Design and Synthesis of Gold Nanoparticle-Based Chemosensor for Detection of Toxic Ions Fluoride, Arsenic, Mercury, Lead and Cadmium

Funding Agency	Department of Science and Technology, Govt of West Bengal
Sanctioned Amount	Rs 14.73 Lakhs
Project Duration	Three years
Project Status	Continuing since June, 2013

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Brief Description of the Project

We have designed and synthesized a variety of fluoroionophore structures having appropriate binding moieties for F^-, Cu^{2+}, Sn^{2+}, S^{2-}, Pd^{2+} ions etc and thus know their properties in solution and in solid phase by NMR, X-ray study as well as live cell imaging study also reported with five international publications. Some fluorescent receptors have also been designed and synthesized for their potential use in aqueous media and also in organic solvents, both are of importance as chemical and biochemical reactions happen in both the media. Also water is the predominant solvent of choice in biological system and probably the most environment-friendly green solvent for future reactions and thus molecular recognition induced reactions in water are of our on-going interest.

Keywords: Fluoroionophore, toxic ions, selectivity, aqueous medium, Density Functional Theory,

Methodologies/Approaches Adopted

1. Design of a variety of synthetic fluoroionophores which serve to maximize the binding interactions towards one particular analyte over other competing ones.
2. Introduction of reactive centre(s) into the binding site of the fluoroionophore; the resulting fluoroionophore probes that sense analytes through optical signal, which is useful for achieving higher selectivity of analyte than supramolecular approach.
3. Application of these sensors in biological and environmental fields.

Project Highlights

This project is related to the design and synthesis of chemosensors and/or chemodosimeters whose performance as analytical detection tools is evaluated by various methods most notable among which is spectrophotometry. To this end we have produced many new molecules targeted towards the detection of various analytes of biological and environmental importance such as toxic analyte such as fluoride, sulphide, copper, tin and palladium. All these substances are essential as well as undesirable depending on their concentrations in a given medium. Tight control of concentration is thus indispensable for the unimpeded running of various biological and environmental processes. The designed sensors show appreciable selectivity and concomitant decisive changes under the influence of electromagnetic radiation in the UV-Vis range of the spectrum. Fluorescence studies have also cemented their efficiency in the field of analyte detection. Finally, economical syntheses using simple, easily available starting materials and impressively low detection limits render our work important to the scientific community at large.

Project Achievements

Design and Synthesis of BODIPY-azaindole fluoroionophore for F⁻ detection:

A new BODIPY-azaindole based fluorescent chemosensor 1 was rationally designed and synthesized as new colorimetric and ratiometric fluorescent chemosensors for fluoride. The binding and sensing abilities of chemosensor 1 toward various anions have been studied by absorption, emission and 1H NMR titrations spectroscopies. Inspection of spectral responses of 1 to fluoride in acetonitrile–water has been observed: an approximately 69 nm red shift in absorption and ratiometric fluorescent response. The striking light yellow to deep brown color change in ambient light and green to blue emission color change are thought to be due to the deprotonation of the indole moiety of the azaindole fluorophore. From the changes in the absorption, fluorescence, and 1H NMR titration spectra, proton-transfer mechanisms have been deduced. Density function theory and time-dependent density function theory calculations were conducted to rationalize the optical response of the sensor. Results were supported by confocal fluorescence imaging and MTT assay of live cells.

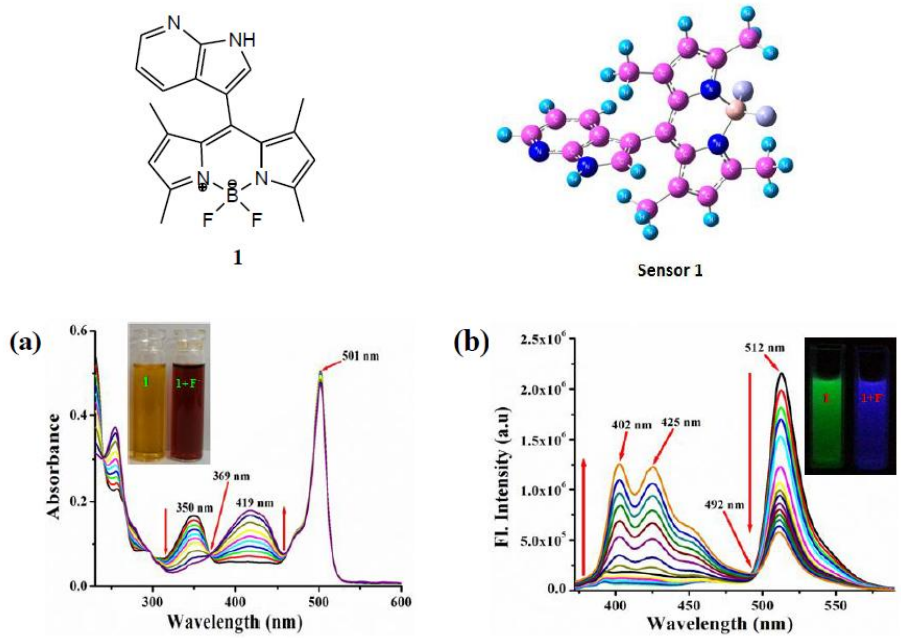


Fig.1:(a) Changes in the UV/vis absorption spectra of cmemosensor 1 (4.5 μM) in 7:3 CH3CN : H2O solution (HEPES buffer, pH 7.2) in the presence of F− anions only (0 – 20 equiv) (b) Fluorescence spectra (excitation at 350 nm) of sensor 1 (4.5 μM) in 7:3 CH3CN:H2O solution (HEPES buffer, pH 7.2) in the presence of 0–200 equiv. of F−

Pyrene thiazole-conjugate as ratiometric chemosensor for sensing of highly toxic tin (Sn4+) and sulphide ions:

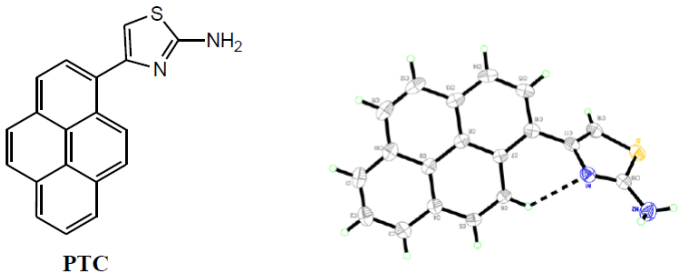


Fig. 2:ORTEP diagram of single crystal XRD structure of PTC at 50% ellipsoid probability.

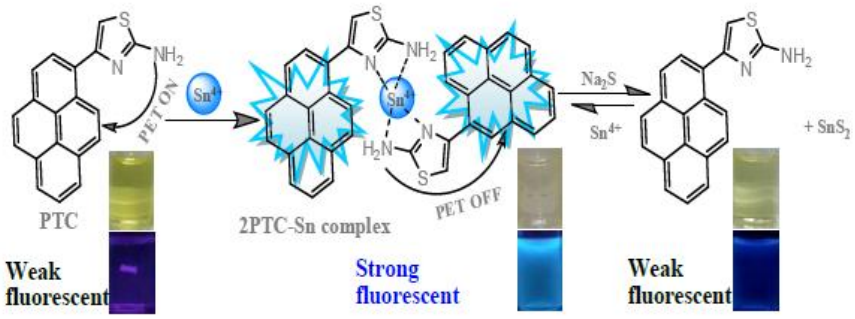
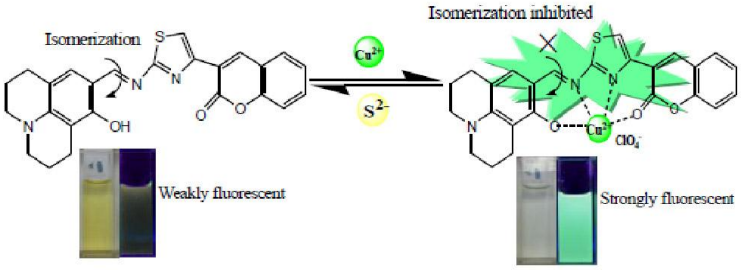


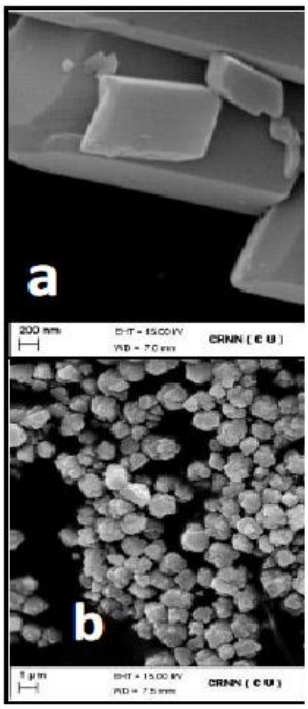
Fig. 3: Schematic presentation showing the possible binding mechanism of PTC with Sn^{4+}.

A new selective chromogenic and turn-on fluorogenic chemosensor for Copper (II) and Sulphide ions:



Scheme: Proposed Mechanism for Fluorescence changes of **L** upon Cu^{2+} (Left Side)

Fig. 4: (a) Monolayer SEM image of L and (b) SEM image of L- Cu^{2+} complex (Right Side)



Publications

1. Ratiometric sensing of fluoride and acetate anions based on a BODIPY-azaindole platform and its application to living cell imaging. Ajit Kumar Mahapatra, Rajkishor Maji, Kalipada Maiti , Susanta Sekhar Adhikari, Chitrangada Das Mukhopadhyay and Debasish Mandal. Analyst, 2014, 139, 309-317.
2. A pyrene thiazole conjugate as a ratiometric chemosensor with high selectivity and sensitivity for tin (Sn4+) and its application in imaging live cells. Ajit Kumar Mahapatra, Sanchita Mondal, Kalipada Maiti, Saikat Kumar Manna, Rajkishor Maji, Debasish Mandal, Sukhendu Mandal, Shyamaprosad Goswami, Ching Kheng Quah and Hoong-Kun Fun. RSC Advances, 2014, 4, 56605-56614
3. A new selective chromogenic and turn-on fluorogenic probe for copper (II) in solution and vero cells: recognition of sulphide by [CuL]. Ajit Kumar Mahapatra, Sanchita Mondal, Saikat Kumar Manna, Kalipada Maiti, Rajkishor Maji,Md. Raihan Uddin, Sukhendu Mandal, Deblina Sarkar, Tapan Kumar Mondal and Dilip Kumar Maiti. Dalton Transactions 2015, 44, 6490-6501

4. An azodye–rhodamine-based fluorescent and colorimetric probe specific for the detection of Pd2+ in aqueous ethanolic solution: synthesis, XRD characterization, computational studies and imaging in live cells. Ajit Kumar Mahapatra, Saikat Kumar Manna,a Kalipada Maiti, Sanchita Mondal, Rajkishor Maji, Debasish Mandal, Sukhendu Mandal, Md. Raihan Uddin, Shyamaprosad Goswami, Ching Kheng Quah and Hoong-Kun Fun. Analyst, 2015, 140, 1229–1236
5. Colorimetric and ratiometric fluorescent chemosensor for fluoride ions based on phenanthroimidazole (PI): spectroscopic, NMR and density functional studies. Ajit Kumar Mahapatra, Parthasarathi Karmakar, Jagannath Roy, Srimanta Manna, Kalipada Maiti, Prithidipa Sahoo and Debasish Mandal. RSC Advances, 2015, 5, 37935–37942

Facilities Developed

1. Shimadzu- UV-vis spectrophotometer

Project Staff

Mr. Kalipada Maiti, M.Sc., JRF; Ms. Sanchita Mondal, M.Sc., JRF

Plan of Future Project Proposal based on the Current Project

Our future plan involves synthesis of more chemosensors and chemodosimeters that will be of significance in the sensing of environmentally and biologically significant analytes. We are aiming for lower detection limits and higher excitation wavelengths preferably in the near infra red region for greater cell penetrability with minimal damage.

Key concepts behind future Project proposals: i) Attachment of synthesized sensing species to polymeric thin films for portable sensing kits; ii) Sensing within micellar cavities; iii) In vivo application of sensing systems