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Short pulse *Z*-scan investigations of optical nonlinearities of a novel organometallic complex: $[(C_2H_5)_4N]_2[Cu(dmit)_2]$ at 532 and 1064 nm

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ABSTRACT A novel dmit organometallic complex: $[(C_2H_5)_4N]_2[Cu(dmit)_2]$ ($dmit^{2-} = 1, 3$-dithiole-2-thione-4,5-dithiolate), abbreviated as EtCu, was synthesized. Afterwards its optical nonlinearities in acetone solution at 532 nm and 1064 nm were studied by the *Z*-scan technique with laser pulses of picosecond duration. The two-photon absorption at 1064 nm and the saturable absorption at 532 nm were observed. The *Z*-scan curves also revealed that EtCu sample solutions exhibited self-defocusing effects at both wavelengths. The origins were analyzed for the differences between the results. All the outcomes suggest that this material is potential for nonlinear optical device applications.

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1 Introduction

Modern development of optical devices calls for new nonlinear optical (NLO) materials with extraordinary properties. Organic and organometallic materials are attracting considerable attention because of their potential uses in various optical telecommunication devices including optical modulation, optical switching and optical limiter [1, 2]. A wide variety of organometallic materials with delocalized conjugated electron systems have been investigated due to their large NLO susceptibilities and ultrafast optical response [3].

As a special π-electron delocalization conjugated system, dmit and related ligand compounds have been used as building underprops for organic, organometallic and coordination compound electrical conductors and superconductors over the past 20 years [4, 5]. Recently, organometallic structures have become an interesting class of potentially highly nonlinear molecular blocks. These structures that contain transition metal ions may exhibit new properties due to the richness of various excited states present in these systems in addition to the tailorability of metal-organic ligand interactions. Also the transfer of electron densities between

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metal atom and the ligands makes this kind of compounds exhibit large molecular hyperpolarizability. So much attention has been paid to the third-order NLO properties of some dmit organometallic compounds [6, 7]. However, most of the investigations to the metal-dmit compounds are using methods such as the optical Kerr gate or degenerate four-wave mixing technique which can not distinguish the contribution of the real and imaginary parts of third-order nonlinear susceptibility $\chi^{(3)}$.

The *Z*-scan technique is a simple and sensitive single-beam method to determine both the nonlinear refractive index and nonlinear absorption coefficient of materials. In previous studies [8–10], we have reported the third-order optical nonlinearity of a series of dmit organometallic compounds newly synthesized by ourselves. The studies have shown that these organometallic compounds possess large third-order optical nonlinearity with sub-picoseconds response times. The present paper is devoted to the synthesis and investigation of the third-order NLO properties of EtCu in acetone solution determined by the *Z*-scan technique at 1064 nm and 532 nm with picoseconds pulse widths.

2 Experimental

The molecular structure of a novel organometallic crystalline complex named EtCu crystal is illustrated in Fig. 1 and its crystal structure has been previously reported by us [11]. Its synthesized procedure was as follows: CS_2 (24 ml) was added to degassed dimethyl formamide (DMF, 48 ml) and the mixture was cooled to 273 K (or 0 °C). Sodium (1.45 g) was added to the solution and the mixture was vigorously stirred with cooling until the reaction was completed. MeOH (2 ml) was slowly added. To this solution, separate solutions of (i) $CuCl_2 \cdot 2H_2O$ (2.66 g) dissolved in 25%–28% NH_3 (40 ml), and (ii) Bu_4NBr (6.60 g) in water (30 ml) were added consecutively while stirring at room temperature. The mixture was stirred overnight, then the product was isolated by filtration and washed with water and MeOH, to reclaim the black crystals of EtCu.

The UV-Vis-NIR absorption spectrum of EtCu in acetone was recorded by using a scanning spectrophotometer (Hitachi U-4100, Japan). The contributions to the spectrum of the liquid cell and solvent (acetone) were subtracted.
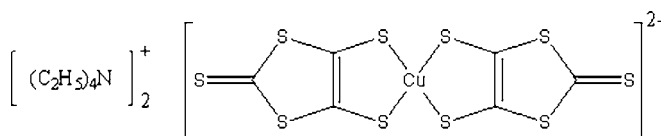
FIGURE 1   Molecular structure of EtCu crystal

The optical nonlinearities of EtCu were investigated by the Z-scan technique [12]. In our measurements, a mode-locked Nd:YAG laser (PY61C-10, Continuum) was used as the light source with a repetition rate of 10 Hz, pulse widths of 40 ps at 1064 nm or 28 ps (both full width at half-maximum, FWHM) at 532 nm. The sample is moved along the optic axis (the Z-direction) through the focus of the lens, while the energy transmitted through an aperture in the far field is recorded as a function of the sample position. The radius of the beam waist (w_0) was determined as 16.7 μm and 39.0 μm (both halfwidth at e^{-2} irradiance at the focus) at 532 nm and 1064 nm, respectively. Accordingly, the Rayleigh lengths, z_0, were calculated to be 1.65 and 4.50 mm, both longer than the thickness of a quartz cell containing the sample. The reference beam and the on-axis transmitted beam energy through a closed-aperture (CA) or an open-aperture (OA) were measured by two energy ratiometers simultaneously. The CA Z-scan is sensitive both to the nonlinear refraction and absorption, while the OA Z-scan only to the latter. The distance between the detector and the focus of the lens is far enough to satisfy the far-field approximation. A program was compiled to collect experimental data and control displacement device using Labview software. At one point of the Z-scan trace, several laser pulses are collected and averaged.

3   Results and discussion

3.1   *The linear absorption*

Figure 2 shows the results of EtCu acetone solution with the wavelength region 400–1400 nm at room temperature. There are two peaks, one at 448 nm and the other at 545 nm due to the n–π^* transition and the d–p interaction, respectively. The d–p interaction can be explained by the specific molecular structure of EtCu: the d orbitals of the central metal ion Cu^{2+} interact with the p orbitals on the two ethylene double bonds through the lone-pair electrons on the four sulfur atoms, and the p orbitals on the thiocarbonyl groups through the lone-pair electrons on the outer four sulfur atoms [13].

3.2   *Z-scan at 1064 nm*

Before measuring this sample, the system was calibrated using CS_2 in a quartz cell as reference. The value was measured to be 3.3×10^{-14} cm²/W, which is well accorded with the literature [12]. The concentration of the sample solution (S1) used in Z-scan measurements is 2.0×10^{-3} mol/L. Figure 3 exhibits the OA, CA and the division of the CA by OA data for EtCu solution sample S1. The OA curve demonstrates a positive nonlinear absorption which is regarded as two-photon absorption but not reverse saturable absorption, which generally occurs in the valley region of the linear spectrum lying in between Q and S (in UV) bands [14]. The
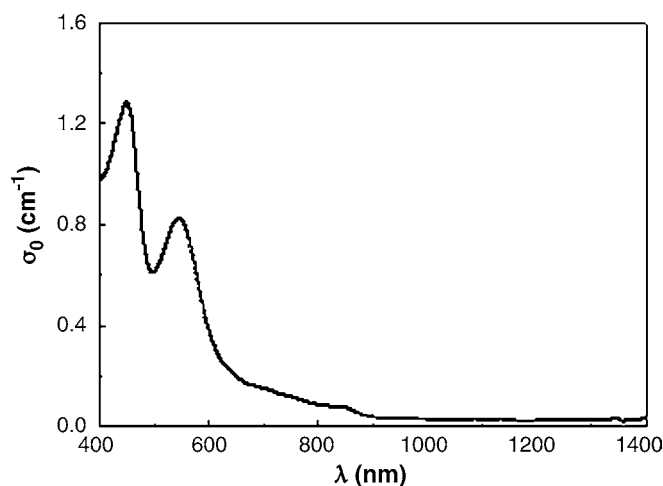

FIGURE 2   UV-Vis-NIR absorption spectrum of EtCu in acetone using acetone as reference at room temperature
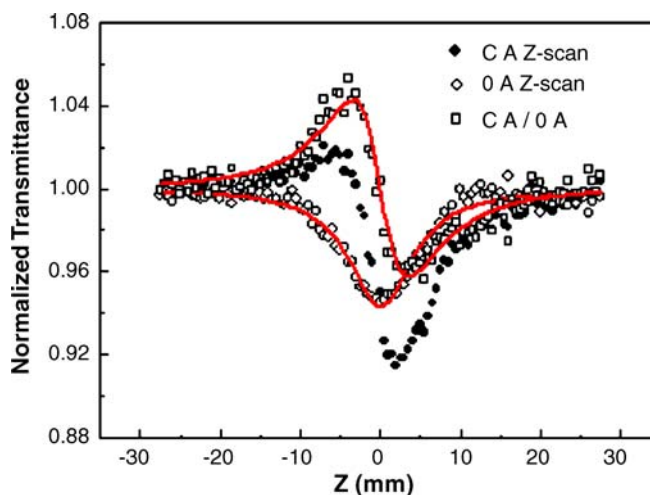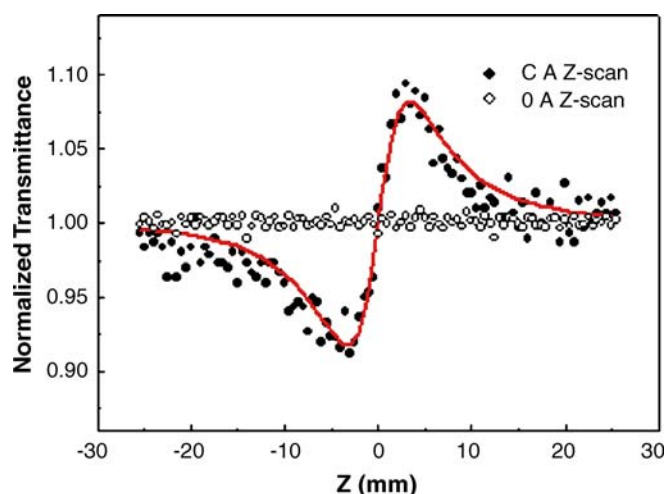

FIGURE 3   Normalized Z-scan transmittance curve of the sample solution S1 with concentration of 2.0×10^{-3} mol/L measured at 1064 nm with the Z-scan. The *solid lines* are the theoretical fit to the experimental data

peak-to-valley configuration of the CA curve suggests that the refractive index change is negative, corresponding to a self-defocusing effect. Meanwhile, measurements on the pure solvent (acetone) in the cell were also performed under the same measuring condition and the Z-scan curves are shown in Fig. 4. The symmetrical valley-to-peak configuration of the CA Z-scan and the horizontal straight line of the OA Z-scan reveal that acetone exhibits self-focusing effect but has not nonlinear absorption. The nonlinear refraction coefficient was 2.3×10^{-15} cm²/W and comparable to that of literature [15]. Therefore, the sample S1 still possessed a negative nonlinear refraction after countering the contribution of the solvent. So the total refraction value of the sample was the sum of the foregoing two.

The nonlinear absorption coefficient β (m/W) can be obtained from a best fitting performed on the experimental data of the OA measurement with the approximate equation [12]

$$T_{OA} = \sum_{m=0}^{\infty} \frac{[-\beta I_0 L_{eff}/(1+z^2/z_0^2)]^m}{(m+1)^{3/2}}, \tag{1}$$

FIGURE 4   Normalized Z-scan transmittance curve of the acetone solvent measured under the same condition as Fig. 3. The *solid line* is the theoretical fit to the experimental data

where T_{OA} is the normalized transmittance for the OA, $L_{eff} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample (L denotes its thickness), α_0 is the linear absorption coefficient of the sample S1 with concentration of 2.0×10^{-3} mol/L at 1064 nm, equaling to $0.2\,\mathrm{cm}^{-1}$, and $I_0 = 18.34\,\mathrm{GW/cm}^2$ is the on-axis irradiance at focus (i.e., $z = 0$).

The on-axis nonlinear phase shifts at the focus, $\Delta\Phi_0$, was obtained through fitting the CA/OA curve with the following approximate equation,

$$T = 1 + \frac{4\Delta\Phi_0 x}{(x^2 + 9)(x^2 + 1)}, \qquad (2)$$

where $x = z/z_0$, and T is the normalized transmittance for the CA/OA curve. Then the nonlinear refraction coefficient n_2 (cm^2/W) can be easily obtained through the equation

$$\Delta\Phi_0 = kI_0 n_2 L_{eff}, \qquad (3)$$

where $k = 2\pi/\lambda$ is the wave vector.

Accordingly, the real and imaginary parts of the $\chi^{(3)}$ and the molecular second hyperpolarizability γ of the sample can also be calculated by the following equations [7]

$$\mathrm{Re}\,\chi^{(3)}(\mathrm{esu}) = \frac{cn_0^2}{120\pi^2} n_2 (\mathrm{m}^2/\mathrm{W}),$$

$$\mathrm{Im}\,\chi^{(3)}(\mathrm{esu}) = \frac{c^2 n_0^2}{240\pi^2\omega} \beta(\mathrm{m/W}), \qquad (4)$$

$$\gamma = \frac{\chi^{(3)}}{N_c F_L}, \qquad (5)$$

where c is the velocity of the light in vacuum, n_0 is the linear refractive index of the sample, ω is the angular frequency of

the light field, N_c is the molecular number density in cm^{-3} and F_L is the local-field correction factor, which may be approximated by $[(n_0^2 + 2)/3]^4$.

The two-photon absorption coefficient β (cm/W), the nonlinear refraction coefficient n_2 (cm^2/W) and the molecular second hyperpolarizability γ (esu) were obtained and listed in Table 1. Considering the fluctuation of the laser energy and the volatilization of the sample solution, the errors of results should be within $\pm 5\%$ accuracy.

We can see that a large nonlinear refraction and positive nonlinear absorption are obtained for the sample S1 at 1064 nm. The two-photon absorption properties of materials are attractive features for optical limiting applications.

3.3   *Z-scan at* 532 nm

In order to verify the resonant origin of the effect, we moved the measurement wavelength from 1064 nm to 532 nm to obtain fully resonant values. Accordingly, the concentration of sample solution S2 was reduced to 0.67×10^{-3} M to avoid the fluence of the accumulative thermal effect at 532 nm. The peak-to-valley configuration of the CA/OA Z-scan curve for EtCu sample solution S2 in Fig. 5 also reveals a self-defocusing effect, and the refractive index change at 532 nm is negative. In addition, the OA curve demonstrates a strong nonlinear absorption which is regarded as saturable absorption for the resonant absorption at 532 nm. This is a very attractive feature for laser locking-mode, laser Q-switching and optical bistability applications. According to the above procedure, the effective excited-state nonlinear absorption cross-section and the nonlinear refraction coefficient were calculated to be $5.03 \times 10^{-17}\,\mathrm{cm}^2$ and $-8.89 \times 10^{-15}\,\mathrm{cm}^2/\mathrm{W}$, respectively.

Through the comparison of the two NLO phenomena at different wavelengths, we can find that the nonlinear effect depends on the wavelength. At the wavelength 532 nm, which locates in the resonant domain of the sample solution, a large saturable absorption occurs and this strongly enhance the third-order NLO effect. However, the wavelength 1064 nm lies in not only the off-resonant region but also two-photon absorption area, in which the NLO effect is not anticipated to be strengthened.

The large third-order optical nonlinearities of sample EtCu are due to the delocalized electronic states formed by the overlapping between p–p and d orbits [7]. The optical nonlinearities of dmit organometallic compounds are closely related to their chemical structures. We can obtain the reason from its structure. The extended electronically delocalized core comprising the central Cu^{2+} ion, four S atoms and the adjacent C=C units is the striking physical characteristic of EtCu. Cu^{2+} takes the place of group 12 metal ions (Zn^{2+}, Cd^{2+} and Hg^{2+}), the electron delocalization is enhanced due to the un-

Sample	Concentration $\times 10^{-3}$ mol/L	λ nm	α_0 cm^{-1}	I_0 $\mathrm{GW/cm}^2$	n_2 $\times 10^{-15}\,\mathrm{cm}^2/\mathrm{W}$	β $\times 10^{-2}\,\mathrm{cm/GW}$	γ $\times 10^{-31}$ esu
S1	2.00	1064	0.20	18.34	−4.64	5.70	0.65
S2	0.67	532	3.03	2.43	−8.89	–	–

TABLE 1   Nonlinear optical properties at 532 and 1064 nm of the samples
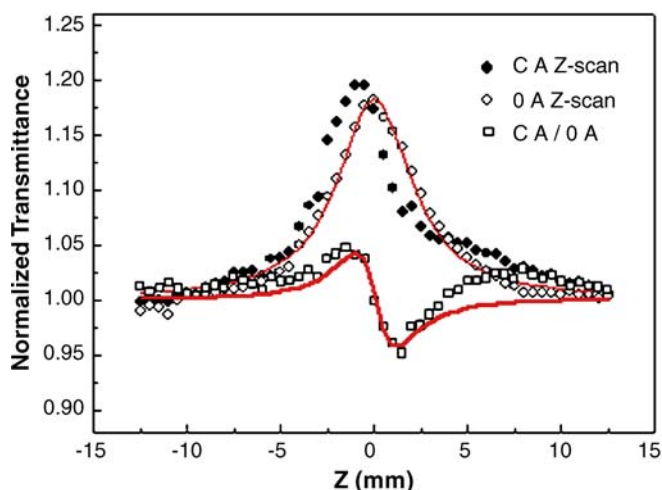
FIGURE 5 Normalized Z-scan transmittance curve of the sample solution S2 with concentration of 0.67×10^{-3} mol/L measured at 532 nm with the Z-scan. The *solid lines* are the theoretical fit to the experimental data

filled d electron shell of Cu^{2+} which allows the possibility of low-energy charge-transfer transitions. In addition, the $3p$ orbitals of S and $3d$ orbitals of Cu^{2+} can overlap to form a highly delocalized system. The delocalization will strongly enhance the hyperpolarizability and the nonlinear susceptibility, and lead to large third-order NLO properties.

4   Conclusions

In summary, a new organometallic compound EtCu was synthesized and its optical nonlinearities in acetone at 532 and 1064 nm were studied by the Z-scan technique with laser pulses of picosecond duration. Z-scan curves show that EtCu sample solution possesses the negative nonlinear refraction and two-photon absorption at 1064 nm and saturable absorption at 532 nm. The investigation can help us learn the material completely and also contribute to demonstration of the relations between molecular structure, linear absorption, third-order optical nonlinearity, and tailoring of the molecule according to practical requirements. Its strong nonlinear absorption and high linear transmittance make EtCu a promising candidate for the optical device applications.

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