



Third-order nonlinear optical investigations of the 1,1'-methylenedipyridinium tetrachloridocuprate(II) using Z-scan technique



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ABSTRACT

We report here the third order nonlinear optical properties of the 1,1'-methylenedipyridinium tetrachloridocuprate(II) in chloroform (CHCl₃) solution using Z-scan technique. Measurements were performed with a CW Diode laser at 635 nm wavelength and 26 mW power. The nonlinear optical absorption coefficient (β) and nonlinear refraction (n_2) were of the order 4.46×10^{-4} cm/W and 3.74×10^{-8} cm²/W, respectively. The operating mechanism is reverse saturable absorption (RSA) as the excited-state absorption cross-section was found higher than ground state absorption cross-section. The magnitude of nonlinear absorption coefficient (β) was found decreasing with on-axis input intensity (I_0). Our results suggest that this material is considered as a promising candidate for future optical devices applications.

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1. Introduction

Organometallic complexes have received significant attention due to their large and fast nonlinear response and potential applications in optical data processing, optical communication, optical switching [1,2], and passive optical limiters in order to protect the human eyes and solid-state optical sensors [3–6]. These materials may provide a viable alternative to traditional inorganic crystalline NLO materials because of their ease in chemical alteration and reduction in cost. Organometallic complexes, which contain transition metal-ions, exhibit new properties due to the richness of the various excited states presented in the system and the ability to tailor the metal–organic ligand interactions. Furthermore, the delocalization of π -electron and the transfer of electron between the metal atom and the ligands make these complexes exhibit large molecular hyperpolarizability, which induces an ultra-fast optical response and larger third NLO effects.

Third order optical nonlinearity has been characterized by various techniques [7]. But, the simplest technique is Z-scan technique;

which is considered to be accurate experimental method to measure intensity dependent nonlinear susceptibilities of third-order nonlinear optical materials [8,9]. At the same time, it is possible to obtain the sign and magnitude of both real and imaginary part of the third order nonlinear susceptibility (χ^3) of nonlinear optical materials. Although, number of organometallic complexes has been reported [10–16], using Z-scan technique, but the investigation of such materials is still limited.

In this article, we report the third-order NLO properties of the 1,1'-methylenedipyridinium tetrachloridocuprate(II) in chloroform (CHCl₃) solution using Z-scan technique at 635 nm wavelength. To our knowledge, there is no report on investigation of the Z-scan measurements of the 1,1'-methylenedipyridinium tetrachloridocuprate(II).

2. Experimental techniques

1,1'-Methylenedipyridinium tetrachloridocuprate(II) was prepared according to the reported literature procedures [17]. The molecular structure of 1,1'-methylenedipyridinium tetrachloridocuprate(II) is depicted in Fig. 1. The Ultra-violet–visible (UV–vis) spectrum of the sample is shown in Fig. 2, which was recorded using a UV–vis spectrophotometer

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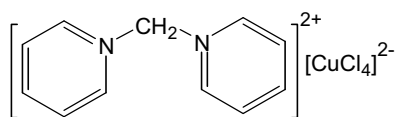


Fig. 1. Molecular structure of 1,1'-methylenedipyridinium tetrachloridocuprate(II).

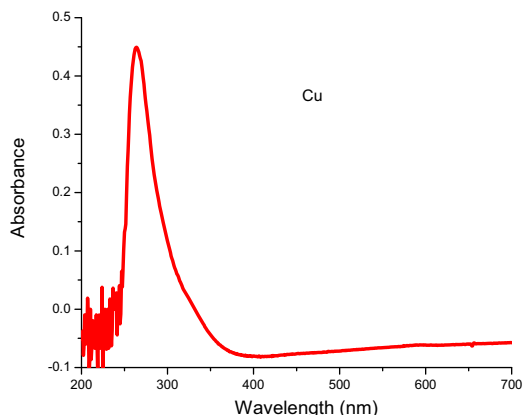


Fig. 2. UV-vis spectrum of 1,1'-methylenedipyridinium tetrachloridocuprate(II).

model UV-3101 PC Shimadzo. The relatively broad absorption band with λ_{max} at 260 nm is due to the combination of π - π^* and intraligand charge-transfer (ILCT) transitions [18]. This π -band is also called the conjugation band as its position and intensity is reported to reflect the extent of conjugation in the pyridyl core. The weak broad spectral feature, which can be distinguished in the spectrum in the range 300–400 nm is more likely to be associated with the ($d \rightarrow d^*$) transition and/or ligand-to-metal charge-transfer (LMCT) in the inorganic part $[\text{CuCl}_4]^{2-}$ of the complex. The same UV-vis spectral feature was observed for the structurally related complex 1,1'-methylenedipyridinium bis[tetrachloridoaurate(III)] [19].

The Z-scan experimental set-up is analogous to that described in Ref. [20]. The excitation source is linearly polarized TEM₀₀ Gaussian beam of a CW diode laser at 16.4 mW ($\lambda \equiv 635$ nm). The experimental parameters were used as follows: the laser beam is focused by a 10 cm focal length lens to a waist radius (ω_0) of 34 μm at the focal point. The diffraction length (Rayleigh length) z_0 is 5.5 mm, the radius of the aperture (r_a) is 0.5 mm and the radius of the laser beam waist (ω_a) is 1 mm on the aperture. The studied samples were dissolved in chloroform with concentration of 10^{-3} M. The sample cell used in this work is a 2 mm thick quartz cell and the cell was hold on an optical rail, and translated across the focal region along the axial direction that is in the direction of the propagation of the laser beam. The transmitted power through the sample is measured as a function of the sample distance z from the waist plane of the Gaussian beam. The transmission of the beam through an aperture placed in the far field is measured with a power meter (ThorlabsPM300E).

3. Results and discussion

The Z-scan method was performed in order to determine the nonlinear absorption coefficient β (with open aperture) and the nonlinear refractive index n_2 (without open aperture) of 1,1'-methylenedipyridinium tetrachloridocuprate(II) in chloroform solution at an input intensity of $I_0 = 465$ W/cm².

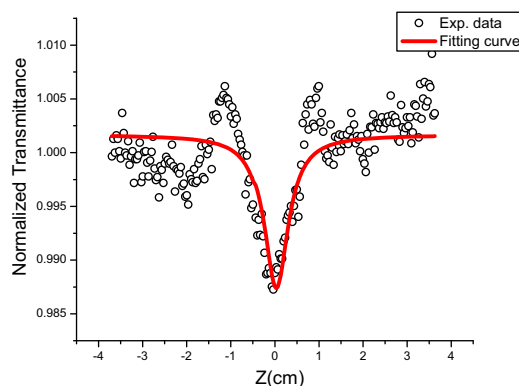


Fig. 3. Open-aperture Z-scan data of 10^{-3} M of 1,1'-methylenedipyridinium tetrachloridocuprate(II) in CHCl_3 . Solid line depict the theoretical fit.

3.1. Open aperture

In open aperture Z-scan experiment, the transmitted light measured by the detector is sensitive only to the intensity variation. The open aperture data of the 1'-methylenedipyridinium tetrachloridocuprate(II) in CHCl_3 at concentration of 10^{-3} M is shown in Fig. 3. Here, the transmission is symmetric with respect to focus ($z=0$), where it reaches a minimum value, showing intensity dependent absorption effect. The shape of the open aperture curve suggests that the used sample exhibited a reverse saturable absorption (RSA) process. A classical five-level model was proposed to explain the nonlinear absorption of organic compounds with extended π -electron system [21,22].

The nonlinear absorption coefficient β can be obtained from a best fitting performed on the experimental data of open-aperture (OA) using the following equation [8,9]:

$$T(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(m+1)^{3/2}} \quad (1)$$

For $q_0 < 1$, Where $q_0(z)$ is a parameter function of I_0 , L_{eff} and β :

$$q_0(z) = \frac{I_0 L_{\text{eff}} \beta}{(1 + z^2/z_0^2)} \quad (2)$$

Solving the summation and for $q_0 \ll 1$;

$$T(z) = 1 - \frac{(I_0 L_{\text{eff}} \beta)}{[2^{3/2} (1 + z^2/z_0^2)]} \quad (3)$$

where $L_{\text{eff}} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, α_0 is the linear absorption coefficient, $z_0 = \pi \omega_0^2 / \lambda$ is diffraction length of the beam, λ is the laser wavelength, and $I_0 = 465$ W/cm² is the intensity of the laser beam at focus $z=0$. In Fig. 3 “symbols” indicate to the experimentally measured transmission data, while “solid lines” are obtained by fitting the experimental data to the nonlinear transmittance given by Eq. (3).

The dependence of excitation intensity I_0 on nonlinear absorption coefficients (β) is shown in Fig. 4 It is noticed that decreases gradually with increasing excitation intensity which is a consequence of sequential two-photon absorption. That is, in the present case, the observed nonlinear absorption behavior is due to the result of TPA and ESA assisted RSA process [23,24]. This feature can be confirmed by comparing magnitude values of cross-section of the ground state (σ_g) and the cross-section of the excited state (σ_{ex}).

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