Abstract

The dissertation entitled "Molecular recognition: Design and synthesis of model receptors for carboxylic acids, carboxylates and urea" embodies in detail the design and synthesis of molecular receptors of different architectures for the recognition of substrates of biological significance such as mono-, di- and tricarboxylic acids, carboxylates and urea. Carboxylic acids and carboxylates are important substrates in molecular recognition. Enzymes, antibodies, amino acids and metabolic intermediates as well as the other natural products, contain a range of carboxylate functionalities that account for the characteristic biochemical behavior. Di- and tri-carboxylates are the essential components of numerous metabolic processes, including for instance, the citric acid glyoxalate cycle. They are also involved in the formation of high-energy phosphate bonds in our body. On the other hand, urea is important as guest species because it is toxic, pollutant and causes serious biological disorders. Urea is end product of nitrogen metabolism and a well-known protein denaturant that can cause damage in concentrations as low as micro molar range. Thus the need to develop structurally simple synthetic receptors capable of detecting urea in low concentration is important in clinical chemistry.

In order to recognize these molecules of biological significance, chemosensors of abiotic origin that are able to bind selectively and reversibly with a concomitant change in one or more properties of the system, such as redox potentials, absorption or fluorescence spectra are of special importance in the area of molecular recognition. Among these, the fluorescence-based chemosensors have achieved significant attention both in terms of their cost effectiveness and high sensitivity and availability of wide number of opportunities for modulation of photo physical properties of a fluorophore (photon, energy and electron transfer, heavy atom effect and change of electron density etc.). Light being a versatile signal and use of micro sized optical fibers can allow analysis at any location. Thus these sensors have found applications both in performing real space
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(biochemists, clinical and medical applications) and real time (analytical and environmental applications) measurements.

However, in the present research program, it was planned to design and synthesize hydrogen-bonding fluororeceptors for effective and selective sensing of different species such as carboxylic acids, carboxylates, urea etc. The content of the thesis has been divided into five chapters. Brief outlook of each chapter is described below.

Chapter-1: This chapter presents an introduction to molecular recognition including the definition and its interdisciplinary nature with various disciplines. This chapter also covers a brief discussion on the nature of different noncovalent forces and their existence in nature. The different physico-chemical methods to study the molecular complexation process are also discussed. At the end of this chapter organization of thesis and aim of the present research program have been cited.

Chapter 2 describes a review on carboxylic acid recognition (especially on hydroxy acids, and their derivatives). Emphasis has been given on the recognition of hydroxy di- and tricarboxylic acids. With a brief discussion on this, work on quinolone and naphthalene-based receptors 28-30, 38, 39, 46-48 has been described. The quinolone-based receptors 28, 38, and 46 shows monomer emission quenching followed by intramolecular excimer emission upon hydrogen bond mediated complexation with hydroxy carboxylic acids guests. The excimer emission has been used to confirm the selective recognition of various hydroxy carboxylic acids guest molecules. In contrast to quinolone-based receptor, naphthalene-based receptors did not show any excimer emission upon complexation of hydroxy acids.
Chapter 3 is divided into two sections. Section 3A deals with the recognition of anionic species (such as mono and dicarboxylates, and also halides, dihydrogen phosphate etc. for comparative purpose) using coumarin-based receptors 82-85, 91 and 92. A brief review on coumarin-based receptors, employed in molecular recognition studies, has also been described. Among the monotopic receptors, receptor 82 is found to be effective as sensor for carboxylates and also fluoride. The ditopic receptor 91 also responded the binding of isomeric dicarboxylates and distinguished them effectively by exhibiting photo physical change of the receptor.
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Section 3B describes the work of pyridine amide appended coumarin receptors that are useful in the discrimination of carboxylic acids from sulphonic acids.

The change in photophysical properties of coumarin or benzcoumarin in 138 and 140 clearly distinguished the guests and also highlights the features of protonation as well as hydrogen bonding phenomena.
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**Chapter 4** describes the work on hetero bis amide receptors 166 and 167 for selective recognition of α-amino and hydroxy acid derivatives. While the receptor 166 is selective for L-N-acetylvaline, receptor 167 exhibits much preference for D-(−)-mandelic acid. Due to flexible nature of the hetero bis amide receptors 166 and 167, the determined binding constant values are less in magnitude. In addition, the crystal engineering of pyridine amide-carbamates 173-176 has been addressed with few examples. In the packing of these conjugates in solid-state water, has been found to play an important role. This has been critically discussed.

**Chapter 5** addresses the recognition of urea by our newly designed synthetic receptors. All the receptors are pyridine amide–based. The macrocyclic receptors 200 and 201 show strong inclusion of urea involving hydrogen bonding. Binding mode in the solid state has been shown through single crystal X-ray structures. Similarly, the open receptors also bind urea and report the recognition event by showing photo physical changes upon complexation. In this aspect, the receptor 28 reports the recognition of urea by showing the formation of excimer. The progress of urea recognition has been introduced in the beginning of the chapter.
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28 $R = C_4H_{17}$