Abstract

Probing the host-guest interaction to identify various environmentally harmful and biologically important substances which are known as target analytes of paramount importance to the scientific communities to sustain peaceful and livelihood life in modern civilization. These are known substances with known chemical, physical, and other properties. They are either known or thought to be in samples, and they must be determined to meet the objectives of the environmental analysis program. The target analytes which are known as guests and chromo-fluorogenic compounds which show signaling in the presence of analytes are known to be hosts. These interactions strategy is broadly accepted, understood, and used in analytical and environmental research, environmental security programs, and many other surveys of investigation. It is employed in most environmental quality surveys and government regulatory compliance monitoring programs. Target analytes include cations, anions, chemical warfare agents (CWAs), pesticides; herbicides used by farmers in cultivation, and food adulteration that negatively affects public health. In very small amounts, many of these are necessary to support life such as cations and anions. However, in larger amounts, they become toxic. They may build up in biological systems and become a significant health hazard. The abuse of CWAs and explosive materials has become a severe issue globally and is used by anti-national terrorist groups for the sake of power. The suppression of abuse of these lethal substances and unwanted crimes for the sake of the livelihood environment and humankind's safety are urgently needed. The researchers are actively engaged in developing and updating the field of detecting these toxic and explosive chemicals. Among the various CWAs, sarin gas and explosive nitroaromatic compounds are highly dangerous, poisonous, and harmful. However, the direct use of some lethal substances such as CWAs is strictly prohibited in laboratories; instead, the use of some surrogate substances has been taken into focus, usually serving as its mimics owing to their similar properties and lower toxicity. Keeping the above facts in mind, in the present thesis, we have introduced various chromo-fluorogenic host molecules that are characterized by diverse conventional analytical techniques which are employed for the detection of some metals, anions, explosive nitroaromatic compounds such as picric acids, sarin gas mimics diethylchlorophosphate exploring the host-guest interaction strategy by versatile spectroscopic contrivances in various environment.

A summary of each chapter of the present thesis is given below, one by one.

Chapter 1: This chapter commences with a concise examination of assorted host-guest systems employed in chemosensors, transitioning to an exploration of the fundamental principles and working mechanisms behind the design of chemosensors based on various photophysical processes, illustrated with relevant examples. A brief survey of the literature on national and international status is also discussed to establish the novelty of the present thesis in the current scenarios. At the end of the chapter main objectives and applications of the current research work within the broader context of scientific advancements are described.

Chapter 2: This chapter discusses the general methods and instruments used throughout the research work.

Chapter 3: This chapter explores the affordable and incredibly sensitive sustainable sensors for recognizing Al^{3+} ions with enormous practical applications. A simple and reliable sensor **DPAB** was developed. by reacting benzene-1,4-diamine with N, N-dimethyl cinnamaldehyde. The sensor is extra highly reputable concerning Al^{3+} ions and exhibits an incredible color change in DMSO and DMSO-H_2O (9:1 v/v) solution, allowing us to visually distinguish Al^{3+} ions from other metals and anions essentially including Al^{3+} and PO_4^{3-} in the **DPAB** solution, the sensor's spectral responses and apparent color shift can be switched backward and forward. This can be conceptualized as a complementary "INHIBIT" logic gate at the molecular phase. We have developed a molecular-scale subsequent memory device based on a reversible and repeatable detection system that exhibits "Writing-Reading-Erasing-Reading" and "Multi-Write" functionalities as binary logic. The lowest detection limits (LOD) for Al^{3+} and PO_4^{3-} ions are determined to be 3.29 nM and 3.89 nM, respectively, considerably lower than other chemosensors described in the literature. Additionally, for on-the-spot detection, the probe may also be utilized in the test strips with a superior selectivity for the detection of Al^{3+} and PO_4^{3-} ions. Moreover, we also performed the smartphone-based technique for the practical utility of **DPAB** in the DMSO-H_2O (9:1 v/v) solution for on-spot detection and quantification. The effectiveness of **DPAB** and **DPAB**-Al^{3+} complex suggests that **DPAB** may be used as a sensitive probe and be applied to the analysis of real samples.

Figure 1: Pictorial demonstration of detecting performances of our introduced imine linkage **DPAB** chromogenic probe for cascade detection of Al^{3+} and PO_4^{3-} ions.

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Chapter 4: In this chapter, a new symmetrical aza-substituted chromo-fluorogenic sensor, **BPH**, for specific detection of sarin gas, one of the fatal G-series nerve agents surrogate, diethylchlorophosphate (DCP) has been introduced. **BPH** shows a noticeable naked eye colorimetric change from pale yellow to light pink in the presence of DCP, displaying highly intense bright greenish cyan color photoluminosity under a 365 nm UV lamp, which is also manifested from the color chromaticity diagram. A **BPH**-staining paper stirps-based test kit experiment has been demonstrated for the onsite detection of nerve agent mimics. A more attractive and efficient application of **BPH** as a sarin gas vapor phase sensor mimics DCP in solid and solution phases. The **BPH**-based chromo-fluorogenic sensor shows excellent selectivity toward DCP with a detection and quantification limit in the μM range. The work invokes a new way for the researchers to detect DCP employing a simple chromo-fluorogenic sensor, which could be prepared by a time-saving, straightforward, handy protocol from the cost-effective starting materials.

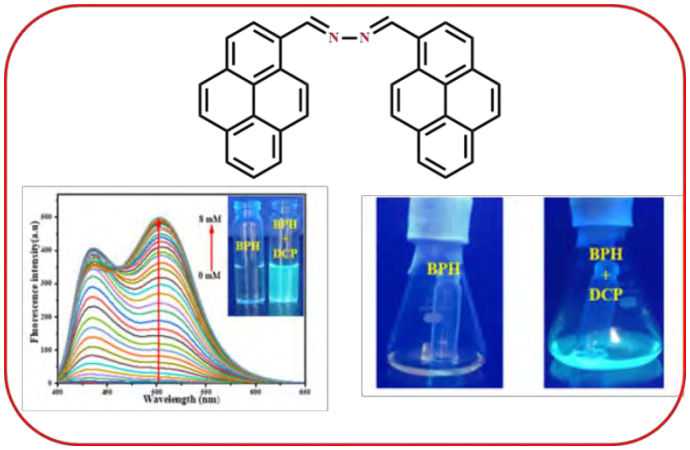

Figure 2: Pictorial representation of detecting performances of our introduced azine-based **BPH** chromo-fluorogenic probe for detection of DCP.

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Chapter 5: This chapter highlights the investigation of the detection of essential trace elements for living organisms such as copper (Cu^{2+}) ions. The Cu^{2+} ions are the most important from kitchen to industrial life. However, Cu^{2+} ions are vital for the human body and are associated with necessary physiological processes; insufficient or excessiveness has many hazardous effects on our bodies. In the present contribution, strategically, we have introduced a julolidine-coupled azine-based (**HDBQ**) reversible chromo-fluorogenic probe for specific detection of Cu^{2+} ions. Probe **HDBQ** exhibits observable orange colorimetric change from yellow, which is visible to the naked eye in daylight. The highly green fluorescence **HDBQ** becomes a non-fluorescent one with the incorporation of Cu^{2+} ions. Interestingly, the colorimetric change and non-fluorescent **HDBQ**-Cu^{2+}complex reverse to the original **HDBQ** in the presence of ethylenediamine tetraacetic acid (EDTA). The detection and quantification limit of **HDBQ** towards the detection of Cu^{2+} ions is found to be in the μM range, which is much lower than the limit (31.5μM) recommended by WHO. We have also performed a colorimetric and fluorometric paper-based test strips-based experiment employing **HDBQ** for real-time on-site detection of Cu^{2+} ions. Using the reversibility characteristics of **HDBQ** for the consecutive addition of Cu^{2+} and EDTA**,** we have established the INHIBIT molecular logic gate. The present report brings a precise and sensitive probe for the detection of Cu^{2+} ions in real environmental and biological samples.

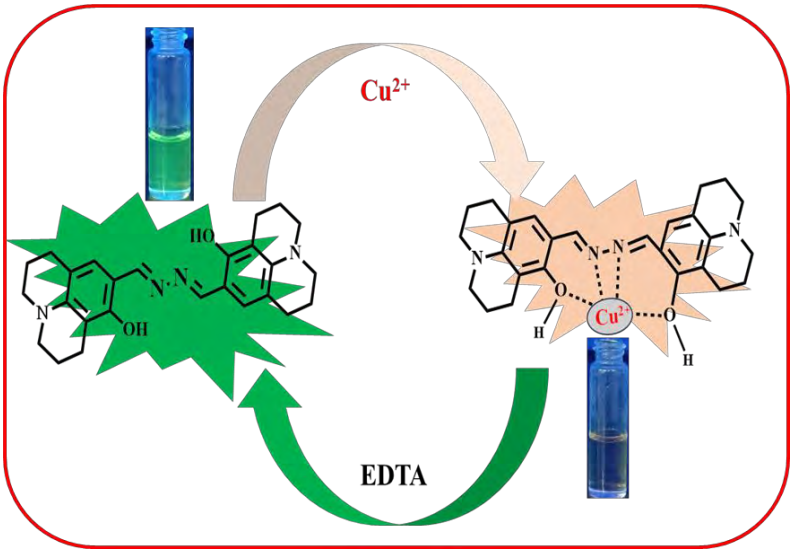

Figure 3: Pictorial demonstration of detecting performances of our introduced julolidine coupled azine-based reversible chromo-fluorogenic probe for specific detection of Cu^{2+} ions having sensitivity in the μM range.

Journal of Fluorescence, https://doi.org/10.1007/s10895-023-03577-64.

Chapter 6: The severe toxicity and easy availability of nerve agents have caused an increase in the need to develop effective methods for identifying these lethal substances. Among the traditional platforms employed for this kind of purpose, chromophore-based chemosensors have garnered a significant amount of attention. In this chapter, we have designed, prepared, and characterized (N^1E, N^4E)-N^1, N^4-bis((Z)-3-(4-(dimethylamino)phenyl) allylidene)benzene-1,4-diamine, **BDPA**, a simple chromogenic probe of symmetrical diimine, having the extreme capability to sensing DCP, the mimic of chemical warfare agent sarin not only in solution but also in solid and vapor phases with highly selective and sensitive manner. In the presence of DCP, a remarkable color change from light yellow to blue is observed in pure acetonitrile solvent and also shows pink color in 10% acetonitrile-water by the naked eye, comes back to its former state after the introduction of triethylamine (TEA) which is found to be five times recyclability by alternately adding DCP and TEA. The detection limit of **BDPA** with DCP has been estimated in the nanomolar range, and also, response time towards sarin surrogate DCP is within a few minutes (~ 5-6 minutes.). To determine its practical usability, we have developed a portable test kit that uses paper strips to assess the capability of **BDPA** for in-situ recognition and measurement of DCP. A dipstick method has also been executed to recognize gaseous DCP within the stores of analogous

hazardous analytes to prove the effectiveness of the sensor, **BDPA**. A smartphone-based readout novel technique, i.e., RGB analysis, has provided an innovative platform for the instant, on-site, visible identification and measurement of DCP in remote areas. The current work presented an incredible probe and method for conveniently and instantly detecting and quantifying sarin gas mimics in actual dangerous circumstances.

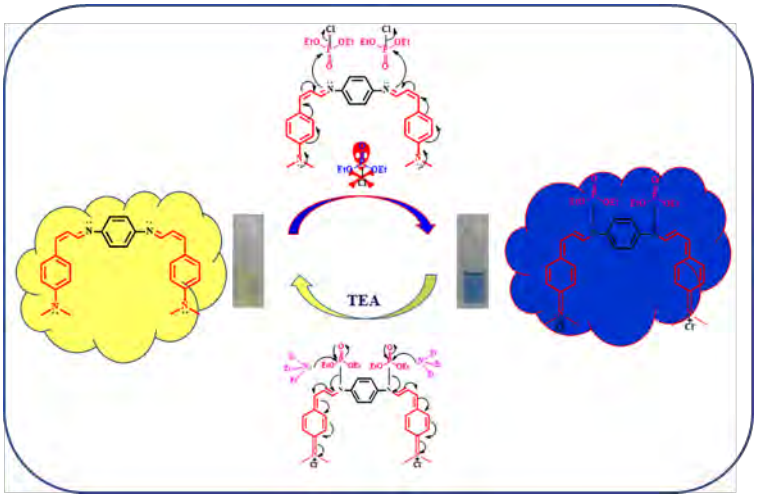

Figure 4: Demonstrate the detecting performances of our introduced imine-linkage simple chromogenic probe, **BPDA** for the detection of sarin gas mimic, DCP with a nanomolar range detection limit.

Microchemical J. 10997 (199) 2024.

Chapter 7: This chapter attempts to introduce a chromone-coupled adenine-based fluorogenic chemosensor (**BD1**) that has been introduced and characterized by different conventional analytical methods. Our developed sensor can selectively and sequentially detect Zn^{2+} and HSO_4^- or Zn^{2+} and picric acid (PA) based on the fluorescence 'OFF-ON-OFF' mechanism. A momentous fluorescence improvement has been observed after the accumulation of Zn^{2+} ions in the **BD1** solution at 475 nm due to the creation of the Zn^{2+} chaleted **BD1** complex. A cyan color fluorescence enhancement is visible under the exposure of a 365 nm UV lamp, which is also manifested in the CIE diagram. The detection limit of our developed sensor **BD1** and Zn^{2+}- **BD1** complex towards the identification of Zn^{2+} and HSO_4^- ions are in the nM and μM range, respectively, in the solution phase. Among the several explosive nitroaromatic compounds (NACs), only PA quenches the fluorescence Zn^{2+} chelated **BD1** complex, and the nature of quenching is both static and dynamic. Zn^{2+} chelated **BD1** complex could detect PA selectively in the μM range among all the tested NACs. We have fabricated a paper strips-based test kit and successfully utilized it for practical on-spot identification of Zn^{2+} ions and PA.

Based on the chemically encoded input as Zn^{2+} ions, PA, and the fluorescence intensity as output, we constructed an INHIBIT molecular logic circuit. The present report evokes a new approach for the development of new chemosensors from bioinspired materials such as adenine, a purine nucleobase.

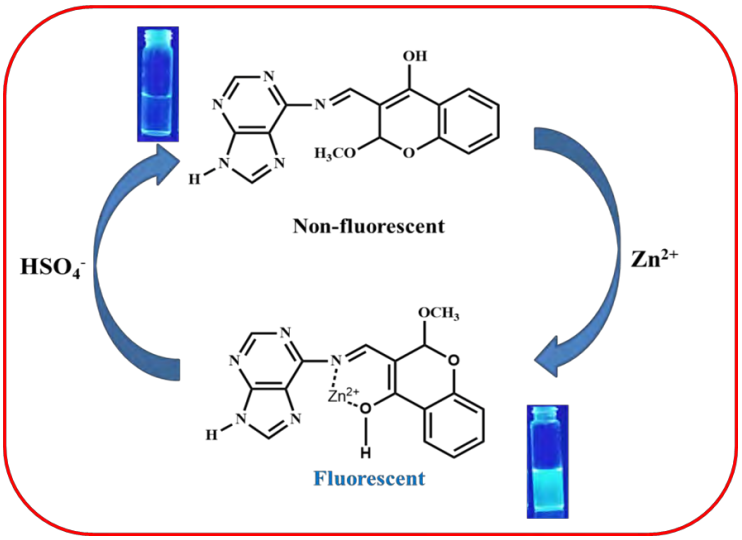

Figure 5: Represent the detection performance of **BD1** for cascade detection of Zn^{2+} and HSO_4^- ions or Zn^{2+} ions and picric acid.

ChemistrySelect, https://doi.org/10.1002/slct.202304947.

Chapter 8: Finally, a summary of the present thesis and the future perspective from the present research work has been delineated in this chapter.