

First Hyperpolarizabilities of η^5 -Monocyclopentadienylmetal Complexes from DFT Calculations

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Organometallic complexes have been studied as potential building blocks for second-order nonlinear optical (SONLO) materials in view of their potential application in the area of integrated optics [1]. Experimental work on η^5 -monocyclopentadienylmetal complexes with benzene based chromophores showed that the first hyperpolarizability decreases with increasing conjugation length of the chromophores [2]. For similar η^5 -monocyclopentadienyliron complexes possessing thiophene based conjugated backbone, an inverse trend on experimental first hyperpolarizability with increasing conjugation length was observed [3]. In addition, the effect of the metal center on the first hyperpolarizability on η^5 -monocyclopentadienylmetal complexes with benzene based chromophores follow the order $\text{Co} < \text{Ni} < \text{Ru} < \text{Fe}$ [2]. No experimental results for the similar complexes containing thiophene chromophores have been yet obtained.

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 crystallographic, spectroscopic and electrochemical data, DFT calculations using the GAMESS-US [4] package were made in model complexes $[\text{MCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)]^+$ ($\text{M}=\text{Fe}, \text{Ru}; n=1-2$). Spatial localization of electron charge has been performed to gain insight into the nature of the chromophores binding to the metal center. First static hyperpolarizabilities has been calculated and correlated to the HOMO-LUMO gaps.

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