



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

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Thesis Title: Proton Transfer and Molecular Logic Functions of a Few Azole Derivatives.

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**SHORT ABSTRACT**

Proton transfer is one of the fundamental reactions in many chemical and biological processes. In the above mentioned thesis, the intermolecular proton transfer, intramolecular proton transfer, excited state double proton transfer were investigated with different molecular systems. The studies revealed that how the proton transfer processes yielded different end products like different tautomer, anion, cation, zwitterion etc. The thesis also described molecular switches, binary subtraction, keypad lock system with simple cation anion interaction with different azole systems. The construction of fuzzy interference system is represented with an azole system to follow the stimuli response of the fluorophore. A brief description of the thesis work is presented below.

The intermolecular proton transfer was studied between 2-(2'-hydroxyphenyl)benzimidazole (HPBI) and different anions. Despite the fact that HPBI exists as *cis*-enol (major) and *trans*-enol (minor) in neutral form, earlier it was reported to exist only in the *trans*-form upon deprotonation in aqueous medium. It was also stated that the dianion formed in the ground state was reprotonated to form the *trans*-anion in the excited state. In the current thesis, it was established that the *cis*-anion and dianion can be obtained upon proper stabilization. It was also demonstrated that the switching between *cis*- and *trans*-anion is possible. Theoretical calculations were also performed to substantiate the existence of *cis*-anion and dianion. In converse to the literature report, it was also proven that not only in protic solvents but also in aprotic solvents 'OH' group is deprotonated before the 'NH' group to form monoanion.

The anion sensitivity and the deprotonation nature of the nitrogenous analogues of HPBI were investigated in a polar aprotic medium. The substitution of pyridyl nitrogen enhances the anion sensitivity. However, despite the enhanced sensitivity of the nitrogenous analogues the deprotonation of these molecules in presence of strong anion is less favoured as compared to HPBI. The anomalous trend observed for the nitrogenous analogs were discussed and explained with theoretical calculations and experimental findings. It was also found that the sensitivity towards anion and the formation of anion depends also on the position of the pyridyl nitrogen.

The intramolecular proton transfer process was demonstrated with a HPBI derivative, 1,4-bis(2-(2'-hydroxyphenyl)benzimidazol-1-ylmethyl)-benzene (BHPBI). The molecule exhibits highly Stokes' shifted normal emission due to the photoinduced planarization. The tautomer emission occurs due to the photoinduced proton transfer. In the excited state, the tautomer undergoes torsional rotation induced isomerization to generate one more tautomer emission. The ground state conformers of the molecule were separated from each other and exploited to produce aggregation induced enhanced emission with different emission color. Thus, a single molecule was used as two distinct color emitting fluorophore.

The consecutive proton transfer process was investigated with (3,5-bis(2'-hydroxyphenyl)-1H-1,2,4-triazole (Tz) molecule. The studies revealed that Tz molecule undergoes excited state single and double proton transfer, and generates a monoketo and a diketo species. The process is initiated with a particular phenol unit. The other phenol unit cannot commence the ESIPT process in solution due to the annular tautomerism. However, in the solid state ESIPT initiates with other phenol unit also to produce three different tautomers in the excited state.

The binding interactions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  with 2-(4'-N,N-dimethylaminophenyl)oxazolo[4,5-b]pyridine (DMAPOP) in acetonitrile were reported earlier. The studies revealed that the binding of metal ions occurs through more than one site. In the present thesis, it was established that the anionic micelle can formulate the metal ion binding at a specific site. In presence of SDS both the metal ion binds at oxazole nitrogen. However,  $\text{Cu}^{2+}$  quenches the fluorescence and  $\text{Cd}^{2+}$  enhances the fluorescence of DMAPOP. The different emission nature of DMAPOP in presence and absence of micelle and metal ions were exploited to construct different logic gates.

BHPBI exhibits tautomer emission from the quasi planar conformer upon photoexcitation. However, in chloroform, upon photoirradiation the ESIPT is inhibited due to the formation of dication species. Here, solvent acts as a proton donor. The interaction of the molecule with fluoride before and after the irradiations are different. This alters the emission characteristics of the molecule. The different emission natures were used to construct molecular INHIBIT, IMPLICATION, TRANSFER, INVERTER logic gates. The input sequence dependency of the emission output was used to construct molecular keypad lock system.

A charge transfer molecule 2-(4'-N,N-dimethylaminophenyl)imidazo [4,5-b]pyridine (DMAPIP-b) was used to construct logic gates with different radices. Taking the advantage of multiple binding sites of the fluorophore, a series of different molecular logic gates were developed using fluorescence intensities at different wavelengths. The high emission of the molecule is drastically quenched in presence of  $\text{Fe}^{3+}$ . However, it regains back by addition of equivalent amount of  $\text{F}^-$ . The fluorescence On-Off nature was used to construct molecular full subtractor and molecular keypad lock system with Boolean logic. Ternary system was generated by considering three defined fluorescence intensities at particular wavelength. The smooth dependency of emission intensities with analyte concentration was utilized to construct infinite valued fuzzy logic system. The fuzzy logic system has been further coupled with neuro adaptation method to predict more accurately the dependency of molecular intensity in presence of external inputs more accurately.