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Photophysical Systems for Proton Coupled Electron Transfer

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Abstract – We report a DFT and TD-DFT study to understand how the presence of an intramolecular hydrogen bonding located at the indol-phenoxyl fragment of molecules **1** and **2** modifies the photochemical properties of a sensitizer, facilitating the charge separation after injection of an electron to a TiO_2 surface.

Many nations count on coal, oil and natural gas to supply most of their energy needs, but reliance on non-renewable energy resources presents a big problem, especially fossil fuels which causes air, water and soil pollution, and produce greenhouse gases that contribute to global warming. Renewable energy resources, such as wind, solar and hydropower, offer clean alternatives to fossil fuels. They produce little or no pollution or greenhouse gases, and are available each year, unlike non-renewable resources which are eventually depleted.

The sun is our most powerful source of energy, and by this reason the application of photovoltaic cell has generated much interest recently, due to that has the potential to be a low-cost energy source. Photovoltaic (PV) cells are photoelectrochemical devices that are based on the dye sensitization on thin (10-20 μm) nanocrystalline fims of TiO_2 nanoparticles in contact with a non-aqueous liquid electrolyte, Figure 1, for which certified solar to electric power conversion efficiencies between 10% and 11% have been obtained[1]. Moreover, when ruthenium complexes are employed as sensitizers, these cells show excellent stability, making practical applications feasible[2].

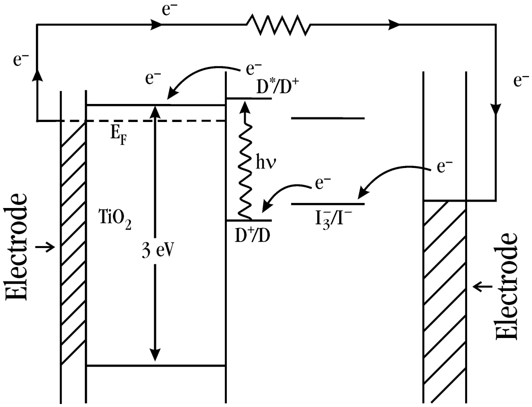

Figure 1: A Photovoltaic (PV) cell Diagram.

The major problems that limit the interconversion efficiencies are: the wavelength range in which the photosensitizer absorbs, the percentage of energy that the photosensitizer can inject to the TiO_2, the efficiency of this injection, the backinjection from the TiO_2 to the photosensitizer and the regeneration of the photosensitizer amongst others.

It is well known that Ruthenium macrocyclic complex containing thiocyanate ligands can absorb light in a large wavelength range, those systems are called Black Dyes[3]. In this way, recent investigations have been focused in the increasing of efficiency of these Black Dyes in PV cells.

On the other hand, a recent study[4] reports the synthesis and functional studies of a bioinspired system, Figure 2a (**1**), in which undergoes a photoinduced electron transfer to a TiO_2 surface coupled to proton motion at the phenolic site. The phenoxyl/phenol couple prevents the reverse injection from the TiO_2, and the system can be recovered in an easier way.

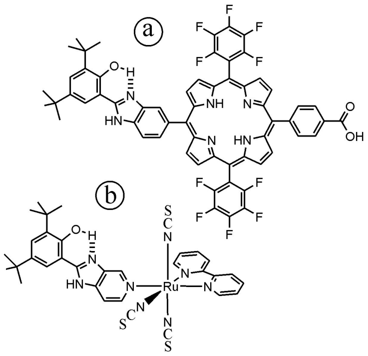

Figure 2: A Bioinspired (a) and a modified Black Dye (b) systems.

Here we explains by means of Density Functional (DFT) and Time Dependent (TD-DFT) methodologies the role of the intramolecular hydrogen bond, and how it affects the photochemical properties of **1**. Also we propose a modified Black Dye system, Figure 2b (**2**), in which the indo-phenolic fragment containing the intramolecular hydrogen bond is included. Also we explain how its presence affects its photochemical properties with the purpose to employ **2** as a sensitizer in PV cells.

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