STRUCTURE-SONLO PROPERTY RELATIONSHIP ON NICKEL COMPLEXES: A TD-DFT STUDY

Ana Barrocas, Paulo J. Mendes and A. J. P. Carvalho

Centro de Química de Évora, Universidade de Évora, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal

E-mail: ana.filipa.barrocas@gmail.com

The search on organometallic compounds for the development of novel nonlinear optical (NLO) materials with large second-order nonlinearities (SONLO) is currently the subject of significant interest in view of their potential application in the area of integrated optics [1]. Experimental and computational systematic studies were made on half-sandwich organometallic complexes presenting the typical push-pull feature in which the metal centre, bound to a highly polarizable conjugated backbone, acts as an electron-releasing or withdrawing group. With this feature, large quadratic hyperpolarizabilities arise from small energy gaps between excited and ground states, large changes in dipole moment upon molecular excitation and large transition dipole moments. The results revealed that η^5-monocyclopentadienylmetal organometallic moieties can be very efficient electron-donor groups in complexes presenting thiophene-based ligands with a nitro group as an electron acceptor [2-4]. Nevertheless, the understanding of the relationship between the structure and experimental molecular NLO phenomena is not completely clear, namely the effect of the conjugation length of the chromophores. The time-dependent density functional theory (TD-DFT) method within the DFT frame provides the satisfactory molecular orbital explanation for the electronic excitation, which is usually recommended for calculating the excited-state behaviours. In the case of organometallic complexes, the TD-DFT method is one of the most suitable choices to calculate accurately the excited energy and first hyperpolarizabilities.

In order to contribute to a clarification on the molecular organometallic structure-SONLO properties relationship and to enhance the SONLO performance of half-sandwich complexes with substituted thienyl chromophores, we report herein a DFT and TD-DFT study on the nickel complexes $[Ni(\eta^5-C_5Y_5)(PR_3)(XC\{SC_4H_2\}_nNO_2)]$ and $[Ni(\eta^5-C_5H_5)(PH_3)(CC\{SC_4H\}(NO_2)_2]$ (Y=H, Me; R=H, Ph; X= N, C; n=1,2) using the Gaussian03W program package. The effect of different monocyclopentadienyl and phosphine co-ligands, the conjugated length of the chromophore and its coordination mode to the metal centre and the number of nitro substitutents on the first hyperpolarizability will be evaluated.

References

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