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Ninth triennial congress of the
**WORLD ASSOCIATION
OF THEORETICAL AND
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Santiago de Compostela (Spain)
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posters

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**Organometallic Complexes for Non-Linear Optical Switching:
DFT Evaluation of the B3LYP, CAM-B3LYP and M06 Functionals**

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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. For obtaining large molecular second-order nonlinear optical (SONLO) responses, *i.e.* large hyperpolarizabilities (β), molecules have to possess typical “*push-pull*” asymmetric structures. η^5 -Monocyclopentadienylruthenium(II) and iron(II) complexes presenting heterocyclic organic chromophores have proven to be promising systems in this field [1,2]. The presence of a transition metal suggests that it is possible to switch the SONLO response of the material by changing its oxidation state, by electrochemical means for example. In this case, two distinct forms would be expected: the “*switched-on*” form, with high β value; and the “*switched-off*” form, with negligible or substantially lower β . The use of SONLO properties of organotransition metal complexes in view of the molecular switching has attracted a considerable interest [3].

Herein, we show the application of Density Functional Theory (DFT) to the studies of SONLO properties of two organometallic complexes bearing a benzo[c]thiophene organic ligand as active NLO chromophore. In order to evaluate the structure-activity relationships and to obtain a validation of the theoretical approach, three different exchange-correlation functionals were tested and the results were compared to experimental Hyper-Rayleigh Scattering measurements. Redox studies on organometallic complexes and organic ligand were performed for the enlightenment of the changes in the electronic density and hence in the factors involved in SONLO switching properties.

References:

- [1] – M. H. Garcia, P. Florindo, *Nova Science Publishers, Inc.*, New York, **2009** (accepted)
- [2] – Paulo J. G. Mendes, T. J. L. Silva, J. P. Prates Ramalho, A. J. Palace Carvalho, *J. Mol. Struct.: THEOCHEM*, 946, **2010**, 1-3, 33-42
- [3] – Benjamin Coe, *Acc. Chem. Res.*, 39, **2006**, 383-393