Chapter I

General Introduction

The present thesis especially focuses on understanding the interaction between the target analyte and chemosensors to design and develop efficient chemosensors for the detection and quantification of various biologically and environmentally vital target analytes. In this context, various target analytes, optical chemosensors, some photophysical properties, several traditional signaling mechanisms based on various photophysical processes, and DFT are discussed briefly. Finally, the literature survey, aim, and objective of the present thesis work are highlighted at the end of the chapter.

1.1. Target analyte

An analyte is a substance or chemical species examined or analyzed by applying a scientific or analytical technique to a sample. It may be a variety of substances, such as elements, molecules, compounds, or ions. An environmental pollutant is an example of analyte. The term "target analyte" describes particular analytes that are the main focus of an investigation or assay. Scientists are trying to accurately detect, quantify, or investigate the target analytes from the assembly of other analytes. There are many ionic and neutral species in living things and environments, as the presence of these species (such as Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, iron, Zn^{2+}, Cu^{2+}, Ag^{+}, F^{-}, AcO^{-}, I^{-}, amino acids, etc.) in right quantities plays a vital role in biological and environmental systems, their overconsumption or deficiency also causes adverse effects on the environment and human body. Heavy metals like Cd^{2+}, Hg^{2+}, Pb^{2+}, As^{3+}, etc., are not considered beneficial heavy biometal ions, but their presence in the environment and the human body is harmful. Molecules or compounds such as explosive nitroaromatic compounds (e.g., picric acid), organophosphate-based nerve agents, or warfare agents (e.g., sarin) are environmental contaminants that are dangerous for the environment and humans. These are all target analytes. To monitor the target analytes, selective identifications, and their concentration estimation are crucial and urgent to the researchers. A brief discussion on several essential target analytes has been done here.

1.1.1. Metal ions

The most prevalent metals, such as sodium, magnesium, potassium, and calcium, have crucial functions in biological systems. They are essential in metabolism, the regulation of osmotic pressure, and as a hormonal messenger. Also, calcium is vital in developing and maintaining healthy bones and teeth. It is known to all that the occurrence of aluminum in our Earth's crust is highest as metal, yet it is a non-essential metal for biological systems. Currently, the use of aluminum is extensively increasing in different application fields such as construction work, transportation, and making for electrical devices, containers, packing materials, drugs, paints, household items, etc[1,2]. Also, Al^{3+} ions significantly function in some biochemical reactions, e.g., biotechnological transformation[3], enzyme-catalyzed reactions[4], etc. Although aluminum is

a non-essential element in the human body, excessive consumption harms health and leads to anemia, Parkinson's disease, Alzheimer's disease, osteomalacia, and osteoporosis[5–8]. In addition, high levels of aluminum in water and soil are dangerous to aquatic plants and animals [9].

Vanadium, chromium, iron, nickel, zinc, copper, molybdenum, and tungsten are essential micronutrients in biology and are necessary for life[10]. Iron is a vital and most common transition element and is necessary for oxygen transport and cellular metabolisms. Overconsumption of iron can lead to the dysfunction of various organs, including the heart, pancreas, and liver, and its deficiency results in anemia. Zinc participates in several crucial biological processes, including enzyme control, in synthesizing DNA and protein. The excess consumption of zinc can cause apoptosis, diabetes, etc, while zinc deficiency can delay puberty, slow down growth, and cause diarrhea.

Similarly, metal ions such as Cu^{2+}, Mo^{2+}, Co^{2+}, Cr^{3+}, Ni^{2+}, and W^{2+} are occasionally utilized by groups of organisms. The antibacterial abilities of silver are well known, and it also has been used in electronic devices, photography[11–13], and jewelry. Prolonged exposure to silver leads to argyria and other health problems such as skin rash, weariness, headache, or more severe problems[14,15]. On the other hand, metal ions such as Hg^{2+}, Cd^{2+}, Pb^{2+}, etc., are not usually considered to be beneficial heavy biometal ions. If the heavy metal ions enter the human body via water and food, several health issues, such as neurological, renal, and digestive illnesses, are seen[16–18].

1.1.2. Anions

Like these many metal ions, anions such as AcO^-, I^-, F^-, Cl^-, HSO_4^-, S^{2-}, etc., are essential to biological and environmental systems. Fluoride ions have an important role in preventing dental caries and in the treatment of osteoporosis; hence, they are often found in toothpaste, toothpowder, tea, food, drinking water, pharmaceuticals, etc.[19]. However, drinking water with fluoride levels exceeding 2 mg/L may lead to serious health issues for people, including thyroid disease, dental fluorosis, bone cancer, and fragility of the bones[20]. Fluoride is frequently employed in the production of fluorinated pesticides as well as the production of ceramics, steel, and aluminum. Soil and water polluted by fluoride coming from industry lead to a lower rate of plant development and yield, and fluoride contamination also affects wildlife. Sodium salts of acetate are applied in various food products, such as poultry, meat, and fish, to inhibit microbiological development and lengthen shelf life[21,22]. AcO^- (acetate ion) plays a more significant role in living organisms as an acetyl-coenzyme. Iodine is a crucial non-metal that exists on Earth. It is a necessary mineral for our bodies as it has a significant role in growth and development during pregnancy and early childhood, especially in the production and function of thyroid hormone from the thyroid gland[23]. Excess intake or lack of iodine results in thyroid malfunction and mental retardation[24]. The elemental forms of iodine are used for the production of pharmaceuticals, dyes, and many other applications[25]. Anion, like cyanide, is used

extensively in various industrial fields, such as the synthesis of pharmaceuticals, metallurgy, gold-silver mining, electroplating, and polymer synthesis[26–28]. Cyanides enter the environment from industrial waste. Cyanogenic glycoside-containing vegetables can also cause cyanide poisoning in both humans and animals. Animals absorb cyanides via the skin, lungs, or digestive systems. Cyanide is a highly toxic species for the human body because it suppresses the process of cellular respiration by binding with cytochrome c oxidase. Moreover, even a minute quantity of cyanide can lead to illnesses in the cardiovascular, endocrine, visual, vascular, central nervous, and metabolic systems.

1.1.3. Molecules or compounds

(a) Nitroaromatic compounds: These substances have an aromatic ring connected to at least one nitro group (-NO_2). Most nitroaromatic compounds (NACs) are synthesized in industry and few produced by biological processes have been found. They are utilized as solvents for manufacturing polymers, dyes, and plastics or have applications in synthesizing bioactive compounds of pesticides, insecticides, pharmaceuticals, etc. Fuel combustion in power stations and automobiles also produces these types of compounds. They are carcinogenic solid or poisonous substances, and their toxicity, carcinogenicity, and metabolic routes in living things have all been studied.

Nitro-aromatic compounds such as 2,4,6-trinitro phenol (TNP), 2,4-dinitro toluene (DNT), and 2,4,6-trinitro toluene (TNT) are mainly applied as explosives. Such explosives are regarded as environmental pollutants and are dangerous for living things. Even picric acid (TNP) is more explosive than TNT. Apart from its use as an explosive, picric acid (PA) is essential in medicines, chemical laboratories, and dye industries[29,30]. Due to its high solubility in aqueous medium and various uses in different areas, it is quickly dispersed into groundwater, aquatic systems, soil, and air as a contaminant. Consumption of PA over 10^{-6} µg/L is dangerous to human health. It creates irritation in the skin or eye and causes kidney problems, anemia, and damage to different organs related to the respiratory system. The design and development of effective optical chemosensors for the detection of PA and other NACs at deficient concentrations is an exciting research area for checking pollution in the environment and stopping terrorist intimidation[31].

(b) Organophosphate compounds: The organophosphorus compounds (OPCs) are employed as agricultural pesticides. Prolonged exposure to organophosphorus-based pesticides causes several difficulties, such as neuropsychiatric problems, cognitive dysfunction, and immediate myocardial damage in farmers. Bioaccumulation of some pesticides also occurs in the environment. This bioaccumulation is harmful to birds like vultures and it causes an adverse impact on aquatic life like Soleasenegalensis and Senegalese sole. Organophosphate-based nerve agents (soman, sarin, tabun, cyclosarin, and Novichok series of compounds) are applied as arms of mass destruction in war as Chemical warfare agents (CWAs) and in terrorist attacks,

for example, the application of sarin gas in recent Syrian civil war and the terrorist attack in Tokyo subway, 1995.

They are highly poisonous to animals and humans because the nerve agents can hamper the pathways through which nerves communicate with organs. They block the hydrolysis of neurotransmitter acetylcholine through their irreversible bindings with acetylcholinesterase. So, a more significant amount of acetylcholine than usual becomes accumulated in cholinergic synapses, and it results in abrupt organ failure, neuromuscular paralysis, an obstruction of muscle relaxation, and death [32–34].

(c) Amino acids: The term "alpha-amino acid" refers to an organic molecule in which two functional groups, essential amino (-NH_2) and acidic carboxyl (-COOH) groups, are generally linked by one chiral carbon atom that has an organic residue[35]. Polymer or an extended change of amino acids forms protein molecules. These amino acids are vital components in biological processes. For example, a proper quantity of lysine is required for animal metabolism and weight gain[36]. Tryptophan has a significant role in biological systems, such as in the biosynthesis of protein, the growth of animals, and the development of plants. Histidine is necessary for the repair and development of tissue and the regulation of the transfer of metal elements in biological bases[37]. Alpha amino acids and their derivatives are usually present in biofluids in the concentration range varying from micromolar (μM) to millimolar (mM). The change in the relative amount of amino acids is associated with and/or indicative of several illnesses[38–40]. For this purpose, a few examples have been given here. When phenylalanine, an alpha amino acid, is present in our body in abnormal concentrations, it leads to Phenylketonuria disease in our body[41]. Several diseases, including aging-related illnesses, inflammatory bowel disorders, neurological problems, ophthalmic diseases, and atopic dermatitis, are linked to abnormal concentrations of histidine as well as its metabolism[42]. An imbalance of the concentration of cysteine in our body can also cause several illnesses, including liver disease, slowed growth, cardiovascular illnesses, cancer, Alzheimer's disease, etc. So, alpha amino acids are significant target analytes in biofluids. Their identification and estimation of concentration in biofluids and water-based medium is essential in molecular diagnostics.

1.2. Chemosensor

Qualitative and quantitative estimation of these target analytes is vital in many areas, such as environmental monitoring, biological system monitoring, forensic science, food safety, pharmaceutical analysis, etc. The design and development of some analytical tools are essential for identifying and measuring the concentration of target analytes and understanding the interaction with target analytes and other necessary parameters. An optical chemosensor sensor is a suitable example of such type of tool.

A chemosensor is a tool (such as a pH electrode) or molecule (such as methylene blue or bromothymol) that can recognize the presence of specific chemical species in its environment and produce a measurable signal as a response.

Most chemosensors usually have three key components: (i) a receptor subunit, (ii) a spacer or transducer, and (iii) a signal subunit (**Figure 1.1**).

Receptor subunit: This component of the sensor generates a response signal by selective binding with a target analyte.

Signaling subunit: Reporting of the binding event is done by this subunit of a chemosensor.

Transducer: The above two subunits may be joined to each other directly or by a spacer. The transducer of a chemosensor functions as an active component whose characteristics are altered when a receptor and an analyte interact with each other, and ultimately, a spacer causes geometrical changes in the system and adjusts the electrical interaction between the two previously mentioned moieties[43]. According to the transducer's basic working principle, there are generally four types of chemosensors: electrochemical, optical, heat-sensitive, and mass-sensitive sensors. Here, only optical chemosensors among four types of chemosensors are discussed briefly.

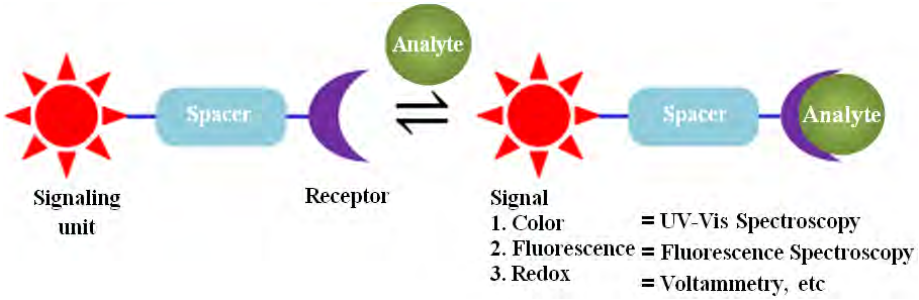

Figure 1.1. Schematic presentation of chemosensor.

1.2.1. Optical chemosensor

Optical sensors, a subclass of chemosensors, provide signals to recognize target analytes using electromagnetic radiation from Ultraviolet to near-IR region and are based on various visual principles (absorbance, reflectance, luminescence, fluorescence). They can measure light intensity as well as different optical parameters like fluorescence lifetime, refractive index, scattering, etc. Generally, they involve interacting with the target analytes by their recognized moiety containing a chromophore or fluorophore that changes the sensors' optical properties (absorbance or fluorescence). The receptor molecule may be an artificial or natural substance that interacts chemically with the target analyte to bind to it specifically through electrostatic interactions, hydrogen bonds, or van der Waals forces. So, optical chemosensors are a powerful tool for identifying and quantifying the concentration of target analytes and for understanding the interaction of sensors with the target analytes. The optical chemosensors have been divided into (a) Colorimetric chemosensors and (b) Fluorescent chemosensors.

(a) Colorimetric chemosensor: The development and design of colorimetric chemosensors for the detection of specific chemical components (ions or neutral molecules) that are significant from the viewpoint of biology and the environment are essential areas for sensing research. A colorimetric chemosensor is commonly defined as a color change that occurs by binding

between the recognition moiety of the sensor and a target analyte. The signaling moiety of colorimetric chemosensors displays a color change when the recognized moiety interacts with a specific target analyte. Colorimetric chemosensors typically function by absorbing UV-visible parts from electromagnetic radiation, and a variety of photoactive species (e.g., rhodamine, coumarin moiety) can be attached to sensors to detect a target analyte[44]. Several advantages of the use of Colorimetric chemosensors are mentioned here.

(i) Visual detection: Colorimetric chemosensors offer a visual indication of the presence or concentration of a target analyte, and color change is frequently observed by the naked eye.

(ii) Rapid response: Colorimetric chemosensors can provide fast response times and real-time monitoring and detect target analytes promptly. The colorimetric change takes place within minutes or even seconds, offering rapid analysis and decision-making.

(iii) Portable and low-cost: Colorimetric sensors can be made into handheld devices appropriate for portable and on-site applications at low cost, avoiding any expensive instrument.

(iv) Selectivity and sensitivity: They exhibit high selectivity and sensitivity for target analyte detection. Colorimetric sensors can detect a specific target analyte, avoiding interference from other substances by employing a variety of recognition components, such as particular chemical indications, enzymes, antibodies, etc.

(v) Versatility: A wide variety of analytes, such as gases, ions, chemicals, biological molecules, and environmental contaminants, can be detected by colorimetric sensors.

(vi) Long-term stability: Many have good long-term stability and keep their performance for long periods.

They have a variety of applications in various areas, such as medical diagnostics (monitoring of drug level in blood), industrial applications, food quality and safety, environmental sensing and monitoring, biological monitoring, etc. The presence of election withdrawing species (-COOH,-NO_2, -CHO, etc.) and election releasing species (-NH_2, -OH, -OEt, etc) in conjugated molecules generally influence the photophysical properties (absorption, shifting of wavelength, etc.) of the sensor. A charge transfer band appears due to the presence of both election-withdrawing species and election-releasing species connected through conjugation in a molecule. Two kinds of colorimetric chemosensors are (i) sensors having the D-A (donor-acceptor) system and (ii) sensors with rhodamine. They are used to understand the detection mechanism of specific analytes. EDG (election donating group) and EWG (election withdrawing group) are commonly introduced to the appropriate location on the chemosensors to design the D-A system. The capacity of the metal ion to donate electrons is reduced when it interacts with EDG. So, the D-A system is nearly changed into an A-A (acceptor- acceptor) system with decreasing conjugation.

Consequently, a blue shift in the absorption band increases the possibility of charge transfer from ligand to metal. The binding of metal ions with EDG increases the strength of the D-A system, and the possibility of charge transfer from metal to ligand increases. Consequently, there

is a red shift in absorption spectra due to the higher stability of the excited state in comparison to the ground state.

(b) Fluorescent chemosensor: It is designed to recognize and measure the concentration of target analytes. The working principle of the sensor is based on the fluorescence phenomenon. When fluorescent sensors interact with a target analyte, they assess the modification of some photophysical properties like shifting in wavelength, fluorescence intensity, fluorescence lifetime, etc. They show high selectivity and sensitivity to recognize and quantify the target analytes. They are applied as essential tools in environmental monitoring, biomedical diagnostics, and other scientific fields. A few photophysical properties related to optical chemosensors are briefly discussed below.

(i) Absorption: In UV-visible absorption, a substance absorbs light from the UV-visible region. An electronic transition occurs in the substance from a ground state to an excited state due to light absorption. Different substances can absorb light of different wavelengths.

(ii) Emission: The process through which a substance emits energy as light after absorbing energy is called emission. Emission generally occurs when electrons in a substance (molecules, atoms, or ions) descend from higher to lower energy levels.

(iii) Fluorescence lifetime (FLT): It is an essential characteristic property of the fluorescent substance. A fluorescence molecule reaches an excited state, absorbing a photon. The fluorescence lifetime (FLT) is the average time it remains excited before it emits a photon and returns to the ground state. A fluorometer or fluorescence life lime spectrometer is used to measure Fluorescence lifetime that is expressed in time units like picoseconds and nanoseconds.

(iv) Fluorescence: Fluorescence is an emission-type physical phenomenon. A substance or a molecule instantly re-emits light of a longer wavelength after absorbing light of a specific shorter wavelength. This phenomenon is known as fluorescence. Fluorescent molecules almost quickly cease glowing after just stopping the light source. Fluorescence has a wide range of applications fields. In this article, it has been utilized to detect target analytes in chemical sensing.

(v) Quantum yield: The effectiveness of the fluorescence process is determined by its quantum yield value. It is expressed as a ratio of the number of photons emitted to the number of photons absorbed in the fluorescence phenomenon. Fluorescence processes that have a higher quantum yield value are more effective.

1.3. Photophysical analysis

This analysis analyzes the photophysical properties (like absorption, excitation, emission, lifetime, quantum yield, etc.) of a substance in light. From the point of view of optical chemosensors, photophysical analysis is the modification of their photophysical properties due to the interaction of the sensor with target analytes. The changes in these properties are experimentally measured, and the estimated information analysis helps us comprehend how an

optical chemosensor interacts with target analytes. A few standard techniques used for photophysical analysis have been given below.

(i) Absorption spectroscopy: This type of spectroscopy is usually utilized to monitor the modification in the absorption spectrum of the optical chemosensor due to the interaction between the sensor and target analyte. When changes in the maxima or new bands have appeared in the absorption spectrum, it signifies that the sensor has formed a new complex with the target analyte.

(ii) Fluorescence spectroscopy: This spectroscopy is extremely sensitive. It is specially applied to measure the changes in emission wavelength, fluorescence intensity, or lifetime of the optical sensor due to its interaction with the target analyte. These modifications in photophysical properties provide some crucial data that help to understand and evaluate binding interaction, selectivity, detection mechanisms, and the sensor's detection limit for the target analyte.

(iii) Time-resolved spectroscopy: Using time-resolved fluorescence spectroscopy techniques like time-correlated single-photon counting (TCSPC), it is possible to study the kinetics of the interaction between the chemosensor and the target analyte. It can determine fluorescence lifetimes and it can provide details regarding binding kinetics, dissociation process, and formation of complex.

(iv) Fluorescence resonance energy transfer (FRET) Technique: It is another effective technique for photophysical studies. It can deliver data regarding optical proximity and binding interaction with the target analyte.

1.4. Signaling mechanisms for optical chemosensors

Several traditional signaling mechanisms based on various photophysical processes are ICT, PET, ESIPT, MLCT, FRET, TICT, AIE, excimer/exciplex formation, and C=N isomerization. The knowledge regarding the above mechanisms helps us to understand the interaction of optical chemosensors with the target analytes and the design and development of new sensors. Some of these mechanisms are briefly discussed here.

(i) Photoinduced electron transfer (PET): Photoinduced electron transfer (PET) is a process in which an election transfer takes place when a specific photoactive substance is exposed to light[45]. PET optical chemosensors are generally classified into (i) turn-on and (ii) turn-off. When this sensor, without binding with the analyte, receives energy, electrons are promoted from the fluorophore's HOMO to the LUMO state. Simultaneously, the HOMO of the higher energy level free receptor allows PET from the free receptor's HOMO to the fluorophore's HOMO. As a result, the emission transition is blocked or the fluorescence is quenched[46,47]. When the receptor (donor) binds with the target analytes, there is a rise in the redox potential of the receptor. So the energy level of the receptor's HOMO becomes lower than that of fluorophore's HOMO. Consequently, the PET process is stopped, and enhancement in fluorescence intensity occurs[48] (Fig.1). In some circumstances, the receptor participates in the photophysical process indirectly.

Suppose the energy level of LUMO of the target analyte is located between the HOMO and LUMO of the fluorophore after binding with the receptor. In that case, it provides a non-radiative route, so fluorescence intensity is quenched (**Figure 1.2**).

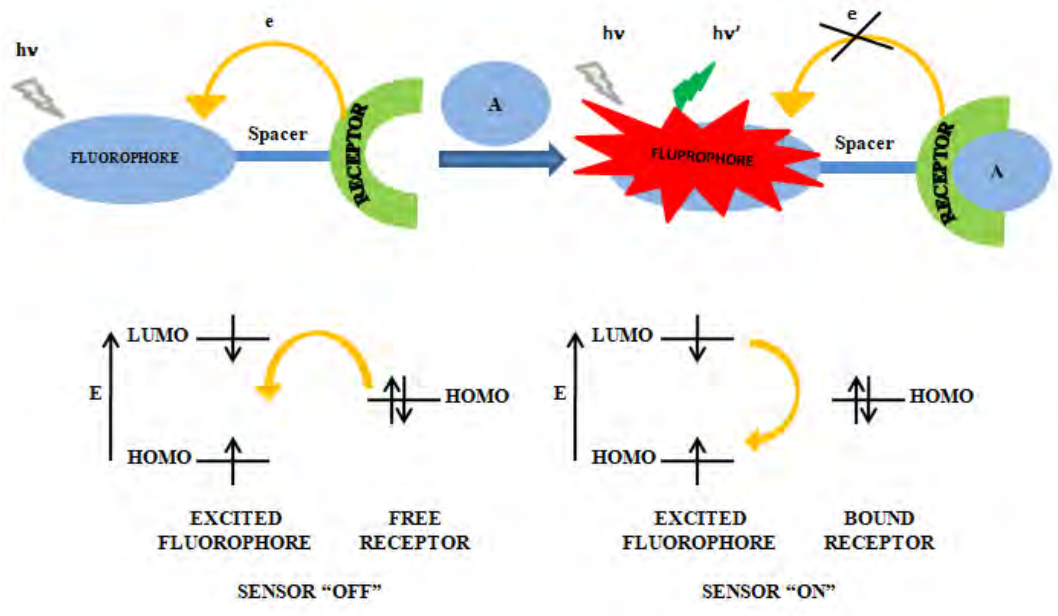

Figure 1.2. Schematic diagram of the PET process.

(ii) Intramolecular charge transfer (ICT): When the molecule becomes excited by absorbing light of a suitable wavelength, an electron density or an electron moves from one part of a molecule to another. The ICT process generally takes place in molecules where electron donating and accepting moiety are connected by a conjugated system[48].

When a cation is bounded at the site containing the electron-donating moiety of a receptor, the ability of the receptor to donate electrons is decreased. So, there occurs a decrease in conjugation, and consequently, a blue shift takes place in absorption and emission spectra. Again, when a cation is bounded at the site containing the electron acceptor moiety of the receptor, a red shift in spectra occurs (**Figure 1.3**).

By analyzing ICT mechanisms with and without an analyte, researchers can collect data regarding the strength, nature of interaction, and modification of the photophysical process of optical chemosensors. Also, incorporating proper donor and acceptor moiety with appropriate linkers in optical chemosensors helps in designing and developing the sensors that show modifications in photophysical properties on interaction with the target analytes. The changes in photophysical properties taken place by the ICT process are utilized to identify, quantify, and distinguish the target analytes.

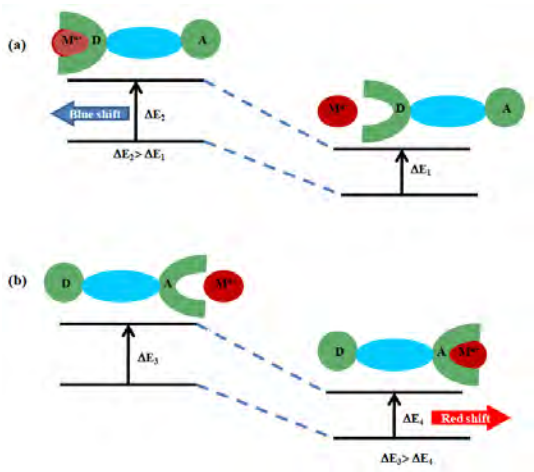

Figure 1.3. (a) Diagram for cation recognition (bounded to donor site) utilizing fluorescent ICT optical chemosensors. **(b)** Diagram for cation recognition (bounded to acceptor site) utilizing fluorescent ICT optical chemosensors.

(iii) Paramagnetic fluorescence quenching mechanism: A considerable number of metal complexes, it is observed that intersystem crossing (ISC) is formally forbidden. Still, it becomes more rapid in the complexes when paramagnetic atoms (such as Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Cr^{3+}, etc.) are present in the closeness of fluorophore. These metal ions can cause quenching in fluorescent intensity. This quenching phenomenon occurs due to strong interaction between half or partially-filled d- electrons present in metal ions of metal complexes and π-electrons present in fluorophore that favors the non-radiative ISC pathway on excitation from S1 to T1 state of the fluorophore (**Figure 1.4**).

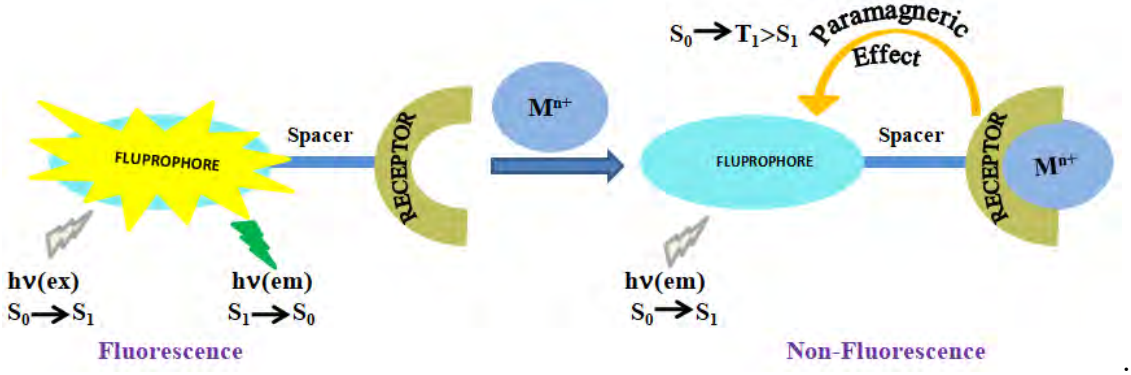

Figure 1.4. Schematic diagram showing paramagnetic fluorescence quenching.

(iv) FRET: When two fluorophores (donor, acceptor) are very close to each other, donor fluorophore at an excited state releases its excited energy that is absorbed by an acceptor fluorophore via a dipole-dipole interaction in a non-radiative pathway. The transfer of excited state energy in such a non-radiative pathway is known as FRET. Then, the acceptor fluorophore at an excited state emits a photon of a larger wavelength than the donor. FRET is utilized in energy transfer microscopy, fluorescence biosensor design, molecular imaging, etc.

A spectral overlap is essential for effective FRET between the donor fluorophore's emission spectrum and the acceptor fluorophore's absorption spectrum. The distance between two fluorophores must be from 1 nm to 10 nm. A metal ion (analyte) can influence the distance between two fluorophores in the FRET process. Both fluorophores either move away or come closer in the presence of metal ions. The binding of the metal ion with fluorophores causes a decrease in the distance between them, and consequently, there is an enhancement in the FRET process (**Figure 1.5**).

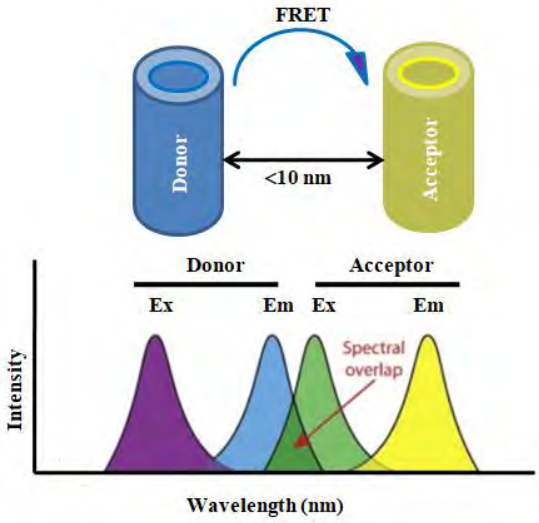

Figure 1.5. Diagram of the FRET approach.

(v) Excited-state intramolecular proton transfer (ESIPT): It is a crucial photophysical process. This process has different applications, such as light-emitting substances, fluorescent chemosensors, etc.[49–51]. The ESIPT commonly occurs in molecules with a particular configuration of functional groups (-OH, -NH, etc.) that generate intermolecular hydrogen bonding. In the process, the transfer of a proton from a proton donor (hydroxyl or amino group) to a proton acceptor (oxygen of carbonyl, nitrogen of imine group) has occurred through an intermolecular hydrogen bond within a molecule on excitation. At the ground state, inter-molecular hydrogen bonding stabilizes the enol form of the chromophore, and on excitation, this enol form changes into keto form through the ESIPT process given in (**Figure 1.6).**

In the ESIPT process, the optical chemosensor shows considerable changes in its photophysical properties (such as fluorescence intensity) related to proton transfer processes due to the binding with the target analytes. So, the sensor can identify the target analyte's presence and quantify the target analyte's concentration. ESIPT process provides a versatile platform for designing and developing optical chemosensors. By altering the molecular structure and adding suitable acceptor and donor functional groups in the sensor, it is possible to fine-tune the ESIPT process to acquire a particular sensing ability. Choosing a proper recognition unit and modifying the molecular environment is very important for designing and developing optical chemosensors with expected selectivity and sensitivity.

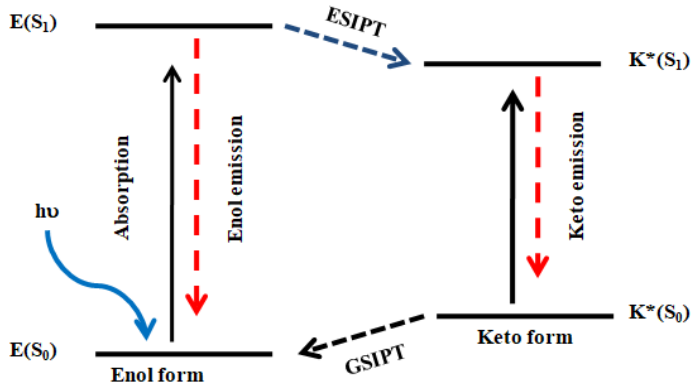

Figure 1.6. Diagram for the photophysical cycle of ESIPT.

1.5 Density functional theory (DFT): It is a computational technique. Based on DFT calculation, properties and the electronic structure of molecules can be predicted. This analysis is very important for understanding the optical chemosensor-target analyte interaction. A few ways are mentioned here where DFT analysis aids in understanding this interaction.

(i) Prediction of molecular structure: The optimal molecular structure of the target analyte and optical chemosensor can be predicted using DFT analysis. DFT aids in identifying the most stable conformations by considering steric and electronic effects and gives details on bond angles, lengths, and intramolecular distances. This information is essential to assess probable binding sites and understand the geometrical criteria for effective interaction.

(ii) Assessment of intermolecular forces: DFT analysis can predict intermolecular interactions of the optical chemosensor with target analytes. It can compute the nature and strength of these interactions, including Vander Waals forces, hydrogen bonding, π-π interactions, etc. Assessing these intermolecular forces helps to understand the driving forces behind binding between the sensor and the target analytes.

(iii) Energy analysis: Calculations based on DFT can provide data on the energy changes related to interactions between optical chemosensors and target analytes. Calculated binding energy, that is, the energy difference from the energy of the formed complex to the energy of the free optical chemosensor and the target analyte, signifies the strength of binding interactions.

(iv) Transitions and optical properties: Electronic transitions and optical features of the analyte-optical chemosensor system can be understood by DFT analysis. DFT can compute spectra (absorption and emission). A comparison between predicted spectra and experimentally obtained spectra aids in evaluating the accuracy of the DFT-based expected model and it reveals how the electrical structure and optical properties of the sensor are modified as a result of binding between the sensor and the target analytes.

(v) Understanding of mechanistic pathway: DFT analysis can predict the mechanism regarding the interaction of optical chemosensors with the target analytes. It aids in the determination of the main steps in binding, like electron transfer or proton transfer processes,

and the knowledge of the theoretically predicted mechanism is essential for the development and design of optical chemosensors.

1.6. Literature survey

International Status: The scientific community worldwide is actively engaged in developing various colorimetric and fluorometric chemosensors for detecting versatile target analytes. In this regard, the research group of Prof. Zheng-yin Yang, Lanzhou University, Lanzhou, China has developed several OFF-ON-OFF chromo-fluorogenic probes for the selective detection of various target analytes. Among all his reports, some reports titled "A simple fluorescent-colorimetric probe for selective switch-on detection of Al^{3+} in ethanol"[52] and "A chromone derivative as a colorimetric and "ON-OFF-ON" fluorescent probe for highly sensitive and selective detection of Cu^{2+} and S^{2-}"[53] are noteworthy in these regards. Prof. Cheal Kim from Seoul National University of Science and Technology, Seoul, Korea contributed significantly in the field of development of sensors for selective detection of several target analyte. His work entitled "A novel fluorescent turn-on probe based on thiosemicarbazide-naphthalene for selectively detecting Zn^{2+}"[54] and "Fluoride detection with a colorimetric and fluorescent dual-mode chemosensor" [55] have taught us how to develop chemosensor with high selectivity towards target analytes in the single molecular platform by modulating the multiple functionalities. In this regard, several reports on the development of fluoro-chromogenic chemosensors by Prof. Jong Seung Kim from Korea University, Seoul, Korea are worth mentioning for the scientific communities who are interested in developing chromo-fluorogenic chemosensors for the detection of various target analytes[56-59]. His report on fluoro and chromogenic chemo-dosimeters for heavy metal ion detection in solution and biospecimens has highly motivated us to work in this field. His reports on fluoride ions sensing Calix luminophores based on regioselective bindings[60] has inspired us to contribute more in this field. Prof. Xiaoqiang Chen's group from China has also reported several chromo-fluorogenic chemosensors to detect various target analytes[61].

National Status: The research and development on chemosensor and their application in the detection of several target analytes have attracted considerable attention from the Indian scientific community. Several groups in India investigate the selective detection of the target analyte based on various optoelectronic signaling. To mention a few, Prof. Anunay Samanta (School of Chemistry, University of Hyderabad) has contributed significantly to the field of sensory materials and their photophysical properties. His report on "A highly selective ′off-on′ fluorescence chemosensor for Cr(III)[62], has given us an understanding of the development of off-on metal ions chemosensors by tunning various photophysical properties. Scientist Vinod Kumar, Defence R & D Establishment, Gwalior, India, and his team report the development of various chromo-fluorogenic sensors for selective detection of sulfur mustard simulants and nerve agents[63-67] which is highly inspired us to work in this field. Recent work of Prof. Ghosh

and coworkers from IACS, Kolkata, also should be mentioned while discussing the multitasking molecules for versatile optoelectronic applications. His recent work based on "Multitasking Behaviour of a Small Organic Compound: Solid State Bright White-Light Emission, Mechanochromism and Ratiometric Sensing of Al(III) and Pyrophosphate"[68] has stimulated us to work further in this field. Subsequently, Prof. Misra and coworkers from Vidyasagar University, Midnapore[69-71], and Prof. Das and coworkers from IIT Guwahati[72,73] have also significantly contributed to sensing the performance of Salen-type molecules in developing various. Last but not least, one has to be mentioned here that the recent contribution of Prof. M. Sarkar from NISER, Bhubaneswar[74-76], towards understanding the various photophysical properties in designing and developing various target analytes to detect and quantify selectively. All the findings and contributions mentioned above have inspired us to work further to design and develop multitasking single, smart molecule to understand their photophysics and their sensory behavior in their solid state and solution. However, the details elucidation of mechanistic in the sensory behavior of various chromo-fluorogenic sensors with density functional theoretical analysis is very scarce to date.

1.7. Aim and objectives of the present thesis work

The main aim and objective of the present research work is to understand the interaction between the optical sensor and target analytes that help in designing and developing various efficient sensor to detect and quantify various target analytes. The main objectives of the present research work are summerized below.

- Design and synthesis of some new optical sensors in the architecture of salen types molecules.
- Investigation of details photophysical aspects in the presence of various target analytes (such as metal ions, anions, explosive nitroaromatic compounds, organophosphate-based nerve agents, etc.).
- The elucidation of sensing mechanistic aspects prevailing spectroscopic and theoretical analysis (DFT).
- Detection of various target analytes.
- Utilization of the developed sensor in diverse practical applications.

The references in my Ph.D. thesis are organized in the following format:

Author names, abbreviated journal name (in italics), year, volume number (bold), and page/article number. e.g.,

M. Rajbanshi, M. Mahato, A. Maiti, S. Ahamed and S. K. Das, *J. Photochem. Photobiol. A Chem.*, 2024, **447**, 115230.

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