



## RUTHENIUM COMPLEXES FOR SONLO: DFT CALCULATIONS OF THE MOLECULAR HYPERPOLARIZABILITY

Tiago J.L. Silva, Paulo J. Mendes and A. J. P. Carvalho

Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671  
Évora, Portugal  
tjlsilva@gmail.com

Nonlinear optical (NLO) materials are of considerable interest because of their possible applications in the emerging technologies of optoelectronic and photonic devices. Fundamental research in this area has been focused in the establishment of detailed structure–activity correlations for first hyperpolarizability ( $\beta$ ), which govern SONLO effects, in view to obtain large intrinsic optical nonlinearities. A combination of fast response time, low-lying intense metal-to-ligand or ligand-to-metal charge transfer (MLCT or LMCT) transitions, and the potential of variable oxidation state, d-electron count, and ligand environment in tuning NLO performance make organometallics very promising systems for nonlinear optics. Organometallic fragments have been demonstrated to be able to act as potential electron donors or electron acceptors in second-order nonlinear optical chromophores. Among organometallic electron donors, CpM(L)<sub>2</sub> (M=Fe, Ru; L=phosphines) moieties seem to be promising candidates. Coplanarity of the metals and the  $\pi$ -electrons of the thiophene-based ligands was suggested to be valuable for second-order optical nonlinearity [1-2]. Theoretical studies using time-dependent density functional theory (TD-DFT) method within the DFT frame has been used to calculate accurately the excited energy and first hyperpolarizabilities of organometallic complexes. These theoretical studies are very useful for a better understanding on the electronic factors that may be responsible for the SONLO properties in order to fine tuning the electronic properties of new compounds. Also, they can be used as a guideline to the molecular design and the time consuming synthetic work. Recently, TD-DFT studies on  $\square^5$ -monocyclopentadienyliron(II) and nickel (II) complexes with substituted thienyl-acetylide ligands has shown a linear dependence of the first hyperpolarizability with the wavelength of the lowest energy electronic transition. Also, it was possible to confirm the better ability of the iron moiety to induce large hyperpolarizabilities [3-4].

We report therein the results of DFT and TD-DFT calculations on the model complexes [RuCp(H<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PH<sub>2</sub>)(CC{SC<sub>4</sub>H<sub>2</sub>}Y)] (Y=NMe<sub>2</sub>, NH<sub>2</sub>, OMe, H, CHO, CN, NO<sub>2</sub>) in view to predict the corresponding first static hyperpolarizabilities and to study the role played by the ruthenium organometallic fragment on the SONLO properties of these complexes. A quantitative correlation with optical data is used in order to compare the results with those found in parent iron and nickel derivatives studies.

### References

- [1] M. Helena Garcia, Paulo J. Mendes, M. Paula Robalo, A. Romão Dias, Jochen Campo, Wim Wenseleers, Etienne Goovaerts, *J. Organomet. Chem.* (2007) 692, 3027-3041
- [2] Clem E. Powell, Mark G. Humphrey, *Coord. Chem. Rev.* (2004) 248, 725-756
- [3] Paulo J. Mendes, A.J.P. Carvalho, J.P. Ramalho, *J. Mol. Struct. Theochem* (manuscript in prep.)
- [4] Paulo J. Mendes, A.J.P. Carvalho, Ana Barrocas, *unpublished results*

### Acknowledgements

This work was funded by Fundação para a Ciência e Tecnologia (Centro de Química de Évora Pluriannual Funding)