

First hyperpolarizabilities of half-sandwich iron (II) complexes with thiophene acetylide ligands: a DFT study

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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 -monocyclopentadienyliron(II) complexes with acetylide and nitrile benzene-based chromophores showed that acetylides have higher first hyperpolarizabilities (β) than the corresponding nitriles.² Also, studies on a series of similar complexes with substituted oligo-thiophene nitrile ligands showed that these complexes have better NLO properties than the corresponding benzenoid structures.³ These results suggest that combination of acetylide thiophene ligands with η^5 -monocyclopentadienyliron moiety would maximize the NLO response.

In order to predict the first hyperpolarizabilities and for a better understanding on the electronic factors that may be responsible for the second-order nonlinear optical behavior of η^5 -monocyclopentadienyliron(II) complexes with substituted thienyl-acetylide ligands, density functional theory (DFT) based calculations as well as time dependent DFT (for the prediction of UV/Vis absorption spectra) were performed for the model complexes $[\text{FeCp}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{CC}\{\text{SC}_4\text{H}_2\}\text{Y})]$ ($\text{Y}=\text{NMe}_2$, NH_2 , OMe , H , Br , CHO , CN , NO_2). Spatial localization of electron charge by means of topological analysis of the electron localization functions (ELF) has been performed to gain insight into the nature of bonding between the acetylide ligands and the organometallic moiety. Calculations were also made in the free acetylide ligands in order to study the role played by the organometallic fragment in the second-order NLO properties of the studied complexes.

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