DFT Studies on the Hyperpolarizabilities of Organometallic Complexes Containing Nitrile Thienyl Derived Ligands

P. Tropecêlo[1], A.J. Carvalho[1], P.J. Mendes[1]

[1]Centro de Química de Évora e Departamento de Química da ECTUE

pedrotro@gmail.com

The research of nonlinear optical (NLO) materials has grown in the past decades due to the potential application in optical device technology, like data storage, communication and bio-sensing. [1] For obtaining large molecular second-order nonlinear optical (SONLO) responses, i.e. large hyperpolarizabilities (β), molecules have to possess typical "push-pull" asymmetric structures. Organometallic complexes presenting heterocyclic organic chromophores have proven to be promising systems in this field. For instance, η5-monocyclopentadienylruthenium(II) and iron(II) complexes containing 1,2-di-(2-thienyl)-ethene and oligothiophene nitrile derived ligands have been studied for this purpose. [2-4] However additional studies using Density Functional Theory (DFT) were found to be very useful in order to understand the SONLO mechanism in these complexes.

This work presents a DFT study on the optical properties and quadratic hyperpolarizabilities (β) of η5-monocyclopentadienyliron(II) and ruthenium(II) complexes containing the cited nitrile derived ligands as chromophores. An attempt to correlate the SONLO properties with the features of the calculated electronic structure and UV/Vis spectra of those complexes, in particular the lowest energy electronic transitions, will be performed. The elucidation of the most important electronic properties determining large β may guide the design of new molecules with interesting NLO properties.

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