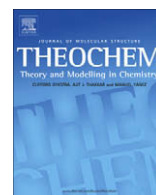




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Role played by the organometallic fragment on the first hyperpolarizability of iron–acetylide complexes: A TD-DFT study

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ABSTRACT

The static first hyperpolarizabilities (β) for a series of both substituted thiophene-acetylide ligands and the corresponding η^5 -monocyclopentadienyliron(II) complexes were determined by density functional theory (DFT) calculations. The effect on the hyperpolarizabilities by various donor and acceptor substituents in the thiophene-acetylide ligands was studied. The nature and role of the electronic excitation contributions to the first hyperpolarizability, using time-dependent DFT (TD-DFT) calculations, are rationalized in terms of the two-level model. Our calculations show that the organometallic fragment can form a very effective push-pull system in combination with electron-withdrawing substituents in the thiophene-acetylide moiety, leading to enhanced static first hyperpolarizabilities. Also, an improvement of the magnitude of β is expected if solvation effects are taken into account.

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1. Introduction

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]. In order to obtain large intrinsic second-order optical nonlinearities, fundamental research has been focused in the establishment of detailed structure–activity correlation. The key to these properties is the existence of strong intramolecular charge transfer excitations in a noncentrosymmetric molecular environment. Thus, strongly asymmetric systems are needed, that lead to the development of typical push-pull donor (D)– π bridge-acceptor (A) systems in which the metal centre, bonded to a highly polarizable conjugated chromophore, acts as an electron-releasing or electron-withdrawing group. With this structural characteristic, large quadratic hyperpolarizabilities arise from intense low energy metal-to-ligand charge transfer (MLCT), ligand-to-metal (LMCT), or intraligand charge transfer (ILCT) excitations. Among the organometallic compounds presenting this structural feature, systematic studies were made on half-sandwich complexes with benzene-based ligands bound to the metal centre via nitrile or acetylide linkages [1–5]. The results revealed that electron-rich CpFe(L)₂ (Cp = η^5 -C₅H₅; L = phosphine) moieties seem to be promising candidates as organometallic electron-donors since these iron-acetylide/nitrile complexes show significant second-order nonlinearities [2–5]. Among these, the compounds possessing acetylide

ligands revealed better SONLO properties than the nitrile analogues, probably due to more favourable metal–ligand π -backbonding interaction.

In the continuation of designing second-order nonlinear optical materials, the attention was focused on the thiophene moiety which has been successfully used in organic chromophores [6–9]. Thiophene chromophores are known to provide a higher level of electronic coupling than benzenoid-based structures because of their more effective electron delocalization (due to reduced aromaticity as compared to benzene), thus yielding a good basis for high second-order NLO responses. Recently, η^5 -monocyclopentadienyliron(II) complexes with substituted thiophene nitrile ligands showed, in fact, an enhanced NLO performance when compared to that observed on analogue benzenoid structures [10]. The overall results suggest that the combination of acetylide thiophene ligands with the best organometallic donor η^5 -monocyclopentadienyliron(II) moiety would maximize the SONLO response of this half-sandwich transition metal family of compounds.

It is well known that theoretical semi-empirical and *ab initio* methods are very useful for fine tuning the electronic properties of new compounds and can be used as a guideline to the molecular design and the time consuming synthetic work. The ZINDO method has been the most widely used semi-empirical method to calculate SONLO coefficients of organometallic compounds [11–15]. At present, the time-dependent density functional theory (TD-DFT) method provides a more satisfactory molecular orbital description of processes involving electronic transitions. In the recent years, this method has been increasingly used to accurately calculate first hyperpolarizabilities of organometallic complexes [16–25].

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