Ruthenium based dyes: Insights from Density Functional Theory

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Ruthenium based dyes, and especially those casting pyridil ligands, have proven to be very effective in photocatalysis and in photovoltaic conversion [1,2]. Their 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. Both are

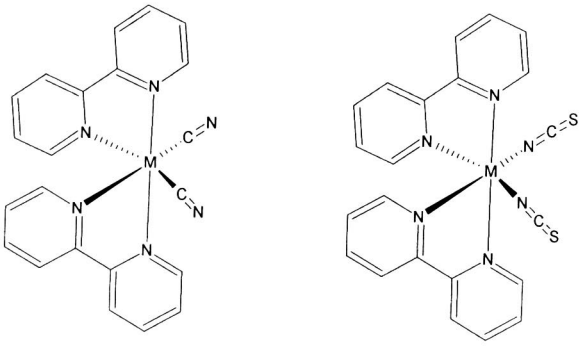

Figure 1. Sketches of the considered Ru and Os complexes.

related to the ability of the dyes to inject (or accept) electrons to (or from) the surface, the most desirable property for photochemical or optoelectronic applications.

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 base on DFT of the ground and excited state potential energy surfaces of $Ru(bpy)_2L_2$ (M=Ru, Os; L=CN,SCN) and of $[Ru(bpy)(tpy)dmso]^{2+}$ complexes, both in the gas phase and in solution.

In our treatment time dependent-DFT (TD-DFT), using the PBE0 model density functional, was applied to computed vertical excitation energies, while the polarizable continuum model (PCM) was considered to mime solvent effects both on structures and on electronic transitions.

This model theory does not only allow to reproduce the avaible experimental data but, more interestingly, offers a trustfull tool for the prediction of investigation of new materials [3,4].

[1] A. Hagfeldt and M. Graetzel, *Acc. Chem. Res.* **2000**, *33*, 269

[2] M. Graetzel and B.O. Reagan, *Nature* **1991**, *353*, 737

[3] J.F. Guillemoles, V. Barone, L. Joubert, and C. Adamo, *Journal of Physical Chemistry A* **2002**, *106*, 11354.

[4] I. Ciofini, C. Daul and C. Adamo, *J. Am. Chem. Soc.*, submitted