INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Programme of Study : Ph.D.

Thesis Title : Modulation of Proton Transfer and Charge Transfer Processes in few Azole Derivatives by Homogeneous and Heterogeneous Media

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Thesis Submitted to the Department/ Center : Chemistry

Date of completion of Thesis Viva-Voce Exam : 20-01-2021

Key words for description of Thesis Work : Azole derivative fluorophores, ESIPT, TICT, Host-Guest interaction, Silver nanoparticle, pH

SHORT ABSTRACT

The photo-physical dynamics of proton transfer and charge transfer based azole derivative photo-switches and control over their dynamics were explored using various experimental techniques and quantum mechanical approaches. The photo-switches have innumerable astonishing applications including in the field of drug delivery. Azole derivative photo-switches are noble fluorescent probes with anti-cancer, anti-malarial, anti-bacterial activity and with many more applications. Proton transfer and charge transfer are two basic and imperative phenomena in several biological processes like photosynthesis, DNA replication, etc. Amongst proton transfer and charge transfer processes, excited state intramolecular proton transfer (ESIPT) and twisted intramolecular charge transfer (TICT) are two photo-process/mechanism which usually lead to dual emission in the fluorophores. Compare to single emissive fluorophores, dual emitting fluorophores are more useful as their emission properties can be controlled by various external factors. Hence now-a-days photo-switches based on more than one reaction coordinate are more desired compared to conventional switches as these are easy to synthesize and have very fast response time. ESIPT and TICT processes result in red shifted emission. ESIPT process happens in intramolecular hydrogen-bonded molecules. TICT occurs upon photoexcitation in molecules that usually consist of a donor and an acceptor part linked by a single bond. The ESIPT and TICT emissions rely upon the nature of the solvents and are sensitive to heterogeneous environment. Hence, modulation of dual emission generated by ESIPT or TICT by solvent of different polarity or by other heterogeneous environment is interesting as this leads to various real-world applications. The thesis comprises the switching of few photo-switches attained by a number of external stimuli factors including simple solvent system, pH, supramolecular host-guest interaction and silver-nano-surface. The motivation behind silver nano-surface was due to their highest efficacy of plasmon excitation, stability, controllable optical properties, wide-

reaching plasmonic application and cost effectiveness. The photoswitches are 2-(2'-hydroxyphenyl) benzoxazole (HPBO) having only one ESIPT reaction coordinate, 3,5-Bis(2-hydroxyphenyl)-1H-1,2,4-triazole (bis-HPTA) having two ESIPT reaction coordinates and 2-(4'-diethylamino-2'-hydroxyphenyl)-1H-imidazo-[4,5-b]pyridine (DEAHPIP-b) having both ESIPT and TICT reaction coordinates. The fluorophore HPBO selectively binds to zinc ion and successfully detaches the zinc ion in presence of a supramolecular cucurbit[7]uril. Hence this can be implemented as a zinc carrier for targeted delivery. The fluorophore bis-HPTA has two unequal ESIPT active sites. However, ESIPT can't be initiated from either side, it strongly depends on the surrounding medium. This fluorophore exhibits a very unique proton transfer process that is proton transfer triggered proton transfer (PTTPT) in non-polar solvents. N,N-Dimethylformamide (DMF) disturbs that proton transfer process and completely alters its reaction path to another ESIPT switch. Further addition of silver nanoparticle to DMF restores its PTTPT like in other non-polar solvents. Another very interesting model system included in the work was DEAHPIP-b. Based on the solvent polarity, it can exhibit either ESIPT or TICT or both ESIPT and TICT. The silver-nano-surface triggers the TICT emission in DMF. On adding surfactants to DMF, TICT switches to ESIPT to different extent based on the nature of surfactants (cationic, anionic, nonionic) and their concentration. Also this fluorophore can be treated as an efficient pH sensor as depending on the acidity or basicity of the medium, a broad range visible emissions were observed which also modulates its proton transfer and charge transfer behavior.