

Basis Functions Search for the Electronic Spectra Simulations of Polypyridyl Ruthenium Sensitizers Applied on DSSCs

Rodrigo Fraga de Almeida¹, André Sarto Polo², Luiz Antônio Sodré Costa¹

¹NEQC – Núcleo de Estudos em Química Computacional, UFJF – Universidade Federal de Juiz de Fora, Rua José Lourenço Kelmer, s/n, 36036-900, Juiz de Fora – MG, Brazil.

²POLO GROUP, UFABC - Universidade Federal do ABC, Avenida dos Estados, 5001, 09210-580, Santo André – SP, Brazil.

Abstract: Nowadays there is a great demand for clean energy once the fossil fuels reserves are limited and the use of these fuels pollute the atmosphere bringing negative effects to the planet. The dye-sensitized solar cells (DSSCs) appear to be a solution to this problem because of its low cost and high efficiency when compared to traditional silicon cells [1,2]. Many kinds of molecules may be used as dye or sensitizer in DSSCs, but from all kinds, the most investigated are the ruthenium(II) complexes. They show high chemical stability, intense absorption in a large interval of visible and extending to near infrared electromagnetic spectrum. The use of sensitizers having such characteristics result in DSSCs that exhibit high efficiency and favorable photo-electrochemical properties [3]. The ruthenium complexes studied here are the *cis*-[Ru(R₂-phen)(dcbpy)(NCS)₂], where dcbpy is 2,2'-bipyridine-4,4'-dicarboxylic acid and R₂-phen is 1,10-phenanthroline with R substituents at the positions 4 and 7 [4, 5], an example is shown in figure 1a. Different substituents in these and other positions at the phenanthroline, change the complexes' photo-electrochemical properties, making them better or worse to be used in DSSCs [4, 5]. One of the properties of importance to apply a molecule as a dye in a DSSC, is the absorption of incident electromagnetic radiation with wavelength lower than 920 nm [6]. In this work is presented a computational study based on DFT using B3LYP functional and the basis functions developed by Barros *et al.* for ruthenium [7], only the basis set used for the ligands were changed, among them are 6-31G(d) and 6-31+G(d). These were tested intending to find a good methodology for UV-Vis spectrum simulation of the *cis*-[Ru(R₂-phen)(dcbpy)(NCS)₂] complexes, for R = H, CH₃, Ph, cbz (carbazole). Figure 1b shows the experimental and simulated spectra (using 6-31G(d)) for the Ph substituent. The geometries were optimized in the gas phase and the TD-DFT calculation were done in

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DMF using the SMD solvation model. This methodology was evaluated by the agreement with experimental data obtained from our collaborators from Polo Group (UFABC). The simulated spectra show reasonably good relative band intensities and band shapes when compared to the experimental spectra and for that may be used as a tool to predict the UV-Vis absorption of similar complexes.

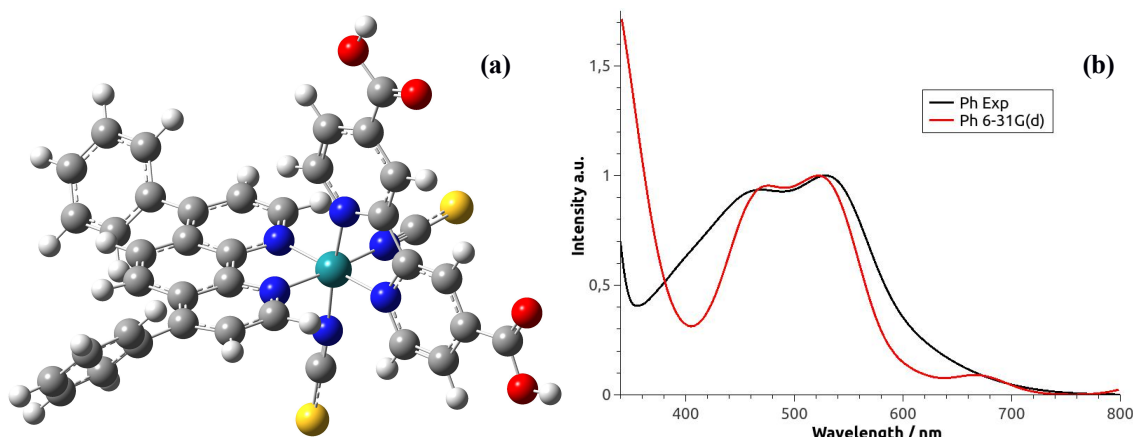


Figure 1. (a) DFT optimized structure of *cis*-[Ru(Ph₂-phen)(dcbpy)(NCS)₂]. (b) Comparison between experimental (black) and calculated (red) UV-Vis spectra.

Key-words: DSSCs, ruthenium(II) sensitizers, DFT, electronic spectra.

Support: FAPEMIG, FAPESP, CNPq

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