

Ab initio Studies of Solvated Fluorophores Undergoing Excited-State Intramolecular Proton Transfer

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During this talk, I will illustrate recent applications of Time-Dependent Density Functional Theory (TD-DFT) and wavefunction electron-correlated approaches (e.g., ADC(2) and CC2) for molecular dyes undergoing Excited-State Intramolecular Proton Transfer (ESIPT). Several families of ESIPT dyes, such as hydroxyphenylbenzoxazoles, hydroxyphenylbenzimidazoles and benzothiadiazoles derivatives, will be considered. These dyes are particularly useful since *i*) they might lead to single-molecule dual-fluorescence when ESIPT is not quantitative; *ii*) several show significant emissions in both solution and the solid-state. The interest of theoretical calculations will be illustrated not only for reproducing experimental spectroscopic data [1] but also for determining transition states on the excited-state surface [1] as well as estimating the relative emission quantum yields of the various forms in a very simplified approach [2]. Theory was also used to design from first principles a series of dual-emitters from single ESIPT dyes [3]. In several cases, it could also induce a re-interpretation of experimental outcomes [4,5]. Finally, the possibilities to design systems encompassing several ESIPT centres [6], ratiometric probes [7], or zwitterionic systems [8] will be discussed.

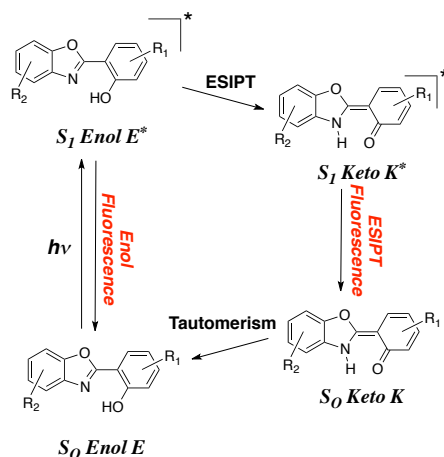


Fig. 1: Representation of a typical ESIPT process

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