

Evaluation of density-functionals to study the emission spectra of cationic and anionic dyes

F. Bettanin⁽¹⁾, J. R. Perussi⁽²⁾, A.B.F. da Silva⁽²⁾, P. Homem-de-Mello^{(1)*}

(1) SSMA, Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia, 166, CEP 09210-170, Santo Andre, SP, Brazil. paula.mello@ufabc.edu.br

(2) Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil.

* Corresponding author.

Abstract – Due to the important applications of the following dyes: Methylene blue (AM), Toluidine Blue (AT), Thionine (TI), Eosin Y (EO), Erythrosin B (ER), Fluorescein (FR), Acridine orange (LA), Proflavine (PF), Safranin (SF), Rose Bengal (RB), Neutral red (VN), we have performed Density Functional Theory calculations to obtain geometries and emission spectra. The functional that provides the best agreement with experimental spectra will be used to calculate important properties (as dipole and atomic charges) to understand the applications of these molecules.

Cationic and anionic dyes have been studied for different applications, and more recently for photodegradation of organic pollutants, electrocatalyses, solar cells, biosensors and photodynamic therapy. These dyes are also being used as probes in the study of microheterogeneous and biological systems (clays, micelles, vesicles, microemulsions, DNA and nucleosides). This is based on their photophysical and photochemical properties, whose strongly depend on the nature of the surrounding environment. In the specific case of clay, the dyes tend to be adsorbed by the external surfaces of its particles, increasing the local concentration and inducing the aggregation of the dye molecules. Studies on the dye-clay interactions are based on spectrophotometric and fluorescence emission measurements, as the spectral behavior of the dye is modified when adsorbed on clay [1,2].

Aiming to understand the interactions whose promote the spectral changes, we have performed Density Functional calculations for the following dyes: Methylene Blue (AM), Toluidine Blue (AT), Thionine (TI), Eosin Y (EO), Erythrosin B (ER), Fluorescein (FR), Acridine Orange (LA), Proflavine (PF), Safranin (SF), Rose Bengal (RB), Neutral Red (VN).

Every group of dyes consists of a system planar tricyclic aromatic ring. The phenothiazine group (AM, TI and AT) has two heteroatoms in the central ring, one nitrogen and one sulfur. The xanten group (RB, EO, ER and FR) has an oxygen and a aromatic radical in the central ring. The acridin (LA and PF) group has one nitrogen in the central ring and the diazinic group (VN and SF) has two.

We have obtained the geometries of these dyes in singlet (for example, frontier orbitals for EO are presents in Fig. 1) and triplet states with B3LYP functional and DGDZVP basis set. To eliminate possible artifacts of specific density functionals, we are also carrying out calculations by employing LSDA and PBE functionals (as implemented in Gaussian 03 package). The methodology which provides best agreement with experimental spectra will be used to calculate important properties (as dipole and atomic charges) to understand the interactions of these molecules.

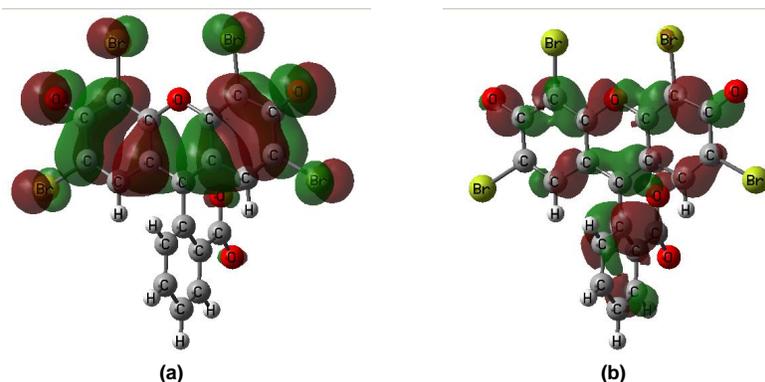


Figure 1: Frontier molecular orbitals for EO singlet state: a) HOMO and b) LUMO.

References

- [1], P. Homem-De-Mello, B. Mennucci; J. Tomasi, A.B.F. Da Silva, *Theor. Chem. Acc* 118 (2007) 305.
[2] M.G. Neumann, C.C. Schmitt, F. Gessner, *J. Colloid Interface Sci.* 177 (1998) 495.