

DFT Conformational Studies on Ruthenium (II) Complexes: Dependence of the First Hyperpolarizability with Planarity of the Conjugated System

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Organometallic complexes find several applications in modern chemistry, ranging from catalytic systems, bioinorganic drugs and materials chemistry. Concerning the latter, great deal of attention has been made on the optical properties of compounds containing transition metals like ruthenium and iron. The incorporation of these organometallic fragments in the development of new and highly active optical devices has been very successful, often overcoming the existing organic compounds. [1]

We recently reported the Non-Linear Optical (NLO) properties of thienyl iron (II), ruthenium (II) and nickel (II) acetylide complexes where it was shown, by means of experimental data and Density Functional Theory (DFT) methods, that these groups of complexes present very good second harmonic generation properties, in particular those having two thienyl rings as conjugated system. [2] Nevertheless, and as far as we are aware, until the present date the orientational averaging of the possible conformers of such molecules in solution was never studied. Thereby in this work we present a first attempt to understand the total contribution of different conformers, using DFT, to the observed experimental value of the first hyperpolarizability, measured by Hyper Rayleigh Scattering. Both the results in gas-phase and in solution show that the highest hyperpolarizability is not achieved by a full planar conjugated system as expected, but when the dihedral angle between the thiophene rings is 30° or even 60°. However, a simple Boltzmann population analysis showed that these conformations have less than 14% and 9% occurrence probability, in gas-phase or solvated case respectively, and hence its contribution for the total hyperpolarizability is relatively low.

[1] a) H. Bozec, V. Guerschais, *Molecular Organometallic Materials for Optics (Topics in Organometallic Chemistry)*, Springer, vol. 28, **2010**; b) M. H. Garcia *et al.*, *Handbook of Advanced Electronic and Photonic Materials and Devices*, chap. 9, **2001**, 127-191

[2] Tiago J. L. Silva, Paulo J. Mendes, Ana M. Santos, M. Helena Garcia, M. Paula Robalo, J. P. Prates Ramalho, A. J. Palace Carvalho, Marina Büchert, Christian Wittenburg, Jürgen Heck, *Organometallics*, *submitted*

Acknowledgements: The authors thank the FCT for funding of the project FCOMP-01-0124-FEDER-007433. Tiago Silva is also grateful for his PhD grant.