

Density Functional Theory Calculations on η^5 -Monocyclopentadienylmetal Complexes with Conjugated Nitrile Chromophores.

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During the past decade, the interest on organometallic compounds for the development of novel nonlinear optical (NLO) materials with large second-order nonlinearities has considerably increased in view of their potential application in the area of integrated optics [1]. Experimental and computational investigations utilizing quantum theory afforded useful insights concerning the molecular structural requirements necessary to induce large second-order nonlinearity response. The strategy to obtain these properties has been the synthesis of compounds with highly polarizable asymmetric structures through the existence of delocalized electronic system bridge (chromophore) between an electron-withdrawing and electron-donating group. Recent experimental work on η^5 -monocyclopentadienylmetal complexes with *p*-substituted benzonitrile and oligothiophene nitrile chromophores showed a correlation between the first hyperpolarizability (β) and the communicability between the chromophores and the organometallic fragments [2]. In addition, some EHMO calculations on nickel and iron complexes had corroborated that the larger values of experimental hyperpolarizability correspond to lower HOMO-LUMO gaps [3].

In order to get a better understanding on the electronic factors that may be responsible for the second-order nonlinear optical behavior of $[\text{CoCp}(\text{dppe})(p\text{-NCC}_6\text{H}_4\text{R})]^{2+}$ and $[\text{FeCp}(\text{dppe})(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)]^+$ complexes and their correlation with experimental spectroscopic and electrochemical data, density functional theory calculations were made in the model complexes $[\text{CoCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(p\text{-NCC}_6\text{H}_4\text{R})]^{2+}$ and $[\text{FeCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{NC}\{\text{SC}_4\text{H}_2\}_n\text{NO}_2)]^+$ ($n=1,2$). Especial emphasis was given to the HOMO-LUMO gaps and their character. Spatial localization of electron charge by means of topological analysis of the electron localization function (ELF) as been performed to gain insight into the nature of the chromophores binding to the metal centers.

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