

## DFT investigation of the Optical Properties of Isoalloxazine Macrocyclical Derivatives

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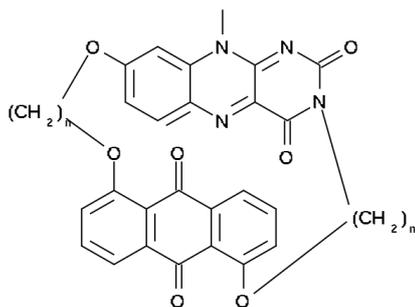
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Keywords: Flavin derivatives, DFT, NLO, Rayleigh scattering

### INTRODUCTION

Organic materials are specially attractive for the design of optoelectronic devices since their electronic and optical properties can be easily modulated from chemical manipulation.<sup>1</sup> Additionally, they present better integration with the conventional microelectronic in comparison with the major photonic materials based on inorganic compounds.<sup>1</sup> In the research of materials with large non-linear optical response (NLO), the recognition of organic molecules that have higher molecular dipole moment and donor–acceptor electron systems (push-pull) is important.<sup>1</sup> In this sense, this work presents the investigation of the polarizability, the first hyperpolarizability and the depolarized light scattering of two isoalloxazine-anthraquinone adducts<sup>2</sup> (Figure 1) through DFT calculations.



**Figure 1.** Molecular structure of the MQ4 (n=4) and MQ6 (n=6) macrocycles.

### METHODS

The molecular geometry and all properties were obtained at M06-2X/6-311++G\*\* theory level. Vertical electronic transitions were computed using a TD-DFT approach and the solvent effect included by the polarized continuum model ( $\epsilon=8.93$ ). The static first hyperpolarizability ( $\beta_0$ ), the projection of  $\beta$  on the dipole moment direction ( $\beta_{vec}$ ), as well as the Rayleigh scattering activities ( $R_{\parallel}$  and  $R_{\perp}$ )

were computed in the CPKS approach. Additionally, the Two Level Model (TLM) was also taken into account in the analysis of the first hyperpolarizability.<sup>1</sup>

### RESULTS AND DISCUSSION

TD-DFT calculations reveals a charge transference (CT) process involving the HOMO-LUMO excitation with the energy gap ( $\Delta E_{gCT}$ ) at about 3.08 eV for both compounds. The  $\beta_0$  values comparison ( $29.30 \times 10^{-30}$  esu and  $38.17 \times 10^{-30}$  esu for MQ4 and MQ6, respectively) shows that the extension of the side aliphatic chains induces changes in this NLO parameter. Moreover, these values are higher than the obtained for the *p*-nitroaniline at the same theory level ( $26.22 \times 10^{-30}$  esu). Similar behavior was observed in the analysis of the  $|\beta_{vec}|$  values. However, these ones have negative signals; which can be understood as result of the reduction in the polarity of these compounds upon the excitation to the CT state ( $\Delta\mu_{gCT} < 0$ ). On the other hand, the change in the extension of the carbon chains does not produce expressive variations in the  $R_{\parallel}$  and  $R_{\perp}$  parameters.

### CONCLUSIONS

A transition involving intramolecular charge transfer has been characterized in both compounds. The results show that the macrocycles formed between isoalloxazine and anthraquinone are good candidates for applications involving materials with higher NLO response.

### ACKNOWLEDGMENTS

Fapesp, CENAPAD

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2. Farrán, A. *et al.* *Photochem. Photobiol. Sci.* **12**, 813–22 (2013).