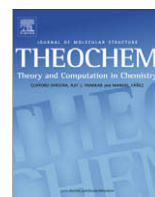




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## DFT studies on thiophene acetylide Ru(II) complexes for nonlinear optics: Structure–function relationships and solvent effects

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## ABSTRACT

Density functional theory (DFT) calculations were employed to investigate the second-order nonlinear optical (SONLO) properties of  $\eta^5$ -monocyclopentadienylruthenium(II) thiophene acetylide complexes. From molecular structure, electronic states, and optical absorption spectra, we have studied the effect of donor or acceptor substituents in thiophene ligands on their first hyperpolarizabilities in vacuum. Calculations in solvated media have also been performed for the complex with the highest first hyperpolarizability obtained in vacuum. The results reveal a significant influence of solvation on the first hyperpolarizability of this compound. The improvement of the second-order nonlinear optical properties in solvated media is due not only to the change of the excitation energies but also to the increase of ground-state molecular polarization and efficiency of metal-to-ligand charge transfer for electronic excitations.

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## 1. Introduction

The design of new organometallic materials with large second-order nonlinear optical properties (SONLO) is currently the subject of extensive research both by theoretical and experimental methods, since they have an important application in the area of integrated optics [1–17]. Usually, compounds possessing large molecular first hyperpolarizability,  $\beta$ , contain donor (D) and acceptor (A) groups linked through a  $\pi$ -backbone. The NLO properties of such polarizable dipolar compounds are caused by intense, lower-energy donor-to-acceptor charge-transfer (CT) transitions. In case of metallo-organic compounds, the metal centre can be bound to a highly polarizable conjugated backbone, acting hence as an electron releasing or withdrawing group. Consequently, strong charge-transfer transitions can occur, leading to high molecular first hyperpolarizabilities ( $\beta$ ). This is the case of the general family of  $\eta^5$ -monocyclopentadienylruthenium/iron(II) complexes presenting benzene- or thiophene-based conjugated ligands coordinated to the metal centre through nitrile or acetylide linkages [18–26], that showed to be much more efficient donor groups for second-order NLO purposes than the traditional organic donor groups. The results suggest that combination of acetylide thiophene ligands with appropriate organometallic fragments would maximize

the second-order NLO response. Our recent experimental results on thiophene acetylide  $\eta^5$ -monocyclopentadienylruthenium(II) [27] derivatives show, in fact, adequate spectroscopic properties for second-order NLO purposes (the measurements of the experimental properties are currently in progress). Also, our recent time-dependent density functional theory (TD-DFT) studies on  $\eta^5$ -monocyclopentadienyliron(II) complexes with substituted thiophene-acetylide ligands gave an insight on the electronic factors that may be responsible for the SONLO properties [28]. Several studies have indicated that the calculated hyperpolarizabilities using the TD-DFT approach match very well with experimental trends [29–35] and this method has been increasingly used to accurately calculate first hyperpolarizabilities of organometallic complexes [5,6,10,11,36–41]. Nevertheless, the majority is lacking in the considerations of the environment effects, namely, the solvation interactions that in some cases are critical for obtaining quantitatively satisfactory results of both the electronic excitations and the first hyperpolarizabilities in comparison with the experimental results. In fact, it is well-known that the solvent polarity influences both the structure and optical properties of conjugated organic molecules and metal complexes and, therefore, their NLO properties. In recent years, however, this subject is attracting increasing attention and several publications have been devoted to the study of solvation effects on the hyperpolarizabilities of organic molecules and organometallic complexes [33,41–44].

In our continuous effort to get a better understanding on the electronic factors that may dictate the SONLO properties of  $\eta^5$ -monocyclopentadienylmetal complexes, we report herein a TD-DFT study

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