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Citation: AIP Conf. Proc. 1288, 151 (2010); doi: 10.1063/1.3521349
View online: http://dx.doi.org/10.1063/1.3521349
View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1288&Issue=1
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NLO properties of a new Au-dithiolene complex

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Abstract. In the present work we report on the investigation of the nonlinear optical response of a recently synthesized Au-dithiolene complex (i.e., Au(dpedt)\textsubscript{2}) using Z-scan technique, employing 35 ps, visible (532 nm) and infrared (1064 nm) laser pulses. In both cases, the nonlinear absorptive and refractive parts of the third-order nonlinear susceptibility $\mathcal{g}^{(3)}$ of the Au-dithiolene have been determined and the corresponding second hyperpolarizability $\gamma$ has been deduced. Au(dpedt)\textsubscript{2} complex was found to exhibit nonlinear refraction and absorption under 1064 nm excitation, while only nonlinear refraction was observed under 532 nm excitation. The present results are compared with previous results concerning similar Ni-dithiolene complexes recently studied by our group.

Keywords: Au-dithiolenes, Ni-dithiolenes, dithiolenes, nonlinear optical properties, Z-scan

PACS: 42.62.Fi, 42.65.-k, 42.70.Jk, 78.47.jh

INTRODUCTION

Metal dithiolene complexes have been an object of significant research efforts during the last three decades due to their interesting electrical, magnetic and optical properties, which make them promising candidates for the development of new conducting, magnetic, and non-linear optical materials. The most interesting aspect concerning the electronic, optical and magnetic properties of metal dithiolenes is that they are easily tunable through modification of the organic dithiolene ligands and/or by replacing the metal. In addition to the possibility of such tuning at the molecular level, their bulk properties can also be tuned via crystal engineering as a result of the strong intermolecular interactions occurring between the sulfur atoms and the other heavy atoms present in these complexes, therefore allowing for a wide variety of crystalline structures to be obtained.

Concerning the optical characteristics of metal dithiolenes, they usually exhibit a characteristic strong IR absorption band, and an almost featureless visible absorption spectrum, providing therefore a high near-resonance NLO response together with a broad spectral range of operation. In addition to the above, the planar system of delocalized $\pi$-electrons exhibited by these complexes together with the charge transfer from the metal are also important factors for their large electronic NLO response making dithiolene complexes very attractive candidates for several applications in photonics and optoelectronics [1–5].

An effective approach in order to maximize the $\pi$-electrons delocalization is through the fusing of organic rings onto the square planar metal dithiolene core, thus increasing planarity and enhancing orbital overlap. An additional advantage of this approach is that it allows for the efficient tuning of the strong characteristic IR band over a relatively large spectral region, permitting the control of the near resonant enhancement of the NLO response. This approach has been followed previously in our group studying the NLO response of several symmetrical and unsymmetrical Ni-dithiolene complexes [6-9]. In the present investigation we report on the NLO response of a recently synthesized Au-dithiolene, namely the Au(dpedt)\textsubscript{2} complex (where dpedt is 1,2-diphenyl-1,2-ethylenedithiolate), and its comparison with the NLO response of similar Ni-dithiolene complexes previously studied.
Materials and Nonlinear Optical Characterization

For the measurement of the NLO response of \( \text{Au(dpedt)}_2 \) dithiolene Z-scan technique [10] has been used since it allows for the easy and simultaneous determination of the nonlinear absorption and refraction of a sample. The NLO response of \( \text{Au(dpedt)}_2 \) was measured both in the infrared, at 1064 nm, and in the visible, at 532 nm, employing 35 ps laser pulses delivered by a mode-locked Nd:YAG laser operating at 10 Hz. For the measurements of the NLO parameters, \( \text{Au(dpedt)}_2 \) solutions of various concentrations have been prepared in \( \text{CS}_2 \). The samples were placed in 1 mm thick quartz cells while the laser beam was focused into the cells by means of a 20 cm focal length lens. From the analysis of these measurements both the refractive and absorptive parts of the third-order susceptibility \( \chi^{(3)} \) were determined and the second-order hyperpolarizability \( \gamma \) was deduced. The details of the experimental setup and the procedure of the analysis of the experimental data can be found elsewhere [8, 9].

![Absorption spectrum of a 0.286 mM solution of \( \text{Au(dpedt)}_2 \) in \( \text{CS}_2 \).](image1)

FIGURE 1. Absorption spectrum of a 0.286 mM solution of \( \text{Au(dpedt)}_2 \) in \( \text{CS}_2 \).

In Figure 1, a typical absorption spectrum of a 0.286 mM solution of \( \text{Au(dpedt)}_2 \) in \( \text{CS}_2 \) is presented. As can be seen, the spectrum is dominated by the presence of a very strong IR band at 1485 nm which is assigned as the low-lying \( \pi-\pi^* \) band which is characteristic for all metal dithiolenes, while the absorption in the visible is featureless. A relatively lower absorption band lying between 300 and 400 nm is assigned to the S\( \rightarrow \)M charge transfer band. The details of the synthesis, the structural, electrochemical and optical properties of the \( \text{Au(dpedt)}_2 \) dithiolene have been reported in details elsewhere [11].

![Divided and open aperture Z-scans of neat \( \text{CS}_2 \) (□) and a 3.63 mM solution of \( \text{Au(dpedt)}_2 \) in \( \text{CS}_2 \) (■).](image2)

FIGURE 2. (a) Divided and (b) open aperture Z-scans of neat \( \text{CS}_2 \) (□) and a 3.63 mM solution of \( \text{Au(dpedt)}_2 \) in \( \text{CS}_2 \) (■). The laser energy was 3 \( \mu \text{J} \), corresponding at a peak intensity of 16.8 GW/cm\(^2\).
In figure 2, some typical Z-scan recordings obtained under 1064 nm laser excitation are shown. In particular, fig. 2a presents the divided Z-scans of a 3.6 mM Au(dpedt)$_2$ solution in CS$_2$ together with the corresponding Z-scan of the neat CS$_2$, while fig. 2b presents the corresponding open aperture Z-scans. The energy of the incident laser was 3 $\mu$J, corresponding at a peak intensity of 16.8 GW/cm$^2$. From the shape of the Z-scan traces of fig. 2a, where a pre-focal valley is followed by a post-focal peak, it becomes evident that both the solvent and the Au(dpedt)$_2$ dithiolene exhibit self-focusing behavior corresponding to positive sign refractive nonlinearity. Accordingly, from the shape of the open-aperture Z-scans, where a decrease of the normalized transmission was found as the incident laser intensity was increasing (approaching the focal plane), a reverse saturable absorption behavior is evident for both the dithiolene and CS$_2$, indicative of a positive sign absorptive nonlinearity.

Similar measurements performed under 35 ps, 532 nm laser excitation have shown that the Au(dpedt)$_2$ dithiolene exhibited only positive sign refractive nonlinearity and negligible nonlinear absorption.

**Results and Discussion**

From the analysis of the experimental data, the third-order susceptibility $\chi^{(3)}$ and the second hyperpolarizability $\gamma$ of the Au(dpedt)$_2$ dithiolene were determined at both excitation wavelengths studied. They were found to be of the order of $10^{-13}$ esu and $5\times10^{-32}$ esu respectively at both wavelengths where measurements were performed. Taking into account that the excitation wavelengths employed here were relatively far from the position of the strong $\pi-\pi^*$ band, which is at 1485 nm, and based on the fact that the nonlinear optical parameters were found to exhibit similar magnitude at both excitation wavelengths it can be assumed that the determined values correspond at an almost non-resonant situation. A similar situation has been confirmed experimentally for some similar Ni-dithiolene complexes [8, 9]. In this case, the laser excitation was again at 532 and 1064 nm, while the corresponding $\pi-\pi^*$ bands of the Ni(pddt)$_2$, Ni(etodddt)$_2$ and Ni(dddt)$_2$ dithiolenes were lying at 940, 1009 and 1039 nm respectively. In fact, it was found that as the laser excitation wavelength was getting closer to the corresponding $\pi-\pi^*$ band, the optical nonlinearities were increasing sharply indicating the increasing role of the resonance enhancement, while the simultaneous increase of the nonlinear absorption played a detrimental role limiting the degree of the observed enhancement. So, although the $\pi-\pi^*$ band of Ni(dddt)$_2$ at 1039 nm was in resonance with the 1064 nm excitation this dithiolene was found to exhibit relatively lower second hyperpolarizability than that of Ni(etodddt)$_2$ whose $\pi-\pi^*$ band was at 1009 nm.

Taken into account the above observations, it can be anticipated that tuning the Au-dithiolene $\pi-\pi^*$ band (e.g. by suitable chemical modification of the ligands) towards longer wavelengths than those currently used for telecommunications, i.e. 1300 and 1550 nm, a significant enhancement of the optical nonlinearities could be possible thus making Au-dithiolene based materials interesting candidates for potential telecommunications related applications.

**REFERENCES**