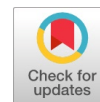


Electron Deficient π -Hole Assisted Hydrazone Based Probe for CN^- And F^- Recognition



Sudha Lakshminarayanan, Kumaraesan Murugesan, Vanthana Jeyasingh, Selvapalam Narayanan, Geetha Das*

Abstract: Novel electron deficient pentafluorophenyl functionalized neutral receptor synthesized and examined the biologically important and hazardous F^- , CN^- recognition via absorption and emission spectroscopic investigation.

Keywords : Anion sensing, hydrazones, π -Holes.

I. INTRODUCTION

Supramolecular chemistry has vast research interest along their importance and applications. Among various directions of Supramolecular chemistry design and synthesis of receptors for anion recognition has more attention by recent researchers[1-6]. Anions are playing ubiquitous roles in many living organisms and biological systems[7-10]. Fluoride and cyanide is highly biologically importance and hazardous among all over anions. Anion recognition was such challenged task because of their different types of structural nature. Many reported hydrazone based receptors struggling with selectivity by non directional hydrogen donor parts[11]. Many receptors designed with urea, amide, sulfonamide, pyrrole, hydrazone and alcohol fictionalization as hydrogen donors which are traditional sources of receptor part of sensor probes[12-15]. Recently pi-holes are used to interact anions and successfully recognized by pi-holes but sensitivity of pi holes are not enough for strong association[16,17].

In our recent report, designed a hydrazone based dinitro substituted receptor with pi-hole assistance where aromatic ring hydrogen's of dinitrophenyl hydrazone also were behaved as hydrogen donor, but the result selectivity struggled with five anion recognition with same signal in

both colorimetric and spectral change[18]. To achieve the selectivity towards particular anion, we designed simple and highly electron deficient monopodal receptor with pi-hole assisted hydrazone part where pi-hole functionalized instead of dinitro substitution. After tuning the receptor part and absence of aromatic hydrogen source the receptor became more directional towards recognizing five to two (F^- , CN^-) anions with clear color change from colorless to yellow and producing new absorption band in UV-VIS absorbance spectrum. Receptor L showing clear new absorbance upon the addition of (F^- , CN^-) anions while no change observed for other anions in both colorimetric and spectrometric investigation.

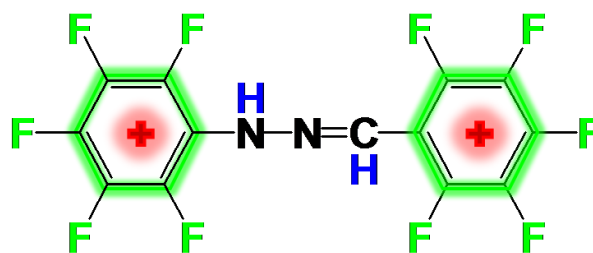
II. INSTRUMENTS AND METHODS

Absorption spectra recorded by double-beam Jasco(V630) UV-Vis spectrophotometer and emission spectrum recorded by Jasco (FP-8300) spectrofluorometer respectively. FT-IR analysis carried by IR-Tracker-100 SHIMADZU.

III. RESULTS AND DISCUSSION

A. Synthesis of receptor L

Receptor L synthesized by 2,3,4,5,6-pentafluorobenzoylchloride(1mmol) and 2,3,4,5,6-pentafluorophenylhydrazine(1mmol) refluxing 10hrs in DCM medium. After 10hrs of reflux the solution mixture evaporation 78% of yield obtained. FT-IR analysis: NH stretching 3362cm^{-1} , C=N stretching 1662cm^{-1} (fig. 7).



Scheme-1: Molecular structure of L

Receptor L was designed with pi-hole assisted hydrazone to enhance the selectivity and sensitivity as we expected receptor L has high sensitivity by the acidic hydrogen donor. In continues curiosity receptor L was taken for anion recognition investigation by absorbance study with various anions in acetonitrile medium.

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* Correspondence Author (s)

Sudha Lakshminarayanan, Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, Tamilnadu, India. Email: sudha28lakshmi@gmail.com

Kumaresan Murugesan, Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, Tamilnadu, India. Email: m.kumaresan@klu.ac.in

Vanthana Jeyasingh, Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, Tamilnadu, India. Email: p.lakshminarayanan@klu.ac.in

Selvapalam narayanan, Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, Tamilnadu, India. Email: n.selvapalam@klu.ac.in

Geetha Das, Department of Chemistry, Kalasalingam Academy of Research and Education (Deemed to be University), Krishnankoil-626126, Tamilnadu, India. Email: geethachem2015@gmail.com

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B. Absorbance and emission titration

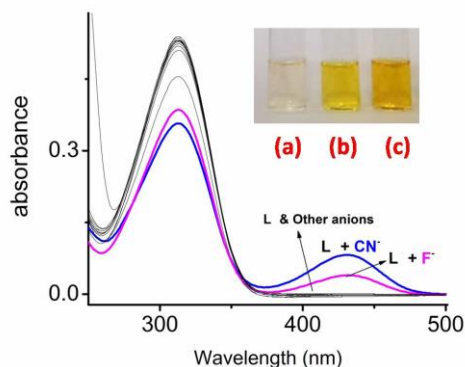


Fig. 1. Absorption bands of receptor L with anions. Insert picture: a) L ; b) L+F⁻; c) L+CN⁻ in acetonitrile medium.

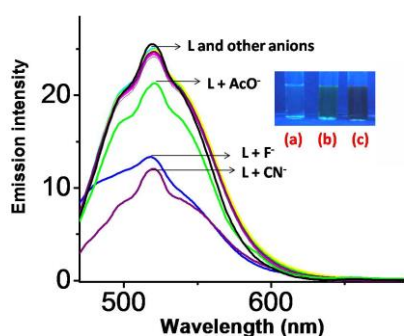
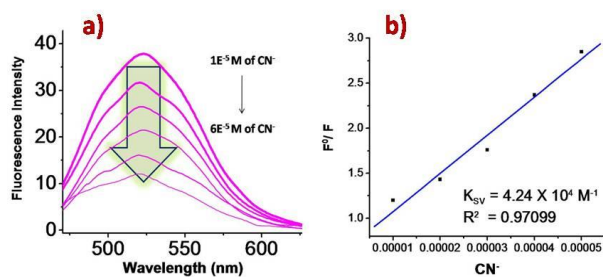


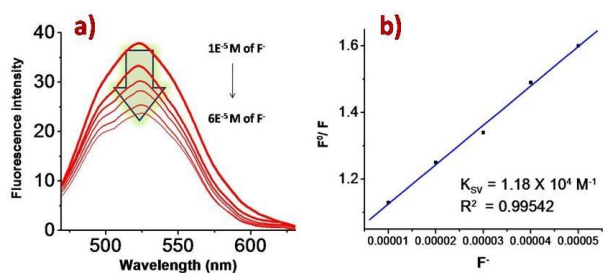
Fig. 2. Emission spectrum of receptor L with anions. Insert picture: a) L ; b) L+F⁻; c) L+CN⁻ in acetonitrile medium.

Fig. 3 . Stern-Volmer method for[L+CN⁻]. a) Emission titration spectrum. b) Stern-Volmer plot and KSV



determination.

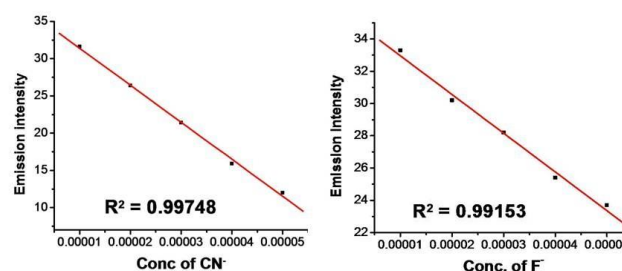
Fig. 4. Stern-Volmer method for[L+F⁻]. a) Emission titration



spectrum. b) Stern-Volmer plot and KSV determination.

For absorbance study the stock solutions of receptor L and anions were prepared 1x10⁻³M concentration and diluted as 1x10⁻⁵M for testing solution preparation. TBA salts used as anion source in both colorimetric and spectroscopic investigation.

To study the anion recognition capability of receptor L, Absorption and emission properties were studied with various anions and the changes observed for (F⁻, CN⁻ and ACO⁻) in both absorbance and emission spectrum when no dramatic changes observed for Cl⁻, Br⁻, I⁻, SCN⁻, FHF⁻, NO₃⁻, N₃⁻, H₂PO₄⁻ and AcO⁻ ions(fig. 1). Spectral changes of L+CN⁻, L+F⁻ observed new maximum absorbance born at 430nm in absorption band and for emission spectrum excitation wavelength fixed at 430nm to examine the emission behavior of receptor L with anions. Receptor L has emission at 519nm when excited at 430nm which quenched upon the addition of F⁻, CN⁻ while other anions didn't give any notable changes(fig. 2). These results assure L has



interaction with F⁻, CN⁻ and the same information obtained in colorimetric study.

Fig. 5. Linear regression analysis of L+CN⁻ and L+F⁻ via emission spectrum.

Electron deficient two pentafluorophenyl moieties give directional pi-hole plane and highly acidic hydrogen available as hydrogen bond donor for anions. Structural restriction environment of pi-holes plays vital role in selectivity via anion-pi interaction. Acidic NH proton and pi-holes capturing anion with Supramolecular interactions which was strongly associated by pi-hole assistance. Supramolecular complexes L+CN⁻, L+F⁻ taken for stoichiometric analysis and association constant determination. Both stoichiometry and association constant of L+CN⁻ and L+F⁻ were calculated by emission studies through Stern-volmer plot. Stern-volmer plot drawn by F/FO vs Conc. of anion.

Where,

$$F = \text{Emission intensity of receptor}$$

$$F^0 = \text{Emission intensity of quenched spectra of receptor with addition of anion}$$

Stoichiometric ratio of L+CN⁻, L+F⁻ complexes were determined as 1:1 ratio with best fit of the plot. Association constants of L+CN⁻ and L+F⁻ were 4.24 x 10⁴M⁻¹ and 1.18 x 10⁴M⁻¹ respectively(fig. 3, 4).

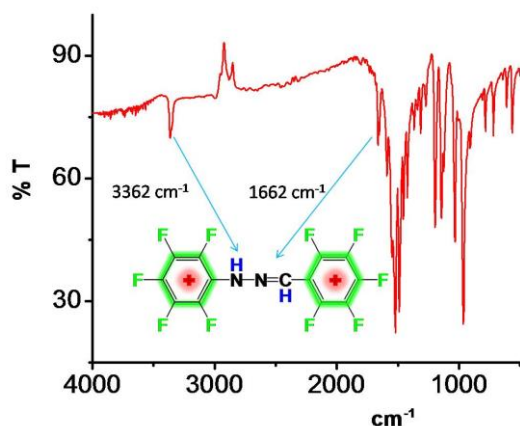
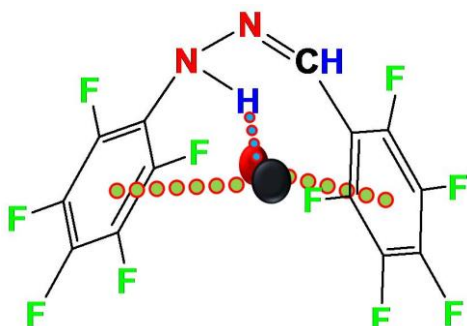


Fig. 6. FT-IR analysis of receptor L in solid state.



In addition linear relationship of $L+CN^-$ and $L+F^-$ examined by emission behavior with uniformly increased anion concentration where got straight fit line obtained with R^2 values above 0.95 which ensures perfect 1:1 complex formation. Obtained R^2 values of $L+CN^-$ and $L+F^-$ complexes is 0.99748 and 0.99153 (fig. 5). Possible binding mode can be assumed as given (fig. 7).

Fig. 7. Possible Binding mode of $L+CN^-$

IV. CONCLUSION

Pi-hole assistance to acidic hydrogen donor provided by pentafluorobenzene moiety which makes structural restriction to anions and it leads selectivity and electron deficient nature to receptor L. As we expect receptor L selectivity enhanced towards two anions from five anions. Anion recognition studies examined with absorption and emission spectroscopy.

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AUTHORS PROFILE



Mrs. Sudha Lakshminarayanan her B.Sc and M.Sc in chemistry from the Sri Paramakalyani College, Alwarkuruchi, India and her M.Phil degree in chemistry from Bharathidasan university, Trichy. Presently She is working as Assistant Professor at JP College of Arts and Science, Agarakattu, Tamilnadu. She is pursuing doctoral degree in Chemistry at Kalasalingam Academy of Research and Education (KARE)

under the guidance of Dr. Geetha Das and Dr. Selvapalam. She has research interest on Host-guest chemistry.

Electron Deficient II-Hole Assisted Hydrazone Based Probe for CN⁻ And F⁻ Recognition

She has published over 5 research article in reputed international journals.



Mr. M. Kumaresan Murugesan received his B.Sc and M.Sc in chemistry from the NGM College and Karunya University respectively. He is pursuing doctoral degree in Chemistry at Kalasalingam Academy of Research and Education(KARE) under the guidance of Dr. Lakshminarayanan Piramuthu. Mr. M. Kumaresan has a research interest on Host-guest chemistry. He has published over 5 research article in reputed international journals.



Ms. Vanthana Jeyasingh, her B.Sc and M.Sc in chemistry from Sri Sarada College for women, Tirunelveli, and APC Mahalaxmi College for women, Tuticorin, India respectively. She is pursuing doctoral degree in Chemistry at Kalasalingam Academy of Research and Education(KARE) under the guidance of Dr. Lakshminarayanan Piramuthu. Ms. Vanthana Jeyasingh has a research interest on Host-guest chemistry. She has published over 5 research article in reputed international journals.



Narayanan Selvapalam received his M.S. and PhD degrees from Mysore University and IIT Delhi respectively. He is presently working as Associate professor at Kalasalingam Academy of Research and Education (Kalasalingam University). His research interests include supramolecular chemistry, chemistry of cucurbiturils and cyclo dextrines, organic synthesis and sensors.



D. Geetha has completed M.Sc., from Bharadhidasan University, M.Phil., from Annamalai university. She completed Ph.D from Jaypee University in 2016. Joined as assistant professor at Kalasalingam University from 2017 onwards. Her field of interest is in bio surfactants. She has published 7 papers in reputed international journals.