PREFACE

Supramolecular chemistry is a highly interdisciplinary field of science covering the chemical, physical, and biological features of chemical species of higher complexity, which are held together and organized by means of intermolecular noncovalent interactions\(^1\). Over the past quarter century, supramolecular chemistry has grown into a major field and has induced numerous developments at the interfaces with biology and physics\(^2\).

As defined by Lehn; “Supramolecular chemistry is the chemistry of the intermolecular bond, covering the structures and function of the entities formed by the association of two or more chemical species.”

Molecular recognition\(^3\) is the soul for dynamics of supramolecular chemistry and eventually forms basis for receptors\(^4\), self-assemblies\(^5\), dynamic combinatorial libraries\(^6\), self-organized entities, molecular devices\(^7\), etc. The concepts that molecules do not act if they do not bind (Paul Ehrlich); binding must be selective (lock and key phenomenon, E. Fisher) and co-ordination / affinity between substrate and receptor (A. Werner) though put individually but collectively laid down the foundation of molecular recognition. However, Pedersen's discovery\(^8\) of solubilization of metal ions by crown ethers in organic solvents provided much impetus to the researches in recognition of variety of targets viz cations\(^9\), anions\(^10\), neutral molecules etc. That molecular recognition between complementary functions is crucial in the phenomenon of specific organization between molecules and has been further conceptualized within the field of supramolecular chemistry and has revealed great opportunities for new generation of chemists.

The crown ethers and their acyclic (podands) and polycyclic (cryptands) analogs constituted the first generation synthetic receptors and were followed by cyclodextrins coined as second generation synthetic receptors and later on the calix[n]arenes have been developed as third generation synthetic receptors. An early landmark in 1967 in the development of receptors for group I metal cations by Pedersen\(^8\), the ensuing decade brought further notable advances through the use of the principles of shape and size complementarity and Cram’s principle of preorganization of binding sites in the design and construction of spherands, cavitands, lariat ethers and macrocyclic ligands with predetermined selectivity for cations\(^11\). Significant contributions by Lehn have transformed humble beginning of molecular recognition into molecular information, functionalized supra-molecular materials, self-

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\(^2\) Supramolecular chemistry is the chemistry of the intermolecular bond, covering the structures and function of the entities formed by the association of two or more chemical species.

\(^3\) Molecular recognition.

\(^4\) Receptors.

\(^5\) Self-assemblies.

\(^6\) Dynamic combinatorial libraries.

\(^7\) Molecular devices.

\(^8\) Pedersen's discovery.

\(^9\) Cations.

\(^10\) Anions.

\(^11\) Calix[n]arenes.
organization, self-assembly and has been extended to constitutional dynamic chemistry\textsuperscript{12}. The trailblazing work of the trio was recognized by the Nobel Prize in Chemistry in 1987.

Since its inception, the field of molecular recognition using synthetic receptors has been also focused on its practical applications - the molecular sensing being the most significant. Molecular sensors combine molecular recognition with some form of reporter so that the presence of the guest can be observed\textsuperscript{13}. Commonly used detection methods involve fluorescence, electrochemical, colorimetric, surface plasmon resonance (SPR) and quartz crystal microbalance (QCM). Each method has its own advantages and disadvantages.

Optical signals based on changes in absorbance or emission both in terms of their intensities and $\lambda_{\text{max}}$ shift are especially attractive with respect to ease in transduction of a modulated signal using cheap, easy to handle and widely used instruments. The change in absorbance, particularly of color, can immediately reveal the presence of a given analyte and can provide semi-quantitative information using naked eye detection only. Colorimetric recognition has also gained popularity in recent years because a shift of an absorption band is often intrinsically ratiometric and avoids the necessity of an internal reference or calibration for quantitative estimation of the analyte. On the other hand, the fluorescence emission allows to realize a very high sensitivity of the chemosensors. In more recent years, fluorogenic chemosensors with shift in their emission maxima on interaction with the target analyte have been realized and have provided emission band ratiometric analysis of target guests.

In literature, in principle two types of \textbf{molecular receptors} named as chemosensors and chemodosimeters have been designed and used for such applications. Chemosensors coordinate with the target analyte through supramolecular interactions to yield measurable optical signal with a real time response, usually less than few seconds. Such interactions are typically reversible where any change in concentration of the analyte is related to the change in amounts of both the free and bound chemosensor. The reversibility of such chemosensors in case of their coordination with metal ions is shown by reversal of the optical response by the addition of a strong chelating agent normally EDTA. They have distinct advantage in terms of their re-usability.

Chae and Czarnik first described the term chemodosimeter\textsuperscript{14} as an abiotic molecule used to achieve analyte recognition with concomitant irreversible transduction of signal. This
approach primarily involves the reaction of the target analyte viz. anion, cation or neutral molecule with the molecular probe called here as chemodosimeter and is associated with significant chemical transformation involving both breaking and forming of covalent bonds. This process results in the formation of products different from starting chemodosimeter concomitantly with optically different properties. Significantly, unlike in case of chemosensors, this process is irreversible and cannot be reversed by using chelating agents like EDTA. These reaction processes, as achieved by specifically designed reactions, are relatively less affected by the environment and provide distinct advantage in terms of high selectivity.

In the present thesis, both the chemosensors and chemodosimeter approaches have been explored for developing chromogenic and fluorescent chemosensors. For achieving these objectives – aminoanthracene-9,10-dione moiety has been used as colored and UV-Vis. spectrophotometric reporter and dansyl group as fluorescent reporter and these results are presented in sections 1.2-1.4 of chapter 1. Consequently, a chemodosimeter for selective estimation of \( \text{Hg}^{2+} \) and a fluorescent chemosensor for ratiometric estimation of \( \text{Cu}^{2+} \) have been developed. The section 1.1 describes a brief commentary on different approaches employed in literature for the development of molecular probes. In chapter 2, the synthesis of all uracil based heterocalixarenes – calix[4]uracil derivatives with different substituents at N-1 of uracil and a substituent at rim of the calix[4]uracil have been synthesized and in brief their complexation behaviour towards alkali and alkaline earth metal ions has been investigated. The discussion on the results has been preceded by literature reports on uracil based cyclophanes.
References


