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# Investigation on Third-Order Optical Nonlinearities of Two Organometallic Dmit$^{2-}$ Complexes Using Z-Scan Technique

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## ABSTRACT

**The third-order nonlinear optical properties of two dmit organometallic complexes, $[(CH_3)_4N][Au(C_3S_5)_2]$ (MeAu) and $[(CH_3)_4N][Ni(C_3S_5)_2]$ (MeNi) in acetone solutions, were characterized using a short pulse Z-scan technique at 1064 nm wavelength. Self-defocusing effects were found in both samples and stronger saturable absorption was observed in MeNi solution comparing with that of MeAu. The origins were analyzed for the differences between the results. Two figures of merit *W* and *T* were also calculated to evaluate the suitability of two materials for all-optical integrated devices. The results of *W*=22.84 and *T*≈0 of MeAu make it an excellent candidate for the all-optical applications.**

**Keywords:** Z-scan Technique; Third-order Nonlinearity; Metal-dmit Complexes; Figure of Merit.

## 1. INTRODUCTION

As the development of optical communication networks progress, the demand for ultrafast optical switching with femtosecond or picosecond response time operation is rising. materials with large third-order nonlinear optical (NLO) properties and ultrafast response time have arose great interest for its widespread applications in optical switching, signal processing, ultrafast optical communications and optical limiting [1-4]. In recent years, π-conjugated organometallic complexes have emerged as a promising class of third-order nonlinear optical (NLO) materials because of 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 [5-6].

Special π-conjugated electron systems, like 4,5–dithiolato-1,3-dithiole-2-thione (dmit) complexes, have been used as building blocks for organic, organometallic and coordination-complex electrical conductors and superconductors [7-10]. Currently, more attention has been paid to the third-order NLO properties of these materials [11-13]. 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 π-electron delocalization and the transfer of electron densities between metal atom and the ligands make this kind of compounds exhibit a large molecular hyperpolarizability which can contribute to ultrafast optical response capability and larger third NLO effects. Usually, assessing the suitability of a material for all-optical switching devices is evaluated through two figures of merit: $W = n_2 I/\alpha_0 \lambda$ and $T = \beta\lambda/n_2$ ( $n_2$ is the nonlinear refractive index, $I$ is incident light intensity, $\alpha_0$ is the linear absorption coefficient, $\lambda$ is wavelength and $\beta$ is the nonlinear absorption coefficient) [2,14]. In order to satisfy the requirement, it is necessary to achieve $W>>1$ and $T<<1$. In this paper, the third-order optical nonlinearity of two dmit organometallic complexes, MeAu and MeNi, were reported using a Z-scan technique at 1064 nm with 20 ps pulse duration and 10 Hz repetition rate. Additionally, $W$ and $T$ of these samples were obtained which were used to evaluate their feasibility of to be applied in all-optical device field.

The Z-scan technique which was firstly reported by M. Sheik-Bahae *et al.* [15], is a simple and sensitive single beam method for measurement of third-order nonlinear optical coefficients. It is based on the self-focusing or

defocusing of a distorted beam of known spatial structure induced by moving a nonlinear sample along the light-propagation direction (Z-axis). Using this method, the magnitude and sign of both the real (nonlinear refraction, NLR) and imaginary (nonlinear absorption, NLA) parts of the nonlinearity of transparent mediums can be immediately obtained based on the relationship of the variation of transmittance in the far field and the sample position. The Z-scan technique can be signed two types: closed-aperture Z-scan and open-aperture Z-scan. For closed-aperture Z-scan both NLR and NLA can be measured simultaneously while for another, the NLA can be independently measured more accurately. To date the Z-scan technique is becoming an increasingly popular approach on measurement of nonlinear optical responses for its convenient operation, higher sensitivity and simple apparatus comparing with other method such as degenerated four-wave mixing, optical Kerr gate, nonlinear interference and so on.

## 2. EXPERIMENTAL

The molecular structures of MeAu and MeNi were illustrated in **Figure 1**. The synthesized procedures were respectively referred by the literatures [14,16]. The linear UV-Vis-NIR absorption spectra of $1\times10^{-4}$ mol/L solution of two materials in acetone were recorded using a scanning spectrophotometer (Hitachi U-4100, Japan). **Figure 2** shows the results with the wavelength region 330-1500 nm at room temperature. Both MeAu and MeNi represent several absorptive peaks in the UV-Vis region which can be regarded as attributing to the *n*-$\pi$ transition and the *d*-*p* interaction [16,17]. In another words, for MeAu, there was so wider a transparent window with no absorption in the wavelength region longer than 500 nm. While for MeNi, it also exhibits a strong absorption band with the peak at about 1137 nm in the NIR region (800-1500 nm) which may be assigned to the low-energy $\pi$-$\pi^*$ transition [18].

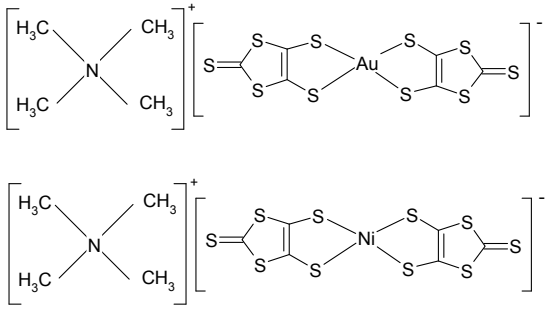



**Figure 1.** Molecular structures of MeAu and MeNi.

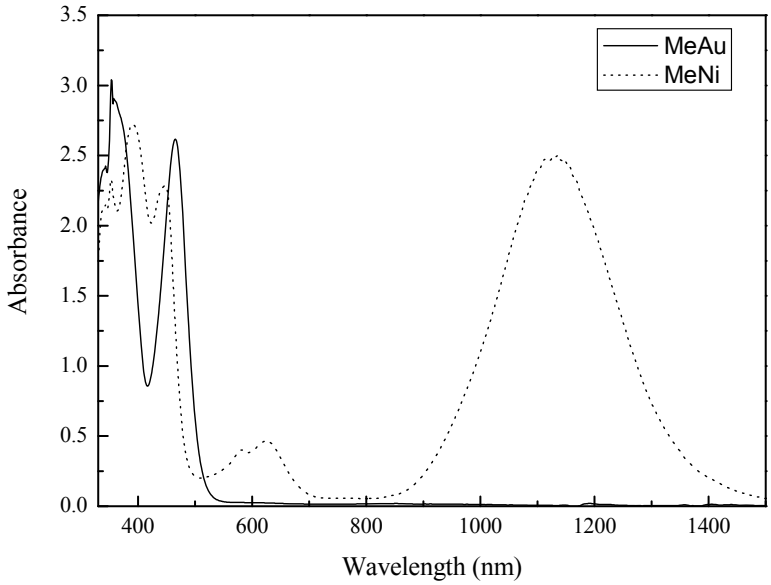



**Figure 2.** UV-Vis-NIR absorption spectra of acetone solutions of MeAu (solid line) and MeNi (dot line) with a concentration of $1\times10^{-4}$ mol/L at room temperature.

The Z-scan technique was used to characterize the third-order nonlinear optical response of the acetone solutions of two materials. In our measurement, a mode-locked Nd:YAG laser (Leopard-10, Continuum) was employed as the Gaussian light source with a repetition rate of 10 Hz, pulse width of 20 ps and wavelength of 1064 nm. The sample is moved along the optic axis (the Z-direction) through the focus of the lens, which has a focal length of 150 mm, 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 39 μm. Accordingly, the Rayleigh length ($z_0$) was calculated to be 4.5 mm, much larger than either the thickness of a quartz cell with the optical length of 1 mm. The incident beam intensity ($I$) performed on the samples was set to be 5.3(±0.3) GW/cm$^2$. Before measuring the samples, the system was calibrated using a standard $CS_2$ solution in quartz cell as reference. Measurements on the pure solvent (acetone) in the cell were also performed under the same measuring condition to verify that the peak-valley configuration in the Z-scan curves all originated from the material, but not from the solvent or the quartz cell [19].

## 3. RESULTS AND DISCUSSION

The concentration of samples used in Z-scan measurements is $1\times10^{-4}$ mol/L. **Figure 3** exhibits the closed-aperture (CA) and open-aperture (OA) data for MeAu in acetone solution. The symmetrical valley-to-peak configuration of the CA curve and the horizontal straight line of the OA curve reveal that the sample shows obvious self-defocusing effect and tiny NLA, which is considered a potential feature for all-optical switching. Then the Z-scan curves for MeNi are shown in **Figure 4 (a)** and **(b)**. The configurations of CA and OA curves in **Figure 4 (a)** both demonstrate single peak,

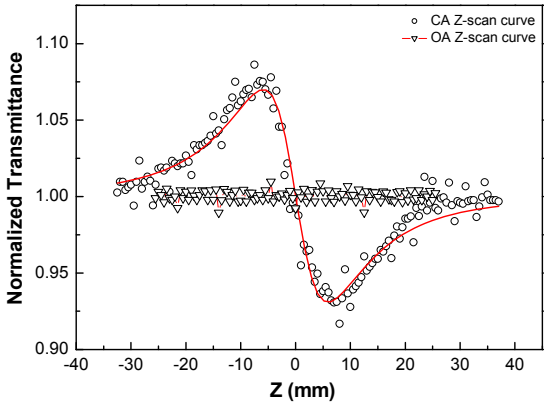
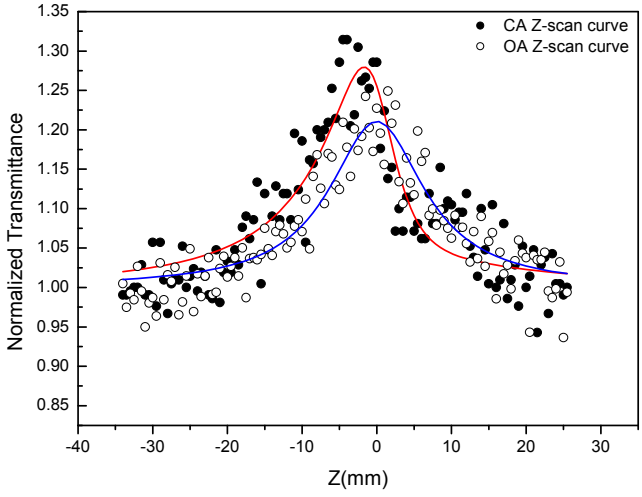
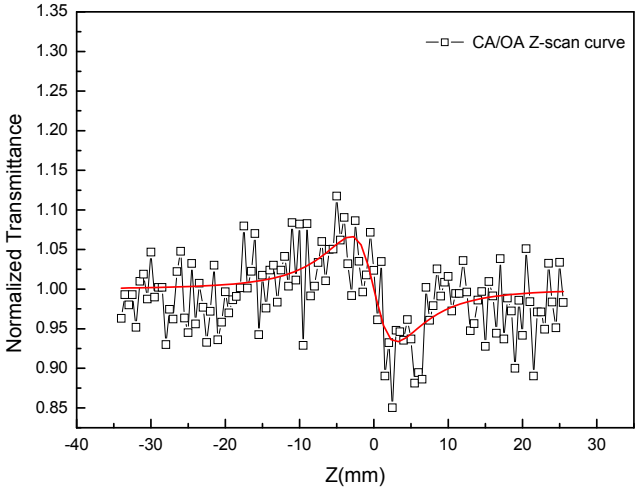



**Figure 3.** Normalized Z-scan transmittance curves of MeAu in acetone solution with concentration of $1\times10^{-4}$ mol/L. The solid line is the theoretical fitting curve. Z is the sample position away from the focus.




**(a)**




**(b)**

**Figure 4.** Normalized Z-scan transmittance curves of MeNi in acetone solution with concentration of $1\times10^{-4}$ mol/L. The solid line is the theoretical fitting curve. Z is the sample position away from the focus.

**Table 1.** Nonlinear optical parameters of MeAu and MeNi at 1064 nm.

| Sample | $\alpha_0$ (mm$^{-1}$) | $n_2$ ($10^{-19}$ m$^2$/W) | $\beta$ ($10^{-12}$ m/W) | $\chi^{(3)}$ ($10^{-13}$ esu) | $\gamma$ ($10^{-30}$ esu) | $W$ | $T$ |
|---|---|---|---|---|---|---|---|
| MeAu | 0.0021 | -9.50 | $-9.17\times10^{-3}$ | 4.58 | 2.65 | 22.84 | ≈0 |
| MeNi | 4.60 | -5.68 | -10.34 | 5.03 | 2.91 | 0.013 | 1.94 |

suggestion that the NLA which is regarded as the saturable absorption, covers the contribution of the NLR and plays a dominant role in the third-order nonlinear process of the sample, which is a very attractive feature for laser mode-locking, laser Q-switching and optical bistability applications [20-22]. **Figure 4 (b)** shows the division curve of the CA by OA data of MeNi, which also reveals a self-defocusing effect for the sample.

In general, to distinguish the NLR and NLA, the normalized transmittance dependence can be presented as follows [23-24]:

$$T = 1 + \frac{4x}{\left(x^2+9\right)\left(x^2+1\right)}\Delta\Phi - \frac{2\left(x^2+3\right)}{\left(x^2+9\right)\left(x^2+1\right)}\Delta\Psi \quad \textbf{(1)}$$

with

$$\Delta\Phi = kn_2 I_0 L_{eff} \quad \textbf{(2)}$$

$$\Delta\Psi = \beta I_0 L_{eff}/2 \quad \textbf{(3)}$$

where $T$ is the normalized transmittance of the sample, $\Delta\Phi$ and $\Delta\Psi$ is the nonlinear phase shifts due to the NLR and NLA, respectively. Here $x=z/z_0$, indicates the dimensionless relative position from the waist, $k$ is wave vector, $L_{eff} = \left[1-\exp\left(-\alpha_0 L\right)\right]/\alpha_0$ is the effective thickness ($L$ denotes its real thickness).

The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ are related to the NLR and NLA coefficients by [15, 25]:

$$\chi^{(3)} = \chi_R^{(3)} + \mathrm{i}\chi_I^{(3)} \quad \textbf{(4)}$$

$$\chi_R^{(3)}(esu) = \frac{cn_0^2}{120\pi^2} n_2(\mathrm{m}^2/\mathrm{W}) \quad \textbf{(5)}$$

$$\chi_I^{(3)}(esu) = \frac{c^2 n_0^2}{240\pi^2\omega}\beta(\mathrm{m}/\mathrm{W}) \quad \textbf{(6)}$$

where $\omega$ is the angular frequency of the light field and $c$ is the velocity of the light in vacuum.

Forwards, the second-order hyperpolarizability $\gamma$ of the sample molecule can be estimated through the equation [26]

$$\gamma = \frac{\chi^{(3)}}{N_c L_c} \quad \textbf{(7)}$$

where $N_c$ is the number density of molecules and $L_c$ is the local field correction factor which equals $\left[\left(n_0^2+2\right)/3\right]^4$.

According to above-mentioned procedure, the nonlinear parameters of the two sample MeAu and MeNi $n_2$, $\beta$, $\chi^{(3)}$, and $\gamma$ can be obtained in succession. Additionally, the results of two figures of merit $W$ and $T$ were also calculated basing on the NLO parameters. All the parameters were listed in **Table 1**. We can see that both

MeAu and MeNi show larger third-order nonlinear optical properties because of the delocalized electronic states formed by the overlapping between *p*-*p* and *d* orbits [10]. But the nonlinear absorption coefficient of MeNi is rapidly larger than that of MeAu. The resonant wavelength of 1064 nm of MeNi gives to the stronger saturable absorption comparing with the weaker nonlinear absorption of MeAu at 1064 nm which locates on the off-resonant field of linear absorption [27]. The figures of merit of MeAu were calculated to be $W$=22.84 and $T$≈0, which finely satisfy the requirement of suitability for all-optical switching devices $W$>>1 and $T$<<1. So the material can be considered to be an excellent candidate to be applied in integrated optics field as all-optical switching devices. While for MeNi, $W$=0.013 and $T$=1.94, the values of two figures of merit don't satisfy the requirement of all-optical devices but may be applied in laser mode-locking, laser Q-switching and optical bistability fields because of its saturable absorption properties.

## 4. CONCLUSIONS

The third-order nonlinear properties of two metal-dmit complexes MeAu and MeNi were investigated using a Z-scan technique at 1064 nm with 20 ps pulse width and 10 Hz repetition rate. Z-scan curves indicated that both MeAu and MeNi show negative nonlinear refraction which are regarded as self-defocusing effects. Meanwhile, tiny nonlinear absorption and stronger saturable absorption was found in MeAu and MeNi, respectively. The figures of merit $W$ and $T$ of two materials were calculated to judge the suitability as all-optical switching devices. The values of MeAu $W$=22.84 and $T$≈0 were considered to be appropriate for applications in all-optical integrated field. While for MeNi, the stronger saturable absorption comparing with nonlinear refraction makes it a fine material to be applied in laser mode-locking, laser Q-switching, optical bistability field and so on.

## 5. ACKNOWLEDGEMENTS

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