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## STUDIES ON SONLO PROPERTIES OF HALF-SANDWICH COMPLEXES USING TD-DFT CALCULATIONS

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During the last decades there's been a growing interest in the use of organometallic complexes as potential building blocks for second-order nonlinear optical (SONLO) materials, namely for photonics and integrated optics applications [1].  $\eta^5$ -Monocyclopentadienylmetal complexes are known to be good candidates for SONLO purposes. Systematic studies in these systems give the basis to predict that the combination of substituted acetylide thiophene chromophores with ruthenium and iron metal centers can enhance the first hyperpolarizability [2,3]. Also, it is well known that the first hyperpolarizability of purely organic push-pull molecules increases strongly with the length of the conjugated chain. Nevertheless, the exploitation of this effect in several  $\eta^5$ -monocyclopentadienylmetal complexes showed contradictory results. The time-dependent density functional theory (TD-DFT) method within the DFT frame provides the satisfactory molecular orbital explanation for the electronic excitation, which is usually recommended for calculating the excited-state behaviours. In the case of organometallic complexes, the TDDFT method is one of the most suitable choices to calculate accurately the excited energy and first hyperpolarizabilities.

In this work we used the TD-DFT method to study the first hyperpolarizabilities of  $[\text{MCp}(\text{P}_\text{P})(\text{CC}\{\text{SC}_4\text{H}_2\}_n\text{Y})]$  complexes ( $\text{M}=\text{Ru}, \text{Fe}$ ;  $\text{P}_\text{P}=\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2, \text{DPPE}$ ;  $\text{Y}=\text{CHO}, \text{NO}_2$ ;  $n=1,2$ ) (Figure 1). The effect of the bidentate phosphine, different electron-withdrawing groups and the conjugated length of the chromophore will be evaluated. Our interest is not only to predict the  $\beta$  values but also to investigate the microscopic SONLO mechanism in these complexes.

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- [2] M.H. Garcia, M.P. Robalo, A.R. Dias, M.T. Duarte, W. Wenseleers, G. Aerts, E. Goovaerts, M.P. Cifuentes, S. Hurst, M.G. Humphrey, M. Samoc,; B.L. Davies. *Organometallics* 21 (2002) 2107.
- [3] M.H. Garcia, P.J. Mendes, M.P. Robalo, A.R. Dias, J. Campo, W. Wenseleers, E. Goovaerts. *J. Organomet. Chem.* 692 (2007) 3027.