

Abstract

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Title of Thesis: Use of absorption and fluorescence spectroscopic techniques for different applications by the newly designed chemosensors.

Our main objective of the research is to explore a special type of molecules who may be excited by absorbing light of definite energy and the excited species may change their emission or mechanical characteristics (structural isomerization, photoisomerization, rotation, cleavage, radical formation etc.) by interacting with specific ions/molecules intricately and can selectively, specifically and sensitively identify the analyte. The Schiff bases (-C=N-) and azo (-N=N-) functions have received much attention in this direction due to their ease of synthesis and structural characterization, use of environmentally benign molecules like, aldehydes/ketones and amines appended with fluorogenic or chromophoric moiety. The Schiff bases are a group of compounds having exocyclic C=N bond(s). The -C=N- can act as a ligating centre and binds to M^{n+} selectively. Hence the Schiff base can act as efficient probe for the detection of several bio-relevant cations at a very low concentration (μM level). The abnormal level of various bio-relevant cations can cause serious health issue. Hence, the recognition of these cations is challenging task for researcher and this can be nicely monitored by the functionalized Schiff bases with fluorogenic moiety. Extensive efforts have been devoted for the design and development of effective chemosensor based on imine moiety (-C=N-) for the selective recognition for sensitive detection of cations. In addition, the UV assisted photochromic behavior is very interesting for researcher because this follows photo-isomerisation which leads to change in various physicochemical properties like refractive index, redox potential and geometrical structure. Due to these change in molecular property, the photochromism i.e. mostly photo-isomerisation can be applied to various photo-switching devices and optical memory media. Our synthesised species also exhibited UV light assisted photochromic behavior. In my research work, four probes based on Rhodamine, Coumarin, Diformylphenol and Chromone moiety, which have been characterized by different spectroscopic techniques (IR, Mass, NMR, elemental analysis) and some of the structure confirmed by Single Crystal X-Ray Diffraction measurements and Hg(II)-halide complexes of 1-alkyl-2-(*p*-nitro-phenylazo)imidazoles also characterized by Single Crystal X-Ray Diffraction measurements and it exhibited UV light assisted photochromic behavior. Benzimidazolyl-hydroxy-coumarinyl diad, serves as fluorescent turn-on Al^{3+} -sensor in acetonitrile-water (2:1, v/v) of pH, 7.2 (HEPES buffer) medium and with the addition of Al^{3+} ions the emission intensity enhanced by twelve times

Mukul Bikash Maity
30/06/2023

Bismita
30/06/2023

Professor of Chemistry
D. Department of Chemistry
Jadavpur University
Kolkata-700 032

and is detailed in **Chapter II**. The probe showed limit of detection (LOD) as $0.62 \mu\text{M}$ for Al^{3+} ions. The anti-metastatic potential of the probe on Human skin carcinoma (A431) and Human lung carcinoma (A549) cells are also examined. Another probe Rhodamine based Schiff base with two fluorogenic motifs is described in **Chapter III**. The probe has been characterized through various spectroscopic techniques. The probe exhibits efficient sensitivity and selectivity towards Al^{3+} , Cr^{3+} and Fe^{3+} ions with the enhancement of fluorescence intensity by 350 fold (Fe^{3+}), 250 fold (Al^{3+}) and 220 fold (Cr^{3+}), in methanol-water (99:1, v/v; HEPES buffer, pH, 7.2) medium. The limits of detection (LOD) are 0.0051 ppm (Fe^{3+}), 0.0029 ppm (Al^{3+}) and 0.0052 ppm (Cr^{3+}); and in addition the probe has been utilized for cell imaging in presence of Al^{3+} , Cr^{3+} and Fe^{3+} ions and the action of probe on human breast cancer cell lines and other different assay like wound healing capacity, nuclear fragmentation, Growth inhibition analysis also examined. Diformylphenol based probe is delineated in **Chapter IV** and it emits light at 610 nm upon excitation at 380 nm and the emission is strongly intensified on interacting with Zn^{2+} ion in DMSO-water (99:1, v/v; HEPES buffer, pH, 7.2) medium and also in solid state. The limit of detection of Zn^{2+} , $0.30 \mu\text{M}$ and the binding constant (K_d) is $4.2585 \times 10^4 \text{ M}^{-1}$. The Intracellular Zn^{2+} ions in living cells of HEK293 have also been identified by the probe using fluorescence microscopic imaging technique. Impact of light on the probe does not only excite to execute emission but also does some mechanical performance like structural isomerization such as trans(E)-cis(Z) isomerization of 1-alkyl-2-(aryloxy)imidazoles and their Hg(II) complex which is known as photochromism. **Chapter V** describes the effect of light irradiation on Hg(II)-halide complexes of 1-alkyl-2-(p-nitro-phenylazo)imidazoles. They have been characterized and the structures have been confirmed by single crystal X-ray diffraction. UV light assisted photochromic behaviour of ligands and the complexes are checked. The rate and quantum yield of E-to-Z isomerisation of the complexes and free ligand also calculated by the experimental data. DFT and TD-DFT calculations also support the experimental data of the rate and quantum yields. Chromone-based probe is noted in **Chapter VI** and has been used for the chromogenic selective recognition of Cu^{2+} ion in EtOH- H_2O (99:1, v/v) medium. The sensor shows excellent selectivity towards Cu^{2+} ion at very low limit of detection, $0.6 \mu\text{M}$ and the binding constant for Cu^{2+} also determined as $4.9346 \times 10^4 \text{ M}^{-1}$. The naked eye change of color of the probe upon the addition of Cu^{2+} ion is very convincing and helps to design paper kits.

From my research work, I have published a total of four original research articles and more results will be published shortly. I have attended a number of national and international conferences and have presented my research results.

Mukul Bikash Maity
30/06/2023

Bismita
30/06/2023

Professor of Chemistry
D-partment of Chemistry
Jadavpur University
Kolkata-700 032