

## NONLINEAR OPTICAL PROPERTIES OF $\eta^5$ -MONOCYCLOPENTADIENYLIRON COMPLEXES FROM DFT CALCULATIONS

P. Mendes<sup>a</sup>, J.P. Prates Ramalho<sup>b</sup>, A. Candeias<sup>a</sup>, M.H. Garcia<sup>c</sup>, M.P. Robalo<sup>c</sup>

<sup>a</sup>*Centro de Química de Évora, Departamento de Química da Universidade de Évora, Colégio Luís António Verney, Rua Romão Ramalho 59, 7000-671 Évora, PORTUGAL*

<sup>b</sup>*Universidade de Évora, Departamento de Química, Rua Romão Ramalho 59, 7000-671 Évora, PORTUGAL*

<sup>c</sup>*Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa Codex, PORTUGAL*

Recently, organometallic complexes have emerged as potential building blocks for second-order nonlinear optical (SONLO) materials in view of their potential application in the area of integrated optics [1]. Unlike organic molecules, whose optical nonlinearities have been extensively studied by computational methodologies using both semi-empirical and ab initio methods, organometallic systems have received much less attention due to the difficulty in the calculation of reliable hyperpolarizabilities in the presence of transition metal atoms. ZINDO has been the most widely used program to calculate SONLO coefficients of organometallic compounds. A more reliable approach, using the density functional theory (DFT) method is less explored but has been increased in the recent years.

Experimental work on  $\eta^5$ -monocyclopentadienyliron complexes with *p*-nitro benzonitrile ligands showed that the first hyperpolarizability decreases with increasing conjugation length of the chromophores [2]. EHMO calculations performed on model complexes  $[\text{FeCp}(\text{PH}_3)_2(p\text{-NCR})]^+$  confirms this behavior and showed that the larger values of experimental hyperpolarizabilities correspond to lower HOMO-LUMO gaps [3]. For similar complexes possessing a thiophene based conjugated backbone, a dramatic increase in experimental first hyperpolarizability with increasing conjugation length was observed [4]. The explanation of this different behaviour was not definitively established. In order to get a better understanding on the electronic factors that may be responsible for the SONLO behavior of these compounds and their correlation with experimental spectroscopic and electrochemical data, high accuracy DFT calculations using GAMESS-US were made in model complexes  $[\text{FeCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)]^+$  ( $n=1-3$ ). Spatial localization of electron charge as been performed to gain insight into the nature of the chromophores binding to the metal center. First static hyperpolarizability was calculated, compared with experimental results and correlated to the HOMO-LUMO gaps.

[1] E. Goovaerts, W.E. Wenseleers, M.H. Garcia, G.H. Cross, *Handbook of Advanced Electronic and Photonic Materials*, Ed. H.S. Nalwa, **2001**, Vol. 9, Ch. 3, 127-191

[2] W. Wenseleers, A.W. Gerbrandij, E. Goovaerts, M.H. Garcia, M. Paula Robalo, Paulo J. Mendes, João C. Rodrigues, A.R. Dias, *J. Mater. Chem.*, **1998**, 8, 925-930

[3] M.H. Garcia, M.P. Robalo, A.R. Dias, M. Fátima M. Piedade, Adelino Galvão, W. Wenseleers, E. Goovaerts, *J. Organomet. Chem.*, **2001**, 619, 252-264

[4] W. Wenseleers, E. Goovaerts, A. Bouwen, M.H. Garcia, M.P. Robalo, P.J. Mendes, A.R. Dias, *Dissertation Abstracts Internat.*, **2000**, B60, 4038

e-mail: pjgm@uevora.pt