A Theoretical Investigation of Eosin Y, an Organic dye for Photovoltaic Applications

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Eosin Y, 2',4',5',7'-tetrabromofluorescein, is a molecular organic dye particular interesting for the photovoltaic conversion in association with the nanoporous semi-conductors, like ZnO. Such molecule does not only show interesting properties itself, but also play a relevant role in determining the global features of hybrid nanostructured materials. For instance a one-step self assembly of ZnO/Eosin Y by electrodeposition has been recently reported [1].

As it concerns the photovoltaic conversion, the dye is present as a monolayer at the interface between the semiconductor surface (ZnO) and an electrolyte containing a redox pair: the molecule of eosin Y get excited by photons, transfer the excess electron into ZnO, and get reduced back by the redox couple I_3^-/I_2.

Even if the overall macroscopic behavior of such materials is well established, the single elementary steps have to be clarified. In particular, we are interested in the mechanism of the growth of this nanoporous hybrid material and its relationship with the different oxidation states of eosin.

In this context, when intermediate species or single interaction cannot be experimentally characterized or quantified, theoretical models can be useful in the interpretations of experimental evidences. Surprisingly very little theoretical work is available on this topic, despite the potential interest of an advanced quantum chemical approach for a better understanding of key issues, like the nature of both the ground and the excited states involved in the absorption and/or photoemission, role played by reduced/oxidized species and the environmental (solvent and/or crystal) effects.

As first step in an complete theoretical study of this ZnO/Eosin material, we have investigate the physicochemical properties of the dye as well as those of its reduced and oxidized forms.

Particularly accurate methods rooted on Density Functional Theory [2] have been used for quantum calculation on the ground electronic state. Excited states have been next investigated using the Time Dependant DFT (TD-DFT) approach, which we have successfully applied to study similar photovoltaic systems [3].

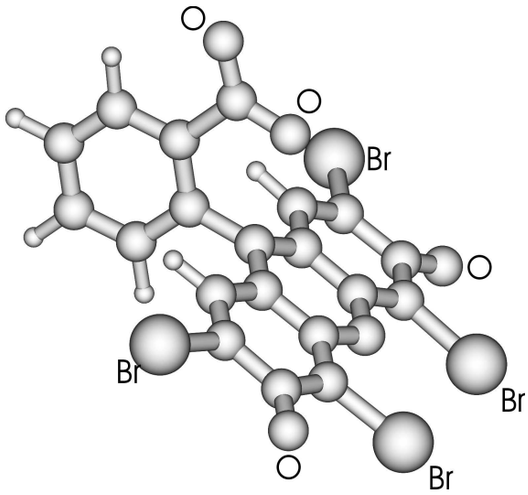

Figure 1. Ground State Structure of Eosin Y.

In particular, our calculations give interesting details about the structural parameters, energetic, spectroscopic (IR) properties as well as electron affinity and ionization potential of such species. We have also shown that a metastable conformation of the eosin is possible, as it has been suggested several years ago [4].

Next, we have considered the interactions of the eosin with Zn^{2+} cation. Here our results explain the strange behavior observed for the eosin Y, either in the neutral or in its reduced and oxidized forms, in aqueous solution containing Zn^{2+}, showed by UV spectra associated with cyclic voltammograms.

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(3) Guillemoles, J.-F.; Barone, V.; Joubert, L.; Adamo, C. *Journal of Physical Chemistry A* **2002**, *106*, 11354 -11360.

(4) Issa, I. M.; Issa, R. M.; Ghoneim, M. M.; Temerk, Y. M. *Electrochimica Acta* **1973**, *18*, 265-270.