DESIGN AND SYNTHESIS OF CHROMOGENIC AND FLUOROGENIC CHEMORECEPTORS FOR SELECTIVE SENSING OF TOXIC ANIONS

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ABSTRACT

Sensing of molecule is a chemical exploration where a synthesized probe can identify a targeted analyte and produces a signal by the alteration of definite and measurable properties. Selectivity and proficiency of the sensory probe are the indispensible features of the molecular sensing. Chemosensors based spectroscopic techniques are specifically alluring, whereas numerous conceptions are developed together with the advancement of chromogenic and fluorimetric probes with the purpose of improving the selectivity, sensitivity as well as the active working range. Nonetheless, electrochemical chemosensors are also grabbing noteworthy attention owing to their low cost, high sensitivity, ease of operation and portability. The exploration of chemosensors capable to recognize anions has acquired substantial attention owing to numerous important roles of anions in several arenas, like, biology, health, medicine, environment and chemical processes. Among numerous toxic anionic components, F^-, CN^-, and AsO_2^- are severely toxic to living creatures in all mode of administration; thereby entail the exploration of new chemical sensors or chemosensors.

In this context, an expansive literature survey was done on the prevailing sensors with the intention of inventing innovative chemosensors. Accordingly, the loopholes and challenges were well-defined which assisted in ascertaining the gaps in this arena and consequently the intents are clearly indicated and well explained. Essentially, chemosensors, comprising potential H-bond donor groups, like –OH/–NH are more desirable in the purview of anion sensing, due to strong interaction of the anions with the highly dissociable protons. Additionally, the presence of apposite electron withdrawing group is another key factor to control the sensing efficacy of the chemosensor. For instance, presence of highly electron withdrawing group within the sensory framework enhances the dissociability of the interacting protons. In this relevance, urea-based chemosensors are effective in sensing anions because of the presence of –NH moieties, which result in H-bond induced π-electron delocalization. Similarly, an efficient Schiff–base chemosensor always possesses a potential H–bond donating group, like –NH within its framework to captivate the anions.

The objective is mainly emphasized on the premeditated synthesis of urea and Schiff base type chromogenic and fluorogenic chemosensors for selective and sensitive detection of F^-, CN^-, and AsO_2^-. In this relevance, certain expedient approaches have been anticipated to attain better sensitivity towards the targeted lethal anions, which steered towards the development of several urea and Schiff-base chemoreceptors: henceforth abbreviated as **S1**, **S2**, **S3**, **S4**, **S5**, **S6**, **S7**, and **S8.** Additionally, analyses of other exclusive features of the synthesized chemosensors have also been accented.

Chapter 1 and 2 essentially focus on the initiatory perceptions regarding the anion recognition chemistry along with a concise literature review for familiarizing various hitherto reported chemosensors. This thesis mainly deals with the purposive syntheses of various chemoreceptors for efficaciously recognizing F^-, CN^- and AsO_2^- along with their harmonized wet-chemical and theoretical sensing studies. In this perspective, the work sequentially proceeded from the sensitive recognition of F^- towards the selective detection of CN^- and AsO_2^- by varying and tweaking the frameworks of the organo-chemosensors.

Chapter 3 contains the exploration of two urea and Schiff-base chemosensors, (**S1** and **S2**), which showed high sensitivity towards F^-. The urea-based chemosensor, **S1** exhibited F^- detection limit of 0.5 ppm. Therefore, the Schiff-base sensor, **S2** has been designed and synthesized by incorporating more electron withdrawing group to enhance its sensitivity towards F^- and fascinatingly it can recognize F^- at a detection limit of 6 ppb.

Chapter 4 comprises the account of another urea and Schiff-base chemosensors (**S3**, **S4**, and **S5**), capable of selectively recognizing CN^-. The urea-based sensor **S3** showed a detection limit of 0.15 ppm towards CN^-. Therefore, the Schiff-base chemosensors, **S4** and **S5** have been sequentially explored to further enhance the sensitivity. Thus, **S4** and **S5** recognized CN^- at the detection limit of 130 and 15 ppb respectively owing to the presence of more dissociable –NH protons.

Chapter 5 includes a Schiff-base chemosensor (**S6**), which has been explored with an eye of detecting both F^- and CN^- by a single multichannel and multianalyte responsive chemosensor. **S6** produced a distinctive colorimetric alteration in presence of F^- and CN^-, while the probe exhibited enhanced sensitivity towards F^- owing to its more electronegativity and smaller size.

Chapter 6 is comprised of an exploratory description of two Schiff-base (**S7** and **S8**) chemosensors, exhibiting noteworthy efficacy towards selective detection of AsO_2^-. The presence of electron donating $-CH_3$ group within the **S7** framework lessened its sensing efficiency towards AsO_2^-, whereas the nonexistence of the $-CH_3$ group within **S8** improved the efficacy of –NH and –CH protons to interact with the O center of AsO_2^-.

All the experiments were demonstrated by using various sophisticated instrumentations, including ESI-MS, FT-IR, SCXRD, UV-Vis, photoluminescence, cyclic voltammetry, ITC, FESM, fluorescence microscopy *etc.* All the wet-chemical evidences have further been validated with the theoretical (DFT and TDDFT) studies. Nevertheless, all the chemosensors contain more than a few inimitable characteristics in addition to their hazardous anion detection efficiencies which are described in the relevant chapters.