STUDIES ON SCHIFF BASE DERIVATIVES AND THEIR POTENTIAL APPLICATIONS AS CHEMOSENSOR

Synopsis submitted to Madurai Kamaraj University

for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

W. ANBU DURAI

(Reg. No. F9708)

DEPARTMENT OF INORGANIC CHEMISTRY

SCHOOL OF CHEMISTRY

MADURAI KAMARAJ UNIVERSITY

(University with Potential for Excellence)

MADURAI-625 021

TAMIL NADU, INDIA

FEBRUARY 2020

STUDIES ON SCHIFF BASE DERIVATIVES AND THEIR POTENTIAL APPLICATIONS AS CHEMOSENSOR

The thesis embodies several novel design and syntheses of naphthalene and pyrene – based chemosensors. As a fluorophore and chromophore probe, they have pulled in an incredible enthusiasm among chemists because of their photophysical properties. Generally naphthalene/pyrene based derivatives weakly fluorescent upon binding with metal ions or anions, made them strong fluorescent probes via Schiff base reaction. Metal ions and anions are essential for the living organisms and assume huge roles in biological, environmental and chemical systems, but excessive amounts having damaging effect on the organisms. Heavy metals, metal-containing compounds and anions are dangerous to health or to the environment, some may cause corrosion, some are carcinogenic or toxic, affecting the central nervous system and other organs like kidney, liver, skin, bones and teeth etc. The development of artificial chemosensor for sensing significant ions, particularly toxic metal ions and anions has presently professed to initiate a colossal enthusiasm for chemical and ecological research. There is constantly a requirement for new, sensitive and improved methods for the detection of certain transition, post transition, toxic metal ions and anions those have significant effects on humans or animals.

At this juncture, the author is to explore a novel series of self designed/synthesized molecules with various denticity and characterization by utilizing various spectroscopic techniques such as NMR and Mass and afterward their potential applications as ions sensing system. In this aspect, the present works have designed with library of chemosensor probes in order to develop chemosensors for effective identification of some biologically and environmentally significant metal ions and anions.

The whole thesis comprises of seven chapters as.

Chapter I gives general introduction and an overview of chemosensors, its types and their necessity. It explains about the different signalling mechanisms associated with the chemosensors and their significance of recognizing for the metal ions and anions as analytes. This section also highlights importance and objectives of the present investigation.

Chapter II gives a brief description of the principles of various methods followed for the entire work. It consists of the name of materials, reagents, and solvents and instruments utilized.

Chapter III: Development of colorimetric and turn-on fluorescence sensor for the detection of Al^{3+} and F^- ions

A new probe, *(E)-1-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)naphthalen-2-ol* (NAATD) is designed for naked-eye colorimetric and turn-on fluorescence chemosensor. The probe NAATD exhibits higher selectivity and sensitivity towards Al^{3+}/F^- ions over other competitive ions in DMSO. The detection limits are found to be 3.14 nM (Al^{3+}) and 9.9 nM (F^-) respectively. The sensing mechanism and stoichiometric ratio are investigated and affirmed by DFT calculations and Job's plot analysis, respectively. The DNA tracking ability of the NAATD-Al^{3+} is investigated by fluorescence technique which indicates that DNA efficiently bind with the probe NAATD and effectively displace the Al^{3+} ions. Further, NAATD practical utilities are successfully demonstrated in environmental applications.

Chapter IV: Turn-on fluorescent sensor for the detection of Al^{3+} ions by a new simple Schiff base probe

A newly designed (*E)-1-(((2-(phenylthio)phenyl)imino)methyl)naphthalen-2-ol* (NAPTA) as efficient chemosensor is synthesized and characterized by using various spectroscopic techniques like ^{1}H, ^{13}C NMR and ESI-MS. The probe NAPTA exhibits highly selective and sensitive towards Al^{3+} ions over the contending metal cations. The 1:1 binding interaction of NAPTA with Al^{3+} has been revealed by Job's plot analysis. The detection limit is calculated to be 13x 10^{-7} M which is very lower level than the permitted value. The DFT calculations have been supported to the proposed mechanism as CHEF and ICT from the obtained spectroscopic data.

Chapter V: Hydrazone based dual – responsive colorimetric and ratiometric chemosensor for the detection of Cu^{2+}/F^{-} ions: DNA tracking, practical performance in environmental samples and tooth paste

In this chapter, a new dual responsive colorimetric, ratiometric chemosensor has been developed with a probe bearing hydrazone moiety for the detection of copper and fluoride ions. These detections are possible with very high selectivity and sensitivity due to facile color changes from pale yellow to yellowish green for copper ions and pale yellow to yellowish brown for fluoride ions. The detection limits for Cu^{2+} (5.8 μM) and for F^{-} (0.025 μM) are observed. The colorimetric recognition has been confirmed by various techniques like NMR, HR-MS, UV-Vis, cyclic voltammetry, differential pulse voltammetry. The DNA tracking ability of the NAPCBH-Cu^{2+} has been investigated by absorption and cyclic voltammetry techniques. All the spectroscopic results are significantly substantiated by the

theoretical calculations. The NAPCBH is found to be regenerated readily with HCl, thus showing its feasibility to be utilized as a re-usable sensor for the convenient detection of Cu^{2+} and F^- ions. The UV-Vis experiments confirm the NAPCBH feasibility and quantitatively determine the Copper and fluoride ions in environmental and toothpaste samples.

Chapter VI: Detection of Pb^{2+}/F^- ions using thiophene based hydrazone ratiometric sensor

In this chapter, a novel ratiometric and visual recognition of Pb^{2+} and F^- ions are developed by utilizing a simple probe bearing naphthalene hydrazone. The color changes works between the interaction of NAPABTH and Pb^{2+}/F^- ions from pale yellow to pink/ pale yellow to dark yellow. The detection limits are found to be very lower level for both Pb^{2+}/F^- ions are to be 1.06 ppm/3.72 nM. This visual detection of Pb^{2+}/F^- ions with satisfactory outcomes are obtained from NMR, Mass, UV-Vis spectroscopy and DFT studies. The sensing mechanism and stoichiometric ratio are explained and confirmed through DFT, Job's plot analysis. This method could offer a new strategy for the forthcoming detection with rapid sensitivity, selectivity.

Chapter VII: Pyrene-thiadiazole based chemosensor probe for the fluorescence turn-on recognition of Pb^{2+} ions

In this chapter, a highly sensitive and selective chemosensor *(Z)-5-((pyren-1-ylmethylene)amino)-1,3,4 -thiadiazole-2-thiol* (PCAT), is synthesized and characterized by ^1H, ^{13}C NMR, ESI-MS. The probe PCAT shows color changes from colorless to pink which can be seen through naked-eye and turn-on fluorescence response towards Pb^{2+} ions over the various metal cations. The stoichiometric ratio is found to be 1:1 from Job's plot analysis.

The detection limit of PCAT-Pb^{2+} ions is found to be7.15×10^{-8} M. Besides, the real sample analysis has been done with the environmental water samples and resulted with an excellent recovery percentage.

Summary

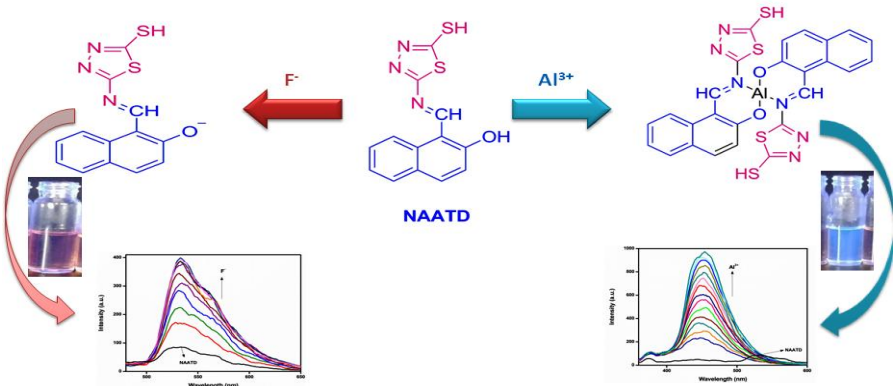
With these highlights of all of the entire research observations are turn out to be pretty important towards biologically active relevant analytes. The probe is based on the moieties like naphthalene and pyrene has been synthesized and analyzed with the diverse metal cations and anions selectively with the experimental evidences. This gives a wider vision to the scientific networks for the forthcoming detection of metal ions and anions from simple organic molecule as sensor with ease of synthesis, high selective and sensitive.

Conclusions

- A new series of Schiff base derivatives have been synthesized from naphthalene and pyrene aldehydes via simple synthetic process that might act as a receptor or chemosensor for specific and selective recognition of metal ions and anions.
- All the synthesized molecules formation has been endorsed through various spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR and LC/HR-MS.
- A diverse fluorescence and colorimetric sensor applications has been achieved for the detection of cations and anions like Al^{3+}, Cu^{2+}, Pb^{2+} and F^{-} ions.
- The binding stoichiometry and binding constants have also been done using the spectroscopic results.
- The different mechanistic pathways have been proposed based on the results obtained and affirmed through Jobs plot and DFT analysis.

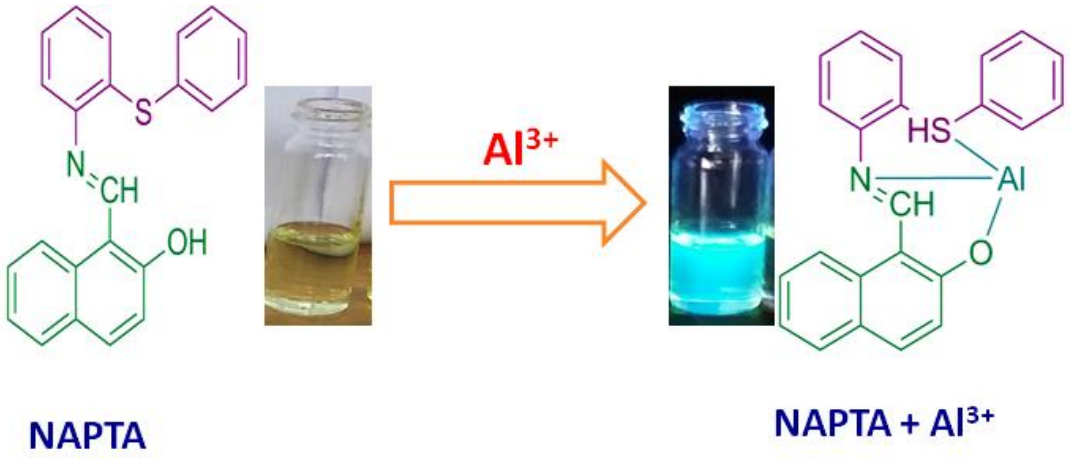
- The experimental data of real sample applications of the chemosensors using environmental water samples and commercially available tooth paste samples are presented and discussed.
- DNA tracking efficiency are also investigated successfully.

Graphical Abstract:

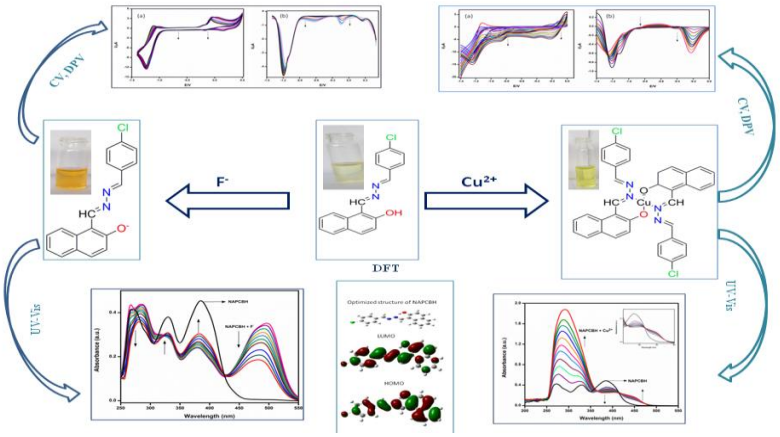


Graphical diagram for the development of Al^{3+}/F^- ions using NAATD (Chapter –III)

(This work is in revision in Chemistry Select, Wiley)



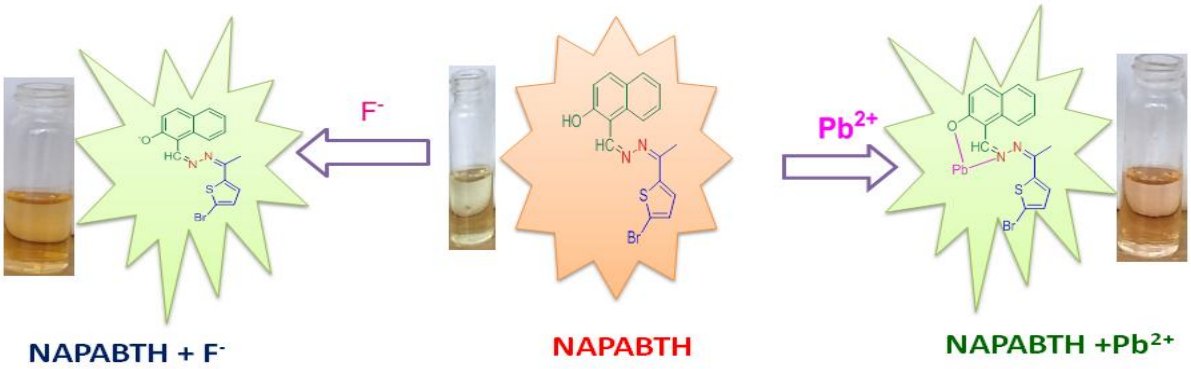
Pictorial representation for the development of Al^{3+} ions using NAPTA (Chapter –IV)



Graphical abstract for the colorimetric sensor for Cu^{2+}/F^- ions by NAPCBH (Chapter –V)

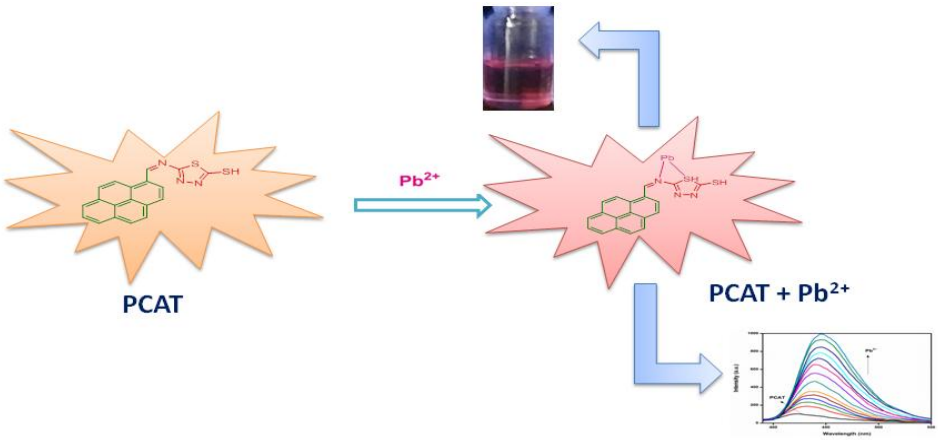
(This work was published in The Journal of Fluorescence, Springer)

(https://doi.org/10.1007/s10895-020-02488-0)



Pictorial representation of colorimetric sensor for Pb^{2+}/F^- ions by the probe NAPABTH

(Chapter –VI)



Graphical diagram for the development of Pb^{2+} fluorescence sensor (Chapter –VII)

Selected References

1 A. Gogoi and G. Das, *RSC Adv.*, 2014, **4**, 55689–55695.

2 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840.

3 P. Marimuthu and A. Ramu, *Sensors Actuators, B Chem.*, 2018, **266**, 384–391.

4 R. I. Khan, A. Ramu and K. Pitchumani, *Sensors Actuators, B Chem.*, 2018, **266**, 429–437.

5 A. Paul, S. Anbu, G. Sharma, M. L. Kuznetsov, M. F. C. Guedes Da Silva, B. Koch and A. J. L. Pombeiro, *Dalt. Trans.*, 2015, **44**, 16953–16964.

6 S. D. Hiremath, R. U. Gawas, S. C. Mascarenhas, A. Ganguly, M. Banerjee and A. Chatterjee, *New J. Chem.*, 2019, **43**, 5219–5227.

7 J. Lv, Y. Fu, G. Liu, C. Fan and S. Pu, *RSC Adv.*, 2019, **9**, 10395–10404.