ab initio Calculations of the Dye Sensitized Solar Cell system

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Ruthenium based dyes, and specially those casting pyridil ligands, have proven very effective in photovoltaic conversion. Their molecular properties, and the possibilities of related applications, are directly related to: (a) the energetic spectrum of the molecules that determines the optical absorption and emission characteristics; (b) the molecular electron density (and its polarizability) which is associated to the reactivity of the molecule. Not only is it desirable to match the absorption to the solar spectrum in photovoltaic applications, but HOMO and LUMO levels should also be matched to those of the sensitized semiconductor and of the redox couple in the electrolyte. It is also generally favorable to have an absorption coefficient as high as possible in such devices. Surprisingly, very little theoretical work is available on this topic as many of the questions above could benefit from the insight given by advanced quantum computations.
Here we present a study based on DFT formalism of the ground and excited states potential energy surfaces of some Ru(bpy)2L2 (M=Ru, Os; L=CN, SCN). In our treatment time dependent DFT (TDDFT) approach, using the PBE0 model density functional, was applied to compute vertical excitation energies, while the polarizable continuum model (PCM) was considered to mime solvent effects on electronic transitions, with significant influence on the results. Both singulet and triplet exited states could be computed. The dye cation states were also computed. Calculations of the I-/I3- redox couple were carried on enabling the evaluation of the reactivity of the dye/electrolyte system. Finally, TiO2 surfaces were also treated. This model theory does not only allow to reproduce the available experimental data but, more interestingly, offer a trustful tool for the prediction of investigation of new materials and devices.