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Effect of External Stimuli on Fluorescent Schiff Bases: Mechanistic Insights and Applications

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Abstract:

Schiff bases are a class of compounds that are characterized by the presence of the azomethine (-HC=N-) group. They are prepared through the simple condensation reaction between an aldehyde and an amine, and their photophysical properties can be fine-tuned by systematically varying the synthons. Moreover, Schiff bases possess extraordinary stability but are reversible under the influence of an external stimulus. They are versatile chelating agents containing multiple donor atoms like O and N which can coordinate to metal ions, anions, and biological molecules or can self-assemble leading to noticeable changes in their optical properties. Owing to these features, Schiff bases have advanced the fields of chemical probes, optical materials, cell imaging agents, and optoelectronic materials. This thesis dissertation is devoted to the design and synthesis of fluorescent Schiff bases and study of their interaction with external stimuli. Chapter 1 discusses the importance of Schiff bases in the field of supramolecular chemistry and their function as chemosensors, photochromic and mechanochromic materials. The importance of appending fluorophores to Schiff bases and the associated photophysical properties are also discussed. Chapter 2 describes the synthesis, chemosensing and photosensitization properties of the tertaphenylethylene derivative A in solution and in the aggregated state. It was observed that A was capable of detecting Cu(II) and Zn(II) in solution with high selectivity and sensitivity. The mechanism of interaction of A with Cu(II) and Zn(II) was elucidated using various experimental techniques and computational modelling. Further, A showed exclusive selectivity for Cu(II) in the aggregated state and interestingly acted as an activatable photosensitizer thus making it a potential candidate for photodynamic therapy. Chapter 3 discusses the synthesis and photophysical properties of a triphenylbenzene based Schiff base B. It exhibited aggregation induced emission and mechanofluorochromism with good fluorescence quantum yield in the solid state. Furthermore, B showed high selectivity and sensitivity for fluoride anions in solution, solid state and cellular conditions. Taking advantage of these properties, we prepared a thin film of B that could successfully detect fluoride under a variety of conditions. Chapter 4 discusses the stimuli responsive behaviour of a pyrene appended Schiff base C in solution and in the crystalline state. C was observed to interact with external stimuli such as Cu(II) and acid vapours with accompanying fluorescence changes. Further, C formed single crystals that exhibited mechanical flexibility which could be modulated using xiiiexternal stimuli. The changes in the mechanical and fluorescence properties of C were employed as input and output to build a crystal-based molecular logic gate demonstrating the potential application of this system in optoelectronics. Chapter 5 examines a coumarin containing Schiff base D capable of interacting with Zn(II) and fluoride ions in the crystalline state. These external stimuli could successfully modulate the fluorescence and the inherent mechanical property of the crystals of D. The binding affinity of D for Zn(II) and fluoride was used to develop a coating on the crystal surface which resulted in varying surface potential leading to a more complex crystalline system.

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