

Theoretical studie of porphyrins for application in Dye-Sensitized Solar Cells

Cassiano Minoru Aono (IC), Paula Homem-de-Mello(PQ)
Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, SP, Brasil

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INTRODUCTION

Porphyrins form a promising class of natural dyes to be applied in DSSC (Dye-Sensitized Solar Cells) since they absorb radiation in visible spectra [1]. The conjugated system π cause a shift to visible region of the spectra and works as a bridge connecting donor (D) and acceptor (A) groups, forming the system D- π -A. In this work, we studied porphyrins bonded to different electron donor groups, focusing on the effects of substitution in meso and β position.

METHODS

Density functional theory (DFT) was employed in geometry optimization, as well as to obtain the vibrational frequencies for porphyrins with one acceptor group, BTB, and the following donor groups: hidroxyl, amine (primary and tertiary), methyl, tert-butyl, methoxy and ethyl. We examined the effects of those substitutions, taking into account meso and β positions. To study the electronic excited states, time dependent DFT (TD-DFT) calculations were performed. M06 functional [2] and 6-311G(d,p) basis set were used in all calculations. Solvent effects (THF) were included with IEFPCM.

RESULTS AND DISCUSSION

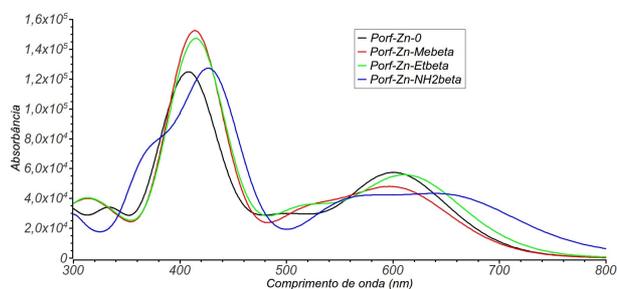


Figure 1: Absorption spectra for studied porphyrins with different substituents in β position

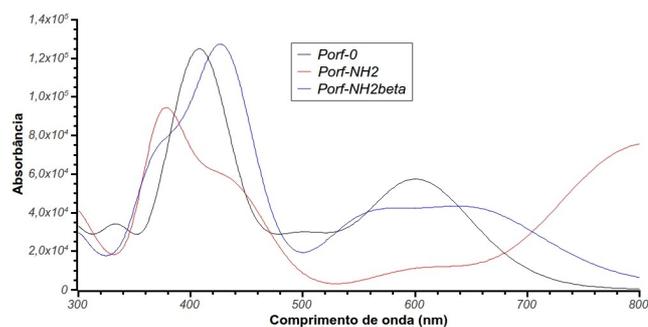


Figure 2: Absorption spectra for porphyrin with -NH₂ in meso and β position

Figure 1 present the absorption spectra obtained for the BTB-porphyrin and for BTB-porphyrin bonded to three different acceptors at β position. These kind of substitution has small effect on the absorption maxima, being the -NH₂ responsible for the most significant shift. On the other hand, substitutions on meso positions have greater effect on the spectra (Fig. 2), since the gap HOMO-LUMO decreases. We observed that this group influences mainly the HOMO energy. This corroborates the red shift in spectra caused by this group and demonstrates his strong donor character. There is a direct correlation between the value of group's Hammett constant and the energy of the orbital.

CONCLUSION

Substitutions on meso positions of porphyrins conducts to greater modifications on absorption spectrum than β substitutions, being the amine groups responsible for the most significant shifts.

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² ZHAO, Y.; TRUHLAR, D. G. Theoretical Chemistry Accounts, v. 120, n. 1-3, p. 215–241, 2007;