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PROGRAMME



Monocyclopentadienyliron (II) and Ruthenium (II) Complexes for NLO Switching

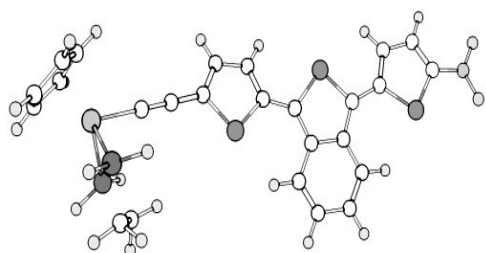
Silva, Tiago J. L., Lisbon/pt, Mendes, Paulo J., Évora/pt, Garcia, M. Helena, Lisbon/pt

Tiago J. L. Silva, University of Lisbon, Campo Grande, 1049-001 Lisbon, Portugal

The limitations on semiconductor-based electronics have inspired many researchers on the development of new photonic molecular materials possessing faster and more accurate responses to external electric or optical stimulus. Non-linear optics (NLO) involves manipulation of laser beams and therefore can be used for electro-optic signaling and data processing. The two most used effects in NLO for these purposes are second harmonic generation (SHG) and frequency doubling, both producing high intensity green laser beams.^[1]

Due to their electronic properties, synthetic tailorability and enhanced stability, monocyclopentadienylmetal complexes of group VIII containing aromatic organic chromophores have proven interesting potentialities for NLO applications, namely SHG. Our recent studies have shown that combining both iron (II) and ruthenium (II) organometallic fragments with acetylide or nitrile thiophene chromophores, the static hyperpolarizability (β_0), related to the SHG signal, will be drastically enhanced by: 1) increasing the metal-to-ligand charge transfer (MLCT); 2) lowering the redox potential of the metal center; 3) increasing the electronic delocalization in the organic chromophore.^[2]

Our ongoing work on the molecular NLO-switching properties of Fe(II) and Ru(II) monocyclopentadienyl compounds, was attracted by benzo[c]thiophene based chromophores, which unique electronic behavior originated by their low HOMO–LUMO gaps, can be potentially on the basis of strong NLO effects.^[3]



This communication presents the synthesis, the electrochemical and the spectroscopic characterization of monocyclopentadienyliron(II)/ruthenium(II) derivatives containing acetylide and nitrile benzo[c]thiophene organic chromophores. Theoretical studies predicting the NLO and switching properties are presented, by the use of Density

Functional Theory (DFT) and Time-Dependent DFT studies. Results will be discussed in order to relate the predicted NLO properties with the spectroscopic and electrochemical data, which can be used, eventually, as an experimental probe.

[1] Coe, Benjamin, *Acc. Chem. Res.*, **2006**, *39*, 383-393. [2] a) Garcia, M. H., *et al*, *J. Organomet. Chem.*, **2009**, *694*, 433. b) Mendes, P. *et al*, *J. Mol. Struct.: THEOCHEM*, **2010**, *946*, 33. c) Mendes, P. *et al*, *J. Mol. Struct.: THEOCHEM*, **2009**, *900*, 110. [3] Friesbie, D. *et al*, *Macromolecules* **2008**, *41*, 5563.