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Nonlinear optical properties of $[(CH_3)_4N]Au(dmit)_2$ using Z-scan technique*

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The third-order optical nonlinearities of $[(CH_3)_4N]Au(dmit)_2$ (dmit = 4,5-dithiolate-1,3-dithiole-2-thione) at 532 nm and 1064 nm are investigated using the Z-scan technique with pulses of picoseconds duration. The Z-scan spectra reveal a strong nonlinear absorption (reverse saturable absorption) and a negative nonlinear refraction at 532 nm. No nonlinear absorption is observed at 1064 nm. The molecular second-order hyperpolarizability γ for the $[(CH_3)_4N]Au(dmit)_2$ molecule at 532 nm is estimated to be as high as $(2.1 \pm 0.1) \times 10^{-31}$ esu, which is nearly three times larger than that at 1064 nm. The mechanism responsible for the difference between the results is analysed. Nonlinear transmission measurements suggest that this material has potential applications in optical limiting.

Keywords: third-order optical nonlinearity, organo-metallic compounds, Z-scan technique

PACC: 4265, 4280W, 7820, 7855K

1. Introduction

Materials with large third-order nonlinear optical (NLO) properties and fast response time are essential to numerous optical device applications including optical switching, signal processing and optical limiting.[1−3] In recent years, organo-metallic complexes have attracted much attention as a new type of NLO material due to their architectural flexibility with a variety of combinations of central metals and ligands as well as the charge-transfer nature of the metal-ligand bonds, which can further enhance the nonlinearity.[4−7]

The synthesis and characterization of 1,3-dithiole-2-thione-4,5-dithiolate (dmit) complexes and related selenium- and oxygen-substituted isologues have been reported in the past two decades.[8,9] As a special π-electron delocalization conjugated system, dmit and related ligand complexes have been used in the assembly of highly electrically conducting radical anion salts and charge-transfer complexes. They are generally used as important building blocks for organic, organometallic and coordination complex electrical conductors and superconductors.[10,11] The π-electron delocalization in conjugated systems can also contribute to the ultrafast response capability and large third-order nonlinearity. Recently, some investigations of the metal-dmit complexes have shown these materials possessing good third-order NLO properties.[12−16] However, most of the results are measured with optical Kerr gate or degenerate four-wave mixing technique and cannot distinguish between the contributions of the real and imaginary parts of third-order nonlinear susceptivity χ.[3]

In this paper, we report the synthesis of a new type of $Au(dmit)_2$ and the investigation of the third-order NLO properties of its sample solution at 532 nm and 1064 nm by using the Z-scan technique with laser pulses of picoseconds duration. In addition, the optical limiting properties at the two wavelengths are also demonstrated.

2. Experiment

The molecular structure of $[(CH_3)_4N]Au(dmit)_2$ is illustrated in Fig.1.

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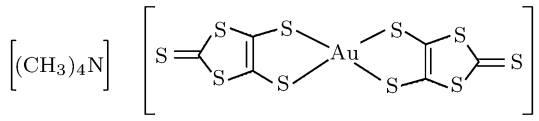


Fig.1. Molecular structure of $[(CH_3)_4N]Au(dmit)_2$.

It was synthesized following the procedure given by Steimecke *et al.*[17] The crystal structure of $[(CH_3)_4N]Au(dmit)_2$ has been reported.[18] In this paper, we used N,N-Dimethylformamide (DMF) as the solvent due to its high solubility to $[(CH_3)_4N]Au(dmit)_2$.

The linear absorption spectrum of a $2.0 \times 10^{-7}\,\mathrm{mol\cdot cm^{-3}}$ solution of $[(CH_3)_4N]Au(dmit)_2$ in DMF was recorded using a UV–Vis – NIR scanning spectrophotometer (Hitachi U-4100, Japan). The contributions of the liquid cell and solvent (DMF) to the spectrum were subtracted. Figure 2 shows the result in the wavelength region 330-1400 nm at room temperature.

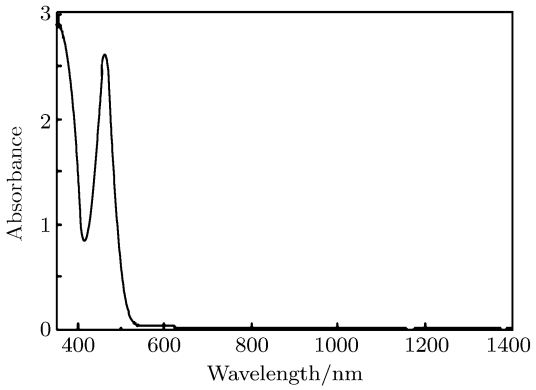


Fig.2. UV–Vis–NIR absorption spectrum of the DMF solution of $[(CH_3)_4N]Au(dmit)_2$ with $2 \times 10^{-7}\,\mathrm{mol\cdot cm^{-3}}$ using DMF solvent as reference at room temperature.

The peak at 465 nm represents the d–p interaction because the d orbitals of the central metal ion Au^{3+} 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.[19]

The Z-scan technique was used to characterize the NLO response.[20] This method is an increasingly popular method of measuring the nonlinear absorption coefficient (β) and the nonlinear refractive index (n_2) of the samples and has the advantage that it can immediately indicate the sign and type of nonlinearity (refraction or absorption). Two setups were used in our measurement, of which parameters are given in Table 1. The mode-locked Nd:YAG laser (PY61C-10, Continuum) provides picoseconds (both full width at half-maximum, FWHM) pluses at 532 nm and 1064 nm with the same repetition rate of 10 Hz. 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 to be 20.6 μm and 43.2 μm (both halfwidths at e^{-2}-fold irradiance at the focus), respectively. Accordingly, the Rayleigh lengths, z_0, was calculated to be 2.5 and 5.5 mm, both are much longer than the thickness of a quartz cell with the optical length of 1 mm including the sample's. The aperture linear transmittance in the far field S was 0.2 and 0.08, respectively. Please refer to Table 1 for the parameters of the measurement apparatus. The reference beam and the on-axis transmitted beam energies through a closed-aperture (CA) or an open-aperture (OA) were measured by an energy ratiometer simultaneously. The CA detector is sensitive to both the nonlinear refraction and absorption, while the OA detector only to the latter. The distance between the detector and the focus of the lens is far enough to satisfy the far-field approximation.

Table 1. Parameters of the measurement apparatus.

Laser type	Wavelength /nm	Pulse width /ps	Focal length /mm	Beam waist /μm	Rayleigh length /mm
PY61C-10	532	28	250	20.6	2.5
PY61C-10	1064	40	150	43.2	5.5

To demonstrate the nonlinear absorption, nonlinear transmission measurements were performed. The setup is similar to that for the OA Z-scan measurement, and the laser pulses were focused on the centre of a 1-mm-pathlength solution cell by a 250-mm-focal-length lens. The nonlinear transmission curves were obtained by varying the input energy (E_{in}) with the help of two polarizers combination and by monitoring input energy (E_{in}) and output energy (E_{out}) measured with two high sensitive detectors.

3. Results and discussion

3.1. Z-scan at 532 nm

Z-scan measurements were performed at 532 nm. As shown in Fig.3, this wavelength is close to that of the absorption cut-off, so the repetition rate 10 Hz can avoid the influence of the accumulative thermal change of refractive index when the light intensity is not large.[21]

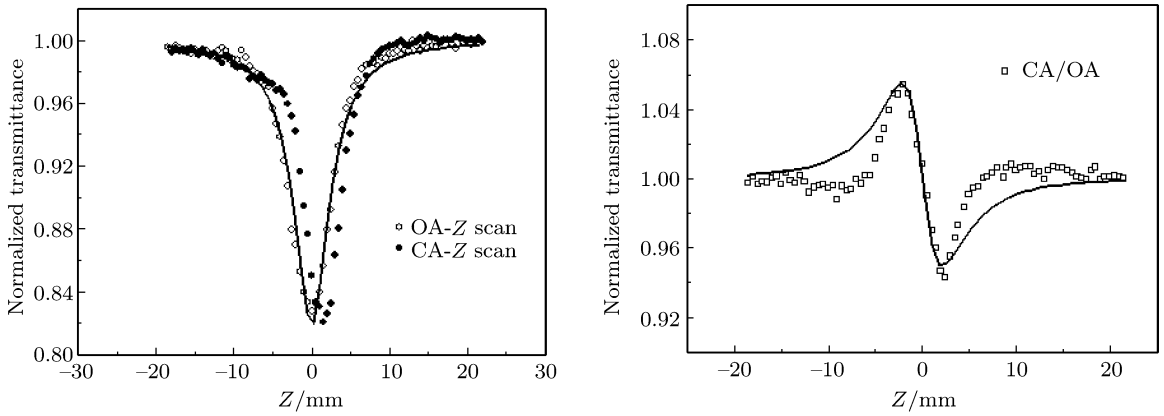


Fig.3. Normalized Z-scan transmittance curves of sample S1 at 532 nm measured with the closed aperture (•) and open aperture (○), and the ratio (□ = •/○). The solid lines are the fitting curves.

The sample (S1) concentration was 1.8×10^{-3} M and the energy of a single pulse was 0.56 μj. Measurements on the pure solvent (DMF) in the cell were performed under the same measuring condition to verify that the valley and peak in the Z-scan curves originated from the material, not from the solvent or the quartz cell. Figure 3 exhibits the OA, CA and the ratio of the CA to OA data for the sample. The OA curve demonstrates a strong nonlinear absorption that is regarded as the reverse saturable absorption for the near-resonant absorption at 532 nm. The curve of CA/OA suggests that the refractive index change is negative, exhibiting a self-defocusing effect. In addition, the configuration of the CA curve shows an asymmetric valley, suggesting that the nonlinear absorption covers the contribution of the nonlinear refraction and plays a significant role in the third-order nonlinear process of the sample, which is a very attractive feature for optical limiting applications. According to the procedure given in Ref.[22], the nonlinear absorption coefficient β (cm/GW), the nonlinear refraction coefficient n_2 (esu) and the molecular second hyperpolarizability γ (esu) were obtained, and they are listed in Table 2.

Table 2. Nonlinear optical properties at 532 and 1064 nm of the samples.

Sample solution	Concentration /10^{-3} mol · cm^{-3}	λ/nm	I_0 /(GW/cm^2)	n_2 (× 10^{-12} esu)	β /(cm/GW)	γ /(× 10^{-31} esu)
S1	1.8×10^{-3}	532	2.8	–2.8 ± 0.2	2.5 ± 0.2	2.1 ± 0.1
S2	4.0×10^{-3}	1064	10.1	-4.1 ± 0.3	0	0.8 ± 0.1

3.2. Z-scan at 1064 nm

The obtained value at 532 nm was considered to be an enhanced value by near-resonant absorption, so we shifted the measurement wavelength to 1064 nm to obtain fully off-resonant values. The repetition was also 10 Hz and the sample (S2) solution had a concentration of 4.0×10^{-6} mol · cm^{-3}. The energy of a single pulse was increased to 12.6 μj. The peak-to-valley configuration of the CA curve of the sample S2 in Fig.4 also reveals a self-defocusing effect at 1064 nm.

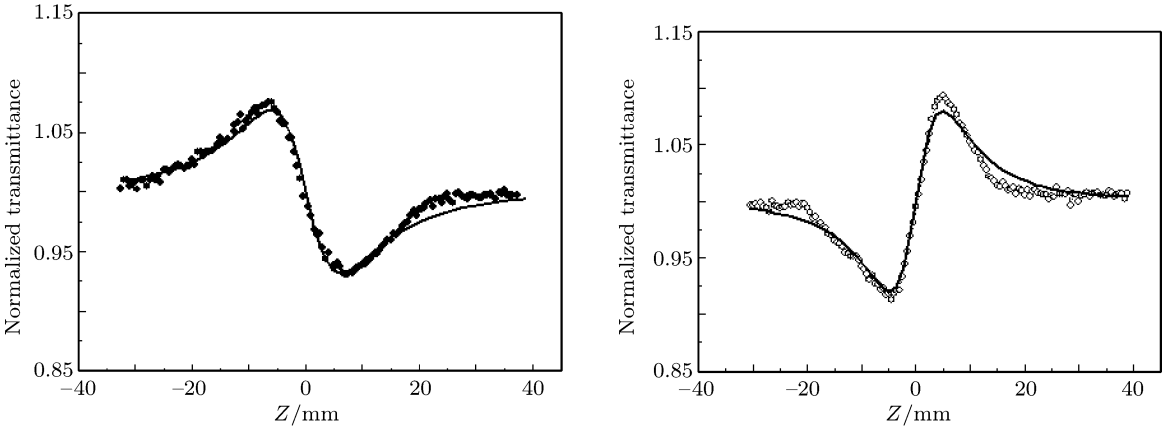


Fig.4. Normalized CA Z-scan transmittance curves of sample S2 and DMF solvent at 1064 nm: (•) is for sample S2 and (○) for DMF. The solid lines are the fitting curves.

The symmetrical trace of the CA Z-scan shows that no nonlinear absorption occurs. For further verification, the OA Z-scan was also carried out in order to obtain the nonlinear absorption information. The result is shown by a horizontal straight line. This suggests that the sample did not have the nonlinear absorption at this wavelength. Under the same condition, a valley-to-peak configuration of the CA Z-scan of the DMF solvent was also observed. Therefore, the sample solution still possessed a negative nonlinear refraction after counteracting the contribution of the solvent. So the total nonlinear refraction value of the sample was the sum of the foregoing two. Please refer to Table 2 for the calculated results.

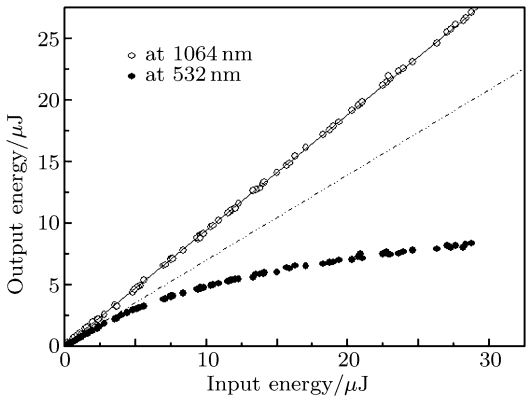


Fig.5. Optical limiting responses for the sample S2 at 532 nm and 1064 nm in a 1-mm cell. The linear transmittances are ≈ 68% (- - -) and ≈ 91% (—), respectively.

3.3. Optical limiting

Optical limiting, a property that is desirable for protection of sensors and human eyes from being affected by intense laser radiation, occurs when the optical transmission in a material decreases with increasing the laser fluence. Figure 5 shows the nonlinear transmission curves for the sample S2 at 532 nm and 1064 nm. In this plot, the straight lines indicate the linear transmittance without nonlinear contributions. When the sample solution is irradiated by the pulses of 532-nm laser light, the transmitted energy linearly increases in the region of low input energy (linear transmittance is ≈ 68%). The output starts from the input of 3.5 μj and then continues to deviate from the linear transmission line due to the contribution of the reverse saturable absorption, implying a strong optical limiting effect. However, there is no energy limiting at 1064 nm. The obtained results are in agreement with the Z-scan measurements very well.

3.4. Discussion

The results exhibit that $[(CH_3)_4N]Au(dmit)_2$ possesses a large third-order NLO properties, which can be understood from its structure. The extended electronically delocalized core comprising the central Au^{3+} ion, four S atoms and the adjacent C = C units is possessed of the striking physical characteristics of $[(CH_3)_4N]Au(dmit)_2$. Au^{3+} takes the place of group 12 metal ions (Zn^{2+}, Cd^{2+} and Hg^{2+}), the electron delocalization is enhanced due to the unfilled d electron shell of Au^{3+}($6d^8$ electronic configuration) that allows the possibility of low-energy charge-transfer transitions. In addition, the 3p orbitals of S and 3d orbitals of Au^{3+} 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.

In general, there are no significant differences in the NLO properties when the pulse duration used in the measurements varies to a small extent in the same

time domain,[23] so we can analyse the results without considering the pulse duration. As we can see from Table 2, the molecular second hyperpolarizability γ at 532 nm is about three times larger than that at 1064 nm. This may be due to the fact that, first, at the wavelength 532 nm that is located in the near-resonant domain of the sample solution, large reverse saturable absorption occurs and this can strongly enhance the molecular hyperpolarizability. However, the wavelength 1064 nm lies in off-resonant region and at the edge of the two-photon absorption (TPA) area, nonlinearity is not anticipated to be strengthened. The investigation on the optical nonlinearities of this sample at different wavelengths can help us learn the material more comprehensively. In addition, this will also contribute to the demonstration of the relations among molecular structure, linear absorption and third-order optical nonlinearity, and tailoring of the molecule according to practical requirements.

In the report of Wang, a large value of γ was obtained with femtosecond optical Kerr effect at 830 nm. We think this result mainly comes from the TPA enhancement effect. It is not strange that our result is 10 times larger than Wang's because the results in ps domain are generally one order higher than those measured using femtosecond pluses.[23]

Z-scan and optical limiting measurements both suggest that this material satisfies the requirements for the application of optical limiter: a strong nonlinear absorption, very fast response speed and relatively high linear transmission at 532 nm. Due to the ease of tailoring and fabrication of dmit salts, we can expect better performance of optical limiting through the mend of chemical structures.

4. Conclusions

A new type of $[(CH_3)_4N]Au(dmit)_2$ is prepared and the NLO properties of its DMF solutions at 532 nm and 1064 nm are investigated by the Z-scan technique with laser pulses of picoseconds duration. The third-order nonlinear refraction coefficient n_2, nonlinear absorption coefficient β and molecular second hyperpolarizability γ are obtained. The strong nonlinear absorption, its very rapid response, and high linear transmittance make $[(CH_3)_4N]Au(dmit)_2$ a promising candidate for the applications in optical limiting.

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