Ab initio Studies of ESIPT Dyes

Denis Jacquemin*,[1]

[1]*CEISAM Laboratory, Univ. Nantes & CNRS, Nantes, France*

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During this talk, I will illustrate recent applications of Time-Dependent Density Functional Theory (TD- DFT) and wavefunction approaches (e.g., ADC(2) and CC2) for 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 as they might lead to single-molecule dual-fluorescence when ESIPT is not quantitative. The interest of theoretical calculations will be illustrated not only for reproducing experimental spectroscopic data [1,2] but also for determining transition states on the excited-state surface [1,2] as well as estimating the relative emission quantum yields of the various forms in a very simplified approach [3]. Theory was used to design from first principles a series of dual-emitters from single ESIPT dyes [4]. In several cases, it could also induce a re-interpretation of experimental outcomes [5,6]. Finally, the possibilities to design systems encompassing several ESIPT centres [7] , ratiometric probes [8], or zwitterionic systems [9] will be discussed.

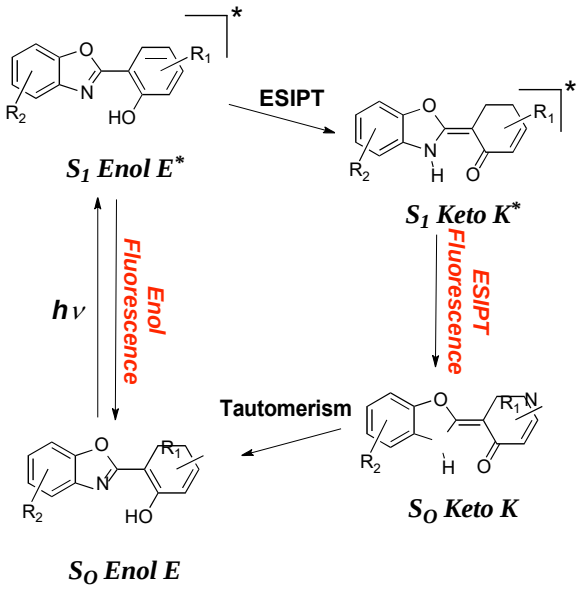

Fig. 1: Representation of a typical ESIPT process

[1]. K. Benelhadj, W. Muzuzu, J. Massue, P. Retailleau, A. Charaf-Eddin, A. D. Laurent, D. Jacquemin, G. Ulrich, R. Ziessel, Chem. Eur. J., **2014**, *20*, 12843-12857. E. Heyer, K. Benelhadj, S. Budzak, D. Jacquemin, J. Massue, G. Ulrich, Chem. Eur. J., **2017**, *23*, 7324-7336. T. Pariat, M. Munch, M. Durko-Maciag, J. Mysliwiec, P. Retailleau, P. M. Vérité, D. Jacquemin, J. Massue, G. Ulrich, Chem. Eur. **2021**, *27*, 3483-3495.

[2]. J. Massue, A. Felouat, P. M. Vérité, D. Jacquemin, K. Cyprych, M. durko, L. Sznitko, J. Mysliwiec, G. Ulrich, Phys. Chem. Chem. Phys., **2018**, *20*, 19958-19963. J. Massue, A. Felouat, M. Curtil, P. M. Vérité, D. Jacquemin, G. Ulrich, Dyes Pigm., **2019**, *160*, 915-922.

[3]. Y. Houari, A. Charaf-Eddin, A. D. Laurent, J. Massue, R. Ziessel, G. Ulrich, D. Jacquemin, Phys. Chem. Chem. Phys., **2014**, *16*, 1319-1321.

[4]. C. Azarias, S. Budzak, A. D. Laurent, G. Ulrich, D. Jacquemin, Chem. Sci., **2016**, *7*, 3763-3774.

[5]. A. D. Laurent, Y. Houari, P. H. P. R. Carvalho, B. A. D. Neto, D. Jacquemin, RSC Adv., **2014**, *4*, 14189-14192.

[6]. Y. Houari, S. Chibani, D. Jacquemin, A. D. Laurent, J. Phys. Chem. B, **2015**, *119*, 2180-2192.

[7]. P. M. Vérité, C. A. Guido, D. Jacquemin, Phys. Chem. Chem. Phys., **2019**, *21*, 2307-2317. P. M. Vérité, S. Hédé, D. Jacquemin, Phys. Chem. Chem. Phys., **2019**, *21*, 17400-17409.

[8]. T. Pariat, P. M. Vérité, D. Jacquemin, J. Massue, G. Ulrich, Dyes Pigm., **2021**, *190*, 109338.

[9]. A. Chrayteh, C. P. Ewels, D. Jacquemin, Phys. Chem. Chem. Phys., **2020**, *22*, 854-863.