# Theoretical study of band alignment in nano-porous ZnO interacting with substituted Phthalocyanines

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The aim of this work is the theoretical study of the band alignment between the two components of a hybrid organic-inorganic solar-cell. The working organic molecules are metal tetra-sulphonated phthalocyanines (M-Pc) and the inorganic material is nano-porous ZnO growth in the 001 direction.

The theoretical calculations are being made using the density functional theory (DFT) using a GGA functional with the SIESTA code, which projects electron wave functions and density onto a real space grid and uses as basis set a linear combination of numerical, finite-range localized atomic orbitals. We also used the DFT+U method included in the code that allows a semi-empirical inclusion of electronic correlations in the description of electronic spectra for systems such as zinc oxide.

Basis set were optimized in order to obtain good ground state energies, cell parameters and bond lengths in bulk ZnO. Furthermore C and N basis set were optimized to minimize the energy in the Pc. First the ZnO and the M-Pc's have been studied individually.

For the M-Pc's we study the more stable geometry and the HOMO and LUMO for different metals (Zn and Cu) finding the most reacting part. The molecule is flat except the sulphonic groups which can freely rotate. The effect of these groups on the interaction with the nanostructure appeared to be very important for the bonding and not only for the molecule solubility.

Different ZnO surfaces have been modeled to find the optimal configuration, in their most stable wurtzite phase, and relaxed to find the minimum energy positions. The (001) growth direction was studied, so the available faces to the dyes will be a perpendicular one as the (100).

After that we study the interaction between the two systems and compared the different electronic energy levels. Different parallel and perpendicular orientations have been tested. We have obtained the total and projected density of states of the system and observed the level alignment. The aim was to determine which metal would be theoretically more efficient in the charge transfer between the dye and the nanostructure. A good estimation of band alignments between the adsorbate and the substrate was achieved with DFT+U, using the correlation corrections that gave good spectra for both systems separately. This theoretical study can be seen as a first step to show how charge transfer would be.

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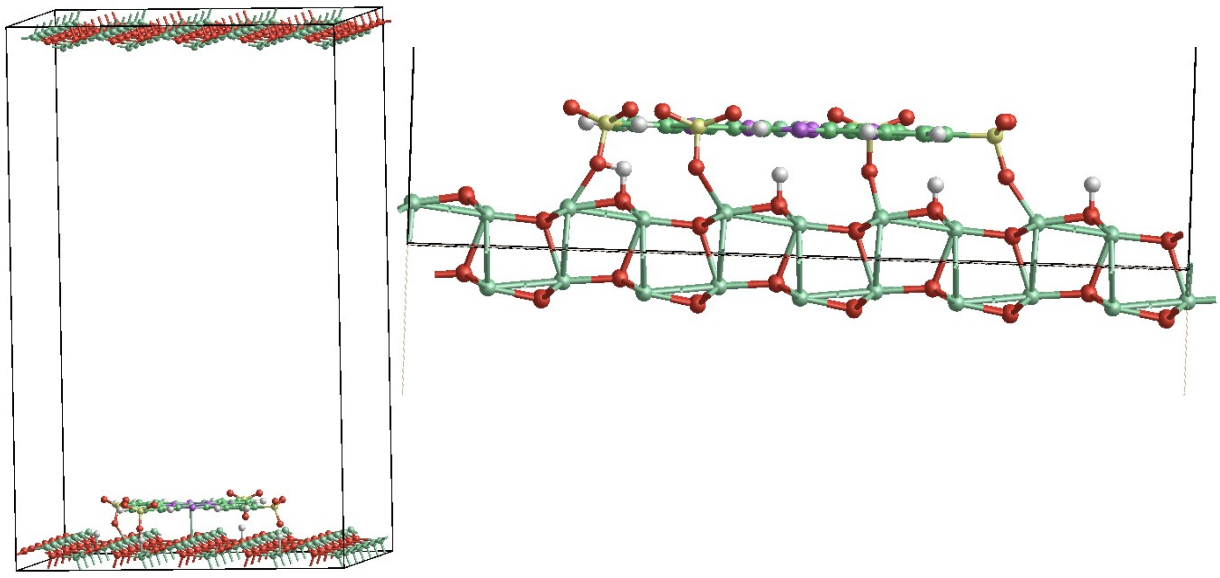
## References

[1] B. Mari, M. Moya, K. C. Singh, M. Mollar, P. Palacios, E. Artacho, P. Wahnon, J. Electroanal. Chem. (2011), doi:10.1016/j.jelechem.2010.12.023.

## Figures



The most stable orientation we expect between the dye and the nano-structure.