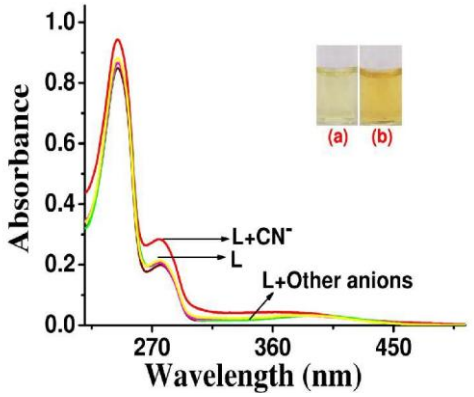


Fig.1. Absorption spectra of the receptor L with in the sight of various anions like F^-, Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, AcO^-, CN^-, N_3^- . Insert picture: (a) receptor L in acetonitrile medium, (b) addition of Tetrabutyl ammonium salts of CN^-.

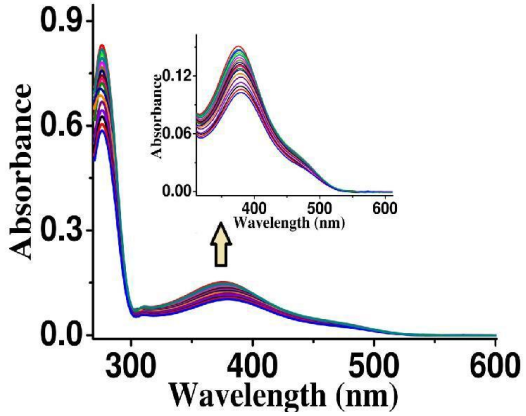


Fig.2. Changes in the UV–vis absorption spectrum of the receptor 1 (1×10-5 M) in acetonitrile upon addition of CN− anions in TBA salts form.

The receptor L treated with the increasing concentration of recognized anion and it showed the λmax at 276 nm increased gradually and at the same time, a new absorbance band occur at 378nm, while addition of cyanide ion respectively to the corresponding acetonitrile solution contains receptor L. Observed spectral changes could be explained on the basis of ICT between urea moieties (anion bound) and electron deficient nitro substituted aromatic moieties.

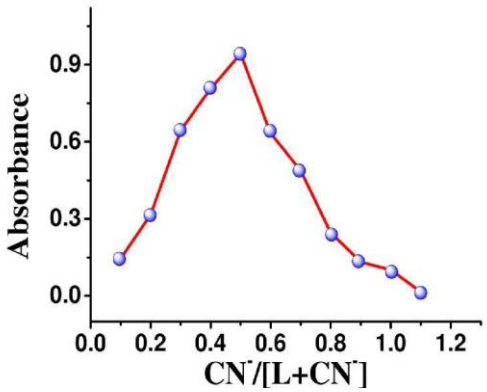


Fig.3. Job's plot to determine the stoichiometry of the receptor L and CN-.

By using Job's plot, the receptor L confirmed the 1:1 stoichiometric interaction with CN^- ion. (fig. 3) were anion concentration increased as continues variation, in addition association constant calculated (Table I). By using Benesi-Hildbrand plot, the binding constant value and stoichiometric value 1:1 are calculated.

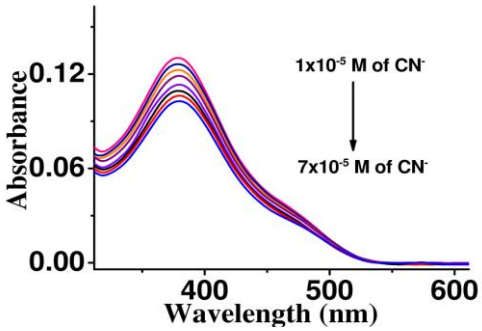


Fig.4. Change in the absorption spectra for the receptor L with the addition of CN- anion.

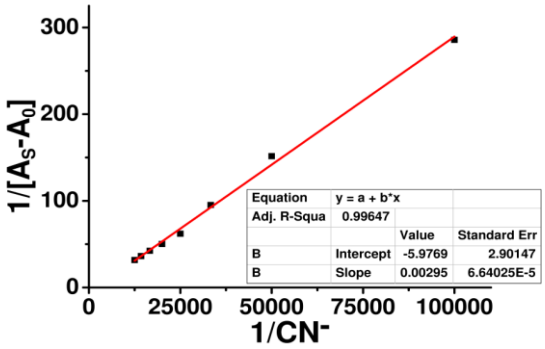


Fig.5. BH plot confirms 1:1 stoichiometric ratio of the receptor L with recognized anions.

For the receptor L, the binding studies are studied by using UV –Visible titrations and it selectively binds cyanide. The association constant of the receptor L at $2.02x10^{3}M^{-1}$ was calculated by using Benesi Hildbrand titrations.

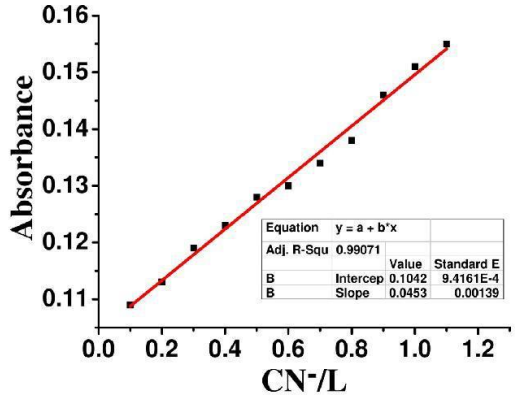


Fig.6. Changes in the UV–Vis absorption spectrum, receptor L upon increasing concentration of TBA salts of cyanide.

LOD are calculated by constant concentration of the receptor L are treated with the decreasing concentration of the recognized anion. The detection limit of the binding receptor L shows $7.217x10^{-6}M$·

A. IR Analysis

In addition, the recognition properties of the receptor L and tetrabutyl ammonium salts of cyanide ion added into the receptor L, (Fig.7), there were a notable disturbance of urea NHs and carbonyl. IR information ensures for L, NH stretching at 3280cm-1 ,C=O at 1614cm-1 and the addition of CN anion into the receptor L , the NH stretching at $3437cm^{-1}$ and for carbonyl at $1699cm^{-1}$.

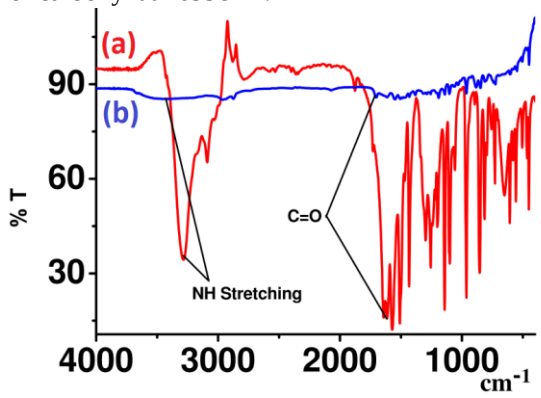


Fig.7. IR Spectra of the receptor L and the recognized anion, (a) L (b) L+CN−.

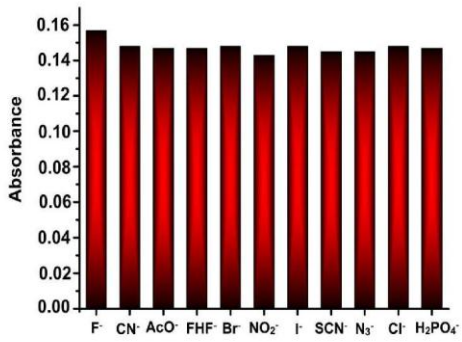
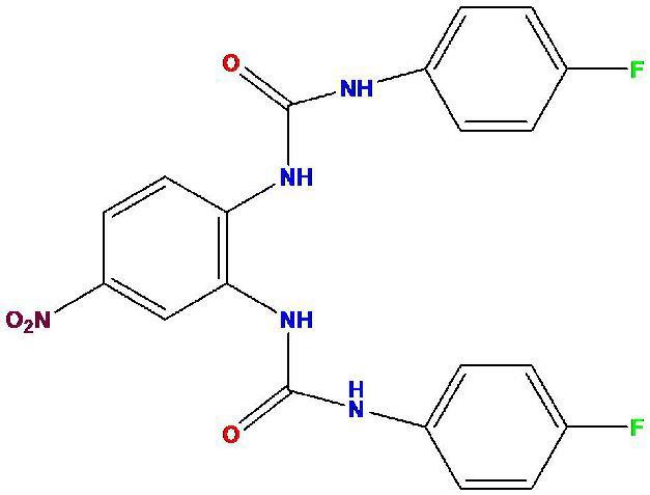


Fig.8. Bar chart review for the receptor L with anions.



Scheme 2: structure of receptor L1.

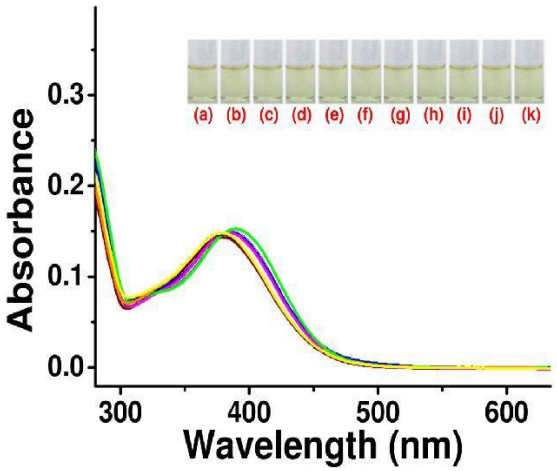


Fig.9. UV–Visible absorption spectra of receptor L1. Insert picture: (a) receptor L1 in acetonitrile, (b) L1 + F− (c) L1 + CN− (d) L1 + AcO− (e) L1 +FHF−(f) L1 + H2PO4− (j) L1 + N3− (k) L1+ Br−.

We have prepared a reference compound L^{1} and it has only one fluoride atom (scheme 2) and it does not recognize any anions while adding tetrabutyl ammonium salts of anions and it can proved by colorimetric experiment and UV titrations.

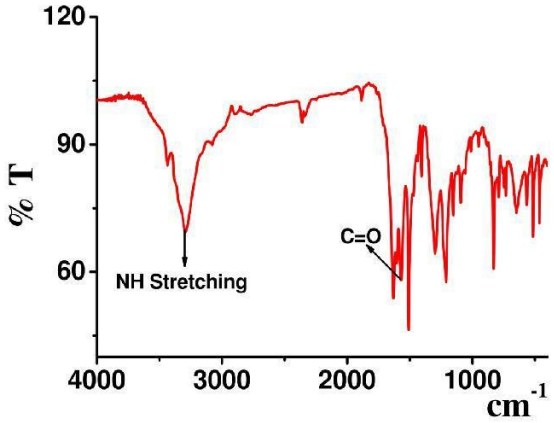


Fig.10. IR Spectra of the corresponding receptor L1.

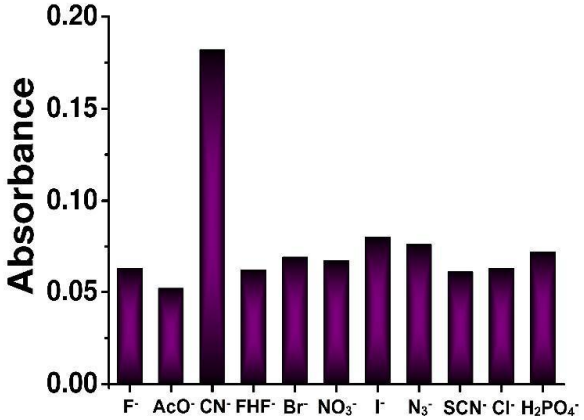


Fig.11. Bar chart review of the receptor L1 various anions.

Table – I: Summarized binding nature of L with CN- calculated with absorption studies

Host	Guest	Stoichiometric Ratio	R^2 value	Association Constant (M^{-1})	LOD (M)	IR (cm^{-1})	
L	CN^-	1:1	0.99071	$2.02X10^3$	$7.217X10^{-6}$	NH	3282
						C=O	1641

IV. CONCLUSION

Bipodal receptor designed with acidic urea based hydrogen donor sites, and acidic nature of the donor sites tuned by Fluoride substitution. Cyanide recognition achieved with high selectivity by Difluoro substitution.

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