Chapter 1

Introduction, Brief Objective and Impacts of the Thesis

The Greenhouse Effect

Some of the solar radiation is reflected by the atmosphere and the Earth's surface.

Some of the infrared radiation passes through the atmosphere and out into space.

Outgoing solar radiation: 100 Watts per m²

Outgoing infrared radiation: 240 Watts per m²

About half the solar radiation is absorbed by the Earth's surface.

Radiation is converted to heat energy, causing the emission of longwave (infrared) radiation back to the atmosphere.
1.1. Introduction

For decades, selective detection of heavy and transition metal ions and anions by developing various ions receptors has received considerable attention due to their indispensable role in biological and environmental processes [1-3]. Though a minute quantity of transition metals are essential for living organisms, excessive amount accumulated in human body causes permanent damage of several organisms like kidney, bones, liver, and central nervous system [4-5]. Similarly, various kinds of anions (such as $F^-$, $Cl^-$, $I^-$, $H_2PO_4^-/PO_4^{3-}$, $CH_3COO^-$ etc.) play the vital role both in environment and biological science. However, excess quantity of such anions causes several serious diseases [6-7]. Some neutral molecules, for example amino acids, proteins, carbon dioxide, sulphur dioxide etc, are also playing an important role considering the biological and environmental issues. Amino acids and proteins are directly related to living organism (e.g. DNA). Carbon dioxide is crucial substrate for the process involved in Photosystem II and for global warming. On the other hand, sulphur dioxide is used for chemical fertilizer. Therefore, recognition and sensing of cations/anions/neutral molecules by proper design of sensors/receptors are currently an expanding area of research within the field of supramolecular chemistry [8-10].

Detection of ions with the use of simple preparation of the receptor and minimal instrumental assistance is desirable towards practical applications. There is always a need for new, sensitive and improved methods for the detection of certain transition, post transition and toxic metal ions, anions and molecules that have significant threat on humans or other animals. Research endeavors, to find a suitable chemosensor for the detection of these ions/molecules, have involved innovative design principles, careful and
thorough development of synthetic strategy and most importantly their characterization using sophisticated spectroscopic and colorimetric techniques. Over the past few years, a great deal of effort has been given for the development of colorimetric and fluorescent chemosensor for the detection of toxic and other metal ions, as colorimetric and fluorometric detection is cost-effective and sensitive one [11]. Traditionally the design of 

**Scheme 1.1: Schematic diagram of Indicator-Spacer-Receptor (ISR) approach**

![Scheme 1.1](image1)

**Scheme 1.2: Schematic representation of Indicator-Displacement-Assay (IDA)**

![Scheme 1.2](image2)

chemosensor involves a chemical system which consists of a covalently bound indicator to a receptor through a linker. The indicator changes color or fluorescence characteristics once the analyte binds to it. This technique is called the Indicator-Spacer-Receptor approach (ISR, Scheme 1.1). In contrast to ISR, Indicator-Displacement-Assay (IDA, Scheme 1.2) utilizes a non-covalent interaction between a receptor (the host), indicator,
and an analyte (the guest) [12]. The host-guest chemistry based methods of designing the chemosensors have gained popularity because of conceptual simplicity, the flexibility that comes with a non-covalent interaction based system and diversity of available media in which the assay can be used. Regarding the development of colorimetric and fluorescent chemosensor, naked-eye color or UV-vis/NMR spectral change and change of fluorescence upon interaction with metal ions are rather commonly used techniques [2, 5-6, 11, 13-14]. But, UV-vis absorption spectroscopy and colorimetric naked-eye detection techniques gain comparatively faster attention than others techniques due to their simplicity, high sensitivity and cost effectiveness [11, 13-14]. Again, the development of chemosensor capable of undergoing colorimetric change and fluorescence intensity enhancement in presence of ions has always been attracting because of easier and more efficient mode of detection. The naked-eye color change or UV-vis spectral change of a receptor/sensor in presence of cations/anions is usually monitored by the charge transfer (CT) mechanism through covalent/non-covalent interaction or deprotonation [13-14]. On the other hand, change of fluorescence intensity of a receptor in presence of metal ion/anion is based on chelation enhanced fluorescence (CHEF) mechanism or charge-transfer (CT) mechanism or followed by restricted photoinduced electron transfer (PET, Scheme 1.3) reaction [5, 11, 13]. The fluorescence quenching effects are mainly due to the photoinduced electron transfer process [13].
Scheme 1.3: Simple Schematic representation of PET process in presence of anions ($A^-$, top) and cation ($M^{n+}$, bottom)

Besides the ions sensing process in the field of supramolecular chemistry, there are huge numbers of receptors/sensors which can detect neutral molecules, such as amino acids, aniline, hydrazine, TNT, carbon dioxide, etc [15-16]. Among these, CO$_2$ detection or aerial carbon dioxide fixation method has great impact in current chemical research. Because, carbon dioxide is one of the most important greenhouse gases responsible for
Chapter I
Introduction, Objective and Impacts

global warming and environmental pollution. Scientific research has been done in the past few decades for minimize the environmental pollution due to excess CO₂ in the air. Many methods have been so far developed for capturing aerial carbon dioxide to minimize the global warming [17]. Several groups have reported various porous materials consist of metal–organic frameworks (MOFs) with a remarkable CO₂ absorption capability, although most MOFs is very expensive and moisture sensitive. On the other hand, several transition metal complexes have been used to absorb carbon dioxide from air and the gaseous CO₂ is converted to bicarbonate or carbonate salts. At present, amino disiloxanes, green-MOFs, neutral organic cages, various amine solutions, aminosilicas, ionic liquids, etc. have been commonly used as efficient CO₂ absorber from the flue gases through a chemical reaction between the amines and CO₂ molecules under variable conditions [18-20]. However, the major problem of the amine–based processes is that it requires high energy to recover the amines for recycling processes as amine can easily react with carbon dioxide and forms carbamate salts. There are only few reported receptors for aerial carbon dioxide fixation, where receptors can efficiently capture aerial CO₂ and then the aerial CO₂ is converted to bicarbonate/carbonate and forms strongly H-bonded receptor-bicarbonate/carbonate complex. In some cases few of these receptors can be re-used for CO₂ fixation cycle [10, 21].

1.2. A Brief Objective of the Thesis and Achievements

Many excellent chemosensors for anion detection have been reported so far. However, they need very complicated synthetic routes or troublesome purification and isolation procedures. The recognition and sensing of cations/anions/neutral molecules by proper design of receptors with multifunctional activity and minimal instrumental
assistance are currently an expanding research area within the field of supramolecular chemistry. Our main objectives included in this thesis are to design and synthesize new sensitive chemosensors suitable for selective sensing of transition metal ions, anions and neutral molecules with minimal instrumental facility. We have followed general principle for designing the basic part of the host. For example, we have introduced the coordinating center for cations, H-bonding center for the anions and Common Organic Backbone (COBs) for neutral molecules. The sensors/receptors are mainly of two types; (i) Chromogenic and (ii) Fluorogenic. In case of chromogenic sensor/receptor we have host with donor-acceptor [like: -NR₂, -OR (R=H, Me, Et, etc.) and -NO₂, CO₂Et/Me₂, -CN, etc. in aromatic rings] functionality. This allows naked eye detection of color change or UV-vis spectral change through charge transfer (CT) process by means of covalent/non-covalent interaction. On the other hand, fluorogenic sensors/receptor involves incorporation of fluorophoric part (may be benzene, naphthalene, imidazole, etc.) into the host molecules.

We have primarily designed and synthesized suitable functionalized organic precursor and their detection behaviors have been investigated towards various cations/anions/neutral molecules in organic and aqueous-organic media with the help of colorimetric, UV-vis, NMR, IR, Mass, fluorescence and time resolve fluorescence (TCSPC) spectral techniques. Host-guest interaction has been precisely analyzed through X-ray single crystal diffraction analysis. We have also investigated the possibility of re-use of the receptors. Structural and spectral properties of receptors experimental findings have been correlated with simple theoretical model optimization. Following the above host designing principle and using the easy synthetic routes and analysis techniques, we
have successfully discovered a library of chemosensors for highly selective, sensitive and multifunctional sensing of cations (\(\text{Cu}^{2+}\) and \(\text{Fe}^{3+}\)), anion (\(\text{F}^-\) and \(\text{AcO}^-\)) and neutral molecules (\(\text{CO}_2\)). As for example, a symmetrical azine Schiff base \(\text{N},\text{N}'\)-bis(4-\(\text{N},\text{N}'\)-diethylaminosalicylidene)hydrazine selectively detects \(\text{Cu}(\text{II})\) ion by means of naked-eye color change as well as UV-vis spectral changes. Using mass spectroscopic analysis we have confirmed 1:1 host-guest adduct formation. We are successful in isolated \(\text{Cu}(\text{II})\) mediated trapping of high energy conformer of the chemosensor, which supports our theoretical model structure calculations. Where as an unsymmetrical azine Schiff base compound, 5-diethyl-amino-2-[(4-diethylamino-benzylidene)-hydrazonomethyl]-phenol, synthesized by a simple modification of the above symmetrical azine compound, can detect both \(\text{Cu}(\text{II})\) and \(\text{Fe}(\text{III})\) ions selectively with dual mode binding approach. Time correlated single photon counting (TCSPC) measurement has been used to explain the host-guest complexation behavior.

We have also designed symmetrical salicylidene based Schiff base \([\text{N},\text{N}'\)-bis(5-nitro-salicylidene)-1,2-benzenediamine\] and reduced Schiff base \([\text{Bis}(2\text{-Hydroxy}-5\text{-nitro-phenyl})\text{-2-aminomethylbenzylamine}\]) which can work for various anion detection. These two compounds selectively detect \(\text{F}^-\) and \(\text{AcO}^-\) ions by means of naked-eye color change as well as UV-vis spectral changes. Self-designed synthetic Schiff base has been used as colorimetric anion receptor for the detection of anions in organic medium, while reduced Schiff base has been used for the preparation of re-usable test kits for the detection of anion in aqueous media. We have shown here that experimental findings are in well agreement with theoretical modeling. An efficient size selective anion binding cleft shaped receptor \([\text{N},\text{N}'\)-Bis-(2-amino-5-nitro-phenyl)-isophthalamide\]} has been designed
and synthesized for the selective detection of anion (here $\text{F}^-$ ion) in aqueous-organic medium. Host-guest interaction has been analyzed through naked-eye color change, UV-vis and $^1\text{H}$ NMR spectral changes. Formation of 1:2 host-guest adducts has been confirmed from X-ray single crystal diffraction analysis, where one fluoride ion is pseudo-encapsulated within the cleft shaped cavity and another fluoride anion is positioned out-side the cavity and forms fluoride-water cluster $\left\{\left[\text{F}_2(\text{H}_2\text{O})_3\right]^2\right\}$.

Again, a series of compounds with low molecular mass of different aromatic subunits constructed with Common Organic Backbone \{COBs: N$^2$-Imidazo[1,2-a]pyridine-2-ylmethyl-4-nitro-benzene-1,2-diamine, 4-Nitro-N$^2$-pyridin-2-ylmethyl-benzene-1,2-diamine and N$^2$-Benzyl-4-nitro-benzene-1,2-diamine\} have been designed and synthesized for efficient atmospheric CO$_2$ fixation. The H-bonded COBs-bicarbonate complexes were formed through \textit{in situ} generated HCO$_3^-$ ion. Complexes have been characterized by IR, $^{13}\text{C}$ NMR and X-ray single crystal structure analysis. Importantly, COBs-bicarbonate salts can be converted to pure COBs with quantitative yield under mild condition for continuation of atmospheric CO$_2$ fixation cycle.

1.3. Results and impacts

The work presented in this thesis will outline a guiding principle for the design of an effective multifunctional chemosensors which are highly sensitive and selective for the detection of toxic material (ions/neutral). Modification of the process, to be well suited for commercial application, will prove to be useful in maintaining low toxicity level of drinking water and other biologically relevant environments. It is found that the host-guest complexes are sometimes used as specific catalyst, adsorbing porous (COBs, MOFs, COFs, etc.) materials, etc. Such catalysts can be useful in pharmaceutical
industries. Adsorbing materials are very much demanding for future generation, especially \( \text{CO}_2 \) and \( \text{H}_2 \) adsorber. Using \( \text{CO}_2 \) adsorber we can minimize the global warming and the adsorbing \( \text{H}_2 \) can be used as fuels. The test kits developed in this process will make the detection technology more available to common people. In the current state of rapidly increasing environment pollution, the project will boost the development of approaches for keeping the environment clean and to keep the people away from any kind of poisoning. Last but not the least, the experiments and its comparison with theoretical modeling will help in gaining a better insight into the host-guest chemistry in organic and aqueous-organic media, which will provide a platform for further development in the field of supramolecular chemistry.

1.4. References


