Summary
Chapter-I Introduction

This chapter deals with the impression of optical chemosensors, necessity of chemosensors and the theory of fluorescence. Sensors that are developed based on different signaling mechanism such as photo-induced electron transfer (PET), intramolecular charge transfer (ICT), twisted intramolecular charge transfer (TICT), fluorescence resonance energy transfer (FRET), and monomer/excimer formation, Aggregation induced emission (AIE), exited state intramolecular proton transfer (ESIPT) and C=N isomerization has been revisited in the thesis. The small molecule based fluorophore (coumarin, rhodamine, anthracene, pyrene, fluorescein, bodipy) containing sensors and their importance in sensing metal ions, anions and neutral analytes are discussed. This section also describes various compounds used in the sensor design and their applications in live cell imaging.

Chapter-II Materials and Methods

This chapter deals with materials, methods, techniques and software employed at various stages of investigation.

Chapter-III Hg$^{2+}$ mediated quinazoline ensemble for highly selective recognition of Cysteine.

In Chapter-III, a fluorimetric sensor for Hg$^{2+}$ ion and Cysteine based on quinazoline platform has been designed and synthesized by one step reaction. It was characterized by using common spectroscopic methods. Time Dependent Density Functional Theory calculation shows that probe behaves as “ON-OFF” fluorescent quenching sensor for Hg$^{2+}$ via electron transfer/heavy atom effect. Receptor has been found to exhibit selective fluorescence quenching behaviour over the other competitive metal ions, and also the receptor-Hg$^{2+}$ ensemble act as an efficient “OFF-ON” sensor for Cysteine. Moreover this sensor
has also been successfully applied to detection for Hg$^{2+}$ in natural water samples with good recovery.

**Chapter-IV Quinazoline Copper(II) ensemble as turn-on fluorescence sensor for Cysteine and Chemodosimeter for NO.**

In Chapter-IV, a fluorescent quinazoline based chemosensor $3$-$((2$-hydroxynaphthalen$\-1$-$y$l) methylene) amino)$-2$-thioxo-$2$, $3$-dihydroquinazolin$\-4$(1H)-one ($QHYN$) had been designed and synthesized. It exhibits high sensitivity and selectivity towards Cu$^{2+}$ over other metal ions in DMSO:$H_2O$ (1:9, v/v) at pH $= 7.4$ [HEPES buffer] by fluorescence quenching. Addition of nitric oxide to a solution of this $QHYN$.Cu$^{2+}$ restores the fluorescence. This is attributed to the reduction of the Cu$^{2+}$ center by nitric oxide to diamagnetic Cu$^+$. The fluorescence response of $QHYN$.Cu$^{2+}$ to NO is direct and specific, which is a significant improvement over commercially available small molecule-based chemodosimeter probes that are capable of detecting NO. The $QHYN$.Cu$^{2+}$ also acts as an efficient “off–on” fluorescent sensor for Cysteine with high sensitivity.

**Chapter-V Colorimetric and turn-on fluorescence detection of Ag$^+$ and Zn$^{2+}$ ion.**

In chapter V, the probes (1-$((anthracen$-9$-y$l)$-$N$-((2$-((anthracen$-9$-yl)methylene) amino)$)$-ethyl)$ disulfanyl) ethyl) methanimine ($Cysan$) and 2-$((anthracen$-9$-ylmethylene)$ amino)$)$-$N$-((2$-((anthracen$-9$-ylmethylene)$ amino)$)$-ethyl) ethan$-1$-amine ($Trian$) based on anthracene platform have been synthesised. The probes were characterized using NMR spectroscopy, UV–visible and mass spectrometry. The probes were tested for its sensing behaviour towards metal ions like Na$^+$, K$^+$, Ba$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, Al$^{3+}$, Cu$^{2+}$, Cu$^+$, Cr$^{3+}$, Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Au$^+$, Hg$^{2+}$ and Ag$^+$ in the CH$_3$CH$_2$OH:$H_2$O mixture buffered with HEPES (pH $= 7.4$) by UV–visible and fluorescent techniques. $Cysan$ and $Trian$ show
respectively high selectivity towards sensing of Ag$^{+}$ and Zn$^{2+}$ ions. Importantly fluorescence enhancement at 440 nm was observed for probes upon complexation with Ag$^{+}$/Zn$^{2+}$ ions over other metal ions. The probe Cysan has been found to be applicable for imaging intracellular Ag$^{+}$ in living cells. This fluorescence enhancement is attributable to the restriction of the C=N isomerization and the prevention of photoinduced electron transfer from nitrogen to anthracene fluorophore. These photonic studies indicate that the probes can be adopted as a selective, sensitive and reversible fluorescent chemosensor for Ag$^{+}$/Zn$^{2+}$ ions.

Chapter-VI Aminoquinoline based highly sensitive fluorescent sensor for Lead(II) and Aluminum(III) and its application in live cell imaging.

In chapter VI, a new anthracene based probe 5-((anthracen-9 ylmethylene)amino)quinolin-10-ol (ANQ) has been prepared and its sensing behaviour towards heavy metal ions such as Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, light metal Al$^{3+}$ ion, alkali, alkaline earth and transition metal ions has been tested by UV-Visible and fluorescent techniques in CH$_3$CN/H$_2$O mixture buffered with HEPES (pH =7.4). It shows very good selectivity towards Pb$^{2+}$/Al$^{3+}$ metal ions upon complexation with 10-fold/5-fold fluorescence enhancement at 429 nm. This fluorescence enhancement is attributed to the prevention of Photoinduced Electron Transfer. The photonic studies indicate that the probe can be adopted as sensitive fluorescent chemosensor for Pb$^{2+}$ and Al$^{3+}$ ions.
Chapter-VII Hydrazide based sensor for naked-eye detection and real time applications of Fluoride ions.

Chapter VII deals with a chemosensor for fluoride ion having pyrene/anthracene appended aminobenzohydrazide as platform. 2-amino-N’-(anthracen-9-ylmethylene) benzohydrazide 1 and 2-amino-N’-(pyren-1-ylmethylene) benzohydrazide 2 were designed and synthesized. The addition of fluoride ion to the receptors caused not only a dramatically observable color change from pale yellow to brown/red but also a fluorescence turn-on response for fluoride ion. $^1$H NMR studies confirmed that the ‘turn-on’ behavior arise from deprotonation of NH protons by F$^-$ ion in both 1 and 2.

Chapter-VIII Pyrazole derivative as colorimetric and fluorescent chemosensor for Cd$^{2+}$ ion.

Chapter VIII deals with a fluorescent chemosensor 5-(((2-hydroxynaphthalen-1-yl)methylene)amino)-1-phenyl-1H-pyrazole-4-carbonitrile (PYHN), which exhibits rapid colorimetric and fluorimetric response for cadmium ion over other competitive ions under mild conditions. The sensor has been synthesized easily by simple one pot condensation. On addition of Cd$^{2+}$, PYHN shows a distinct colour change from colourless to orange that is perceptible to naked eye. The new fluorescent probe exhibits a turn-on fluorescence response towards Cd$^{2+}$ under physiological conditions with high sensitivity and selectivity.