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7 AUTHORS, INCLUDING:

Cheng-Bao Yao

Jin Li
Northeastern University (Shenyang, China)

Ping Yuan
Harbin Institute of Technology

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Third-order nonlinear optical properties and optical limiting behavior of 1,1-ferrocenedicarbaldehyde

Cheng-Bao Yao [a,b], Yun-Dong Zhang [a,*], Hai-Tao Yin [b], Qing-Yu Meng [b], Chang-Qiu Yu [a], Jin Li [a], Ping Yuan [a]

[a] National Key Laboratory of Tunable Laser Technology, Institute of Optoelectronics, Harbin Institute of Technology, Harbin 150080, China
[b] Key Laboratory of Photonic and Electric Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, China

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ABSTRACT

We investigated nonlinear optical properties of 1,1-ferrocenedicarbaldehyde (FePz) with a nanosecond Nd:YAG laser pulse at 532 nm. The nonlinear absorption coefficient and nonlinear refractive index were measured using standard Z-scan technique. The experimental results show that the values of the nonlinear absorption coefficient and nonlinear refractive index were 43.32 cm/GW and -1.65×10^{-10} esu, respectively. Moreover, the transmission measurement technique was used to study the optical limiting of FePz. These molecules exhibit an interesting optical limiting performance with nanosecond laser pulses. With good excellent nonlinear optical coefficient, the samples were expected to be the potential applications in optical devices.

1. Introduction

Ferrocene has attracted the attentions of worldwide scientists because of its numerous applications in chemical sensing, asymmetric catalysis and material science [1]. To integrate a ferrocene unit into macrocyclic architectures has been recognized as an attractive way to endow molecules with secondary functionalities. On the other hand, it is well known that third-order optical nonlinearity is associated with bandgap, the smaller the bandgap of a Π-conjugated polymer, the higher the third-order optical nonlinearity. The above results of the ferrocenophanes have been verified in various photonics devices, such as all-optical switching (A-OS), optical limiting (OL), etc. Nalwa [2] investigated the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of ferrocene-containing polyazines by the third harmonic generation. The $\chi^{(3)}$ values of 2.23×10^{-11} esu at 1.8 μm for ferrocene-containing polyazine were observed. Up to now, experimental result about third-order nonlinear optical properties and OL behavior of 1,1-ferrocenedicarbaldehyde have been seldom reported.

In this Letter, the Z-scan [3–5] and transmission measurement technique [6,7] are used to study the nonlinear optical properties and OL of a 1,1-ferrocenedicarbaldehyde (FePz), which shows large nonlinear absorption coefficient and strong reverse saturated absorption. This material is especially convenient for nonlinear investigations because of its high durability, simple process ability, and low linear absorption. The results reveal that the OL efficiency is dependent on the one-photon absorption (OPA)-induced excited-state absorption (ESA) process, and the FePz exhibits strong OL effect at nanosecond laser pulses. The experimental results provide reliable reference for the application of ferrocene in all-optical switching and OL.

2. Synthesis and experiment

All reagents were purified and dried before it could be used according to standard procedure. FePz was synthesized according to the literature [8,9]. In 50 mL flask, 0.92 mL (4.64 mmol) triethyl phosphonoacetate was added in 15 mL anhydrous THF, under −78 °C. Then, 2.5 mL (4.64 mmol) *n*-BuLi was added by drop wise. After half an hour, 0.51 g (2.11 mmol) 1,1-ferrocenedicarbaldehyde in 5 mL tetrahydrofuran (THF) was dropped. The reaction was kept in −78 °C for 2 h, and then was placed under the room temperature for 10 h. It was quenched by adding water, and was extracted with 15 mL CH_2Cl_2 three times. The combined organic layer was dried with Na_2SO_4. The product was separated through column chromatograph, eluted with petroleum ether:ethyl acetate = 4:1 (v/v). Red solid 0.65 g, yield: 73.5%. The absorption spectra of FePz were recorded by UV–VIS–NIR spectrophotometer, as presented presented in Figure 1. Clearly, FePz exhibits a strong linear absorption band with a peak at $\lambda_{abs} = 340$ nm and highly transparent in the near infrared range; and therefore, one may choose the excitation wavelength λ_{exc} of 532 nm for FePz in order to fulfill the requirements ($\lambda_{abs} < \lambda_{exc} < 2\lambda_{abs}$) of two-photon absorption (2PA) studies [10,11]. The molecular structure of FePz is shown in inset (a) of Figure 1.

The Z-scan technique is used to measure the nonlinear optical properties, which shows great advantages due to its simplicity

* Corresponding author at: National Key Laboratory of Tunable Laser Technology, Institute of Optoelectronics, Harbin Institute of Technology, Harbin 150080, China.
E-mail addresses: yaochengbao5@163.com (C.-B. Yao), ydzhang@hit.edu.cn (Y.-D. Zhang).

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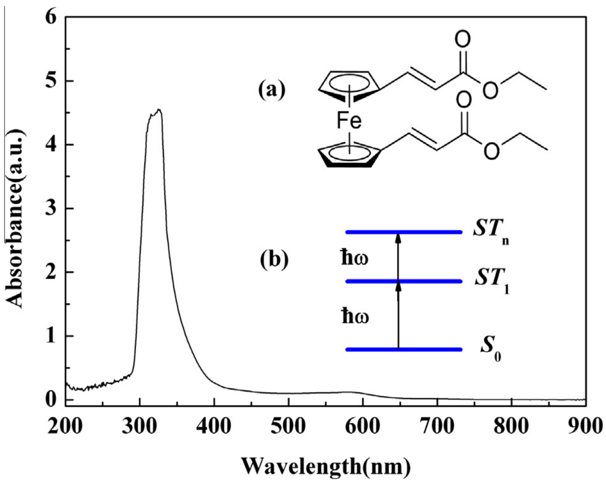

Figure 1. The linear absorption spectra of samples in *N*,*N*-dimethylformamide (DMF) solution. The insets (a) and (b) are the molecular structure of FePz and the three-level model two-step (2PA) we presented, respectively.

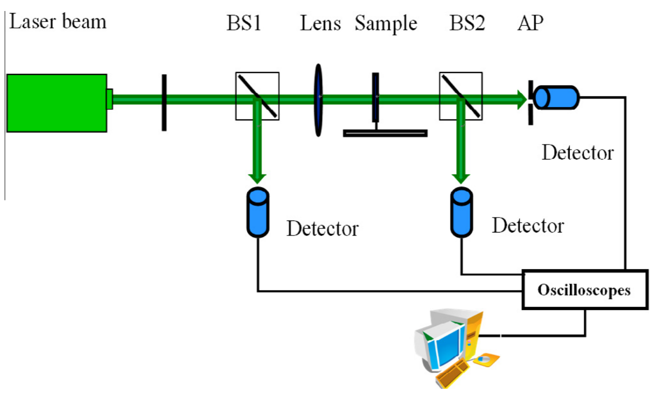

Figure 2. The setup of the Z-scan experiment. BS1-2, beam splitter; AP, aperture.

and high sensitivity. The experimental setup is shown in Figure 2. This technique is described in detail elsewhere [12], which enables simultaneous measurement of nonlinear refraction and nonlinear absorption. Basically, in this technique the nonlinear sample is scanned through the focal plane of a tightly focused Gaussian beam. Meanwhile, the changes in the far-field intensity pattern with and without aperture are monitored. Experiments are performed using a Q-switched, frequency doubled Nd:YAG laser producing 10 ns laser pulses at 532 nm and a pulse repetition rate of 10 Hz. For the optical power limiting study, the samples are kept at the focus of the laser beam. The measurements of OL are performed using the setup reported by Refs. [13–15]. The measurements are done with frequency-doubled Nd-YAG laser system. The laser pulses are guided onto the sample through a lens with a focal length of 100 mm. In order to avoid damaging the sample, it is not located at the focus point; the radius of the laser beam at the sample is approximately 1 mm in the $1/e^2$ diameter. The experiments are performed at room temperature.

3. Results and discussion

The magnitude of nonlinear absorption coefficient for FePz solution is estimated by performing the open aperture Z-scan (i.e. without keeping aperture in front of the detector), which is related to the imaginary part of third-order optical susceptibility $\chi^{(3)}$. Figure 3 shows the curves for the closed- and open-aperture Z-scans, which are obtained at various concentration of FePz solution and a fixed peak intensity $I_0 = 3.92 \times 10^9$ W/m^2. It can be seen from the transmittance curve of the closed-aperture Z-scan that the signal profile with a peak followed by a valley indicates a negative (self-defocusing) optical nonlinearity. The normalized transmittance for the standard closed aperture Z-scan is expressed by the relation:

$$\Delta T = 0.406(1-S)^{0.25}|\Phi_0| \tag{1}$$

where ΔT_{p-v} is the measured peak-valley transmittance difference, $\Delta\phi_0 = kn_2I_0L_{eff}$ is the on-axis phase-shift and I_0 is the peak intensity at focus and S is the linear transmittance of the aperture given by $S = 1 - \exp[-2(r_a/w_a)^2]$, where r_a is the radius of the aperture and w_a is the radius of the laser spot before the aperture.

The theoretical analyses of 2PA have been reported by Ref. [16]. If $q_0 < 1$, the normalized transmittance for the standard open aperture Z-scan is expressed by the relation:

$$T(z, S=1) = \sum_m^\infty \left([-q_0]^m/(m+1)^{3/2}\right) \tag{2}$$

where $q_0(z) = \beta I_0 L_{eff}/(1 + z/z_0)$, z_0 is the Rayleigh range, $L_{eff} = (1 - \exp(-\alpha_0 L))/\alpha_0$ is the effective length with α_0 is the linear absorption coefficient and L is the thickness of the sample. A fit to Eq. (1) to the closed aperture data Z-scan indicates that the nonlinear refractive index n_2 is -1.65×10^{-10} esu for the FePz. A fit to the Eq. (2) to the open aperture data Z-scan indicates that β is 43.32 cm/GW for the FePz.

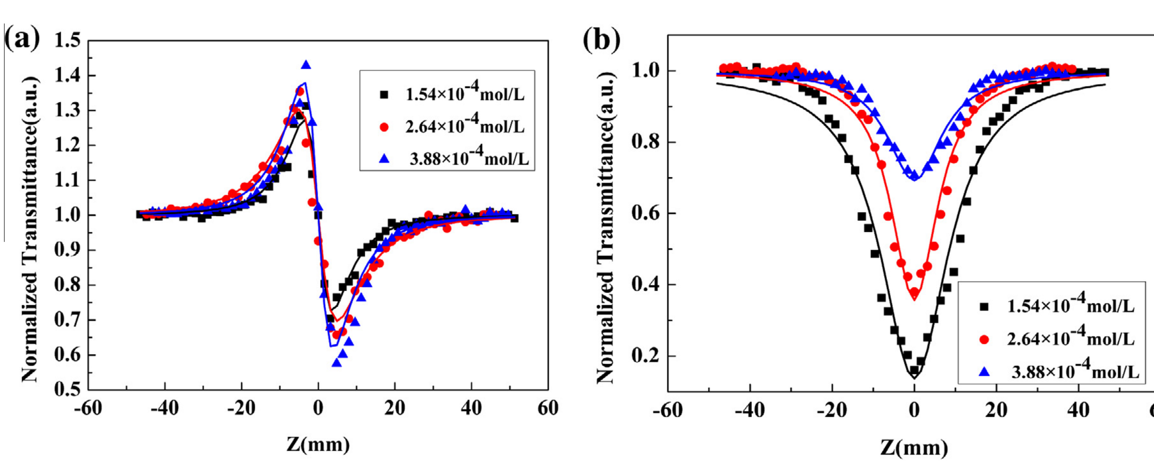

Figure 3. Normalized Z-scan transmittance curves of FePz measured at 532 nm. (a) closed-aperture Z-scans; (b) open-aperture Z-scans.

Table 1
Third-order nonlinear optical coefficients of FePz in solutions at same concentrations (2.64×10^{-4} mol/L).

Sample	n_2 ($\times 10^{-10}$ esu)	β (cm/GW)	σ_g ($\times 10^{-19}$ cm^2)	σ_{exc} ($\times 10^{-17}$ cm^2)	Re χ ($\times 10^{-12}$ esu)	χ ($\times 10^{-12}$ esu)
FePz solution	−1.65	43.32	9.72	3.23	−1.521	0.483

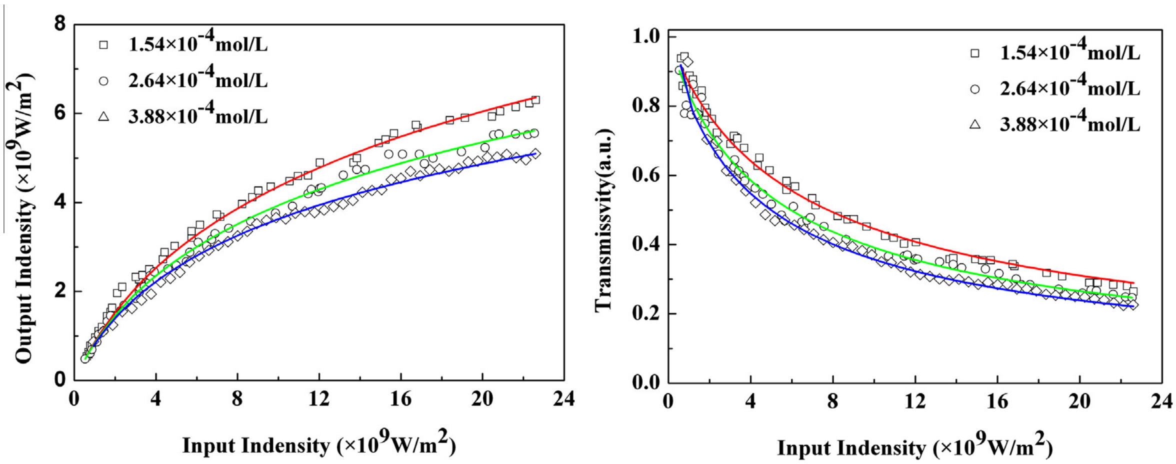

Figure 4. Optical limiting curve and transmittance curve of FePz.

The nonlinear refractive index n_2, and nonlinear absorption coefficient β, are related to the real and imaginary part of third-order nonlinear optical susceptibility $\chi^{(3)}$, respectively:

$$\begin{aligned} \mathrm{Re}\,\chi^{(3)} &= 2n_0^2 c\varepsilon_0 n_2 \\ \mathrm{Im}\,\chi^{(3)} &= n_0^2 c\varepsilon_0 \lambda\beta/2\pi \end{aligned} \tag{3}$$

The excited-state absorption cross-section (σ_{exc}) is measured from the normalized open aperture Z-scan data [17]. The ground-state absorption cross-section, σ_g, was calculated by:

$$\sigma_g = \frac{\alpha_0}{N_a C} \tag{4}$$

where N_a is the Avogadro's number and C is the concentration in mol/L. The values of nonlinear absorption coefficient, nonlinear refractive index, the real and the imaginary part of third-order nonlinear optical susceptibility $\chi^{(3)}$, and the ground-state absorption cross-section σ_g of the FePz in solution are given in Table 1.

The best known reverse saturable absorbers are fullerene (C_{60}), indocyanine green and phthalocyanines [18–21,7]. Due to a larger value of excited-state absorption cross-section compared to that the ground-state absorption cross-section of FePz, we expect that the major nonlinear optical process causing the limiting behavior is the reverse saturable absorption (RSA). Maybe the ferrocene ring alone induces the metal–ligand charge transfer interaction, which contributes to the $\chi^{(3)}$ enhancement. Each of these states contains the number of vibrational levels. Here, we present a three-level two-step 2PA model [22], as illustrated in the inset (b) of Figure 1, in which first singlet excited state S_1 and first triplet excited state T_1 (with the higher singlet excited state S_n and higher triplet level T_n) are combined to ST_1 (ST_n). In our model, the system absorbs one photon, promoting an electron from ground-state (S_0) to ST_1. Subsequently, the electron is excited to ST_n by absorbing another single photon, resulting in one-photon absorption (OPA)-induced excited-state absorption (ESA). To implement this excited process, the population of the excited states (S_1 and/or T_1) must be numerous so that the probability of photon absorption from that will be high. In nanosecond time scale singlet transition will not deplete the population of S_1 level appreciably, since atoms excited to S_n decay to S_1 itself with in picoseconds. From S_1, electrons transfer to T_1 via inter system crossing (ISC), from where transitions to T_n occurs. If more absorption occurs from the excited state than that from the ground state it is usually called RSA. The triplet excited-state absorption may result in RSA if the absorption cross-section of triplet excited state is greater than that of singlet excited state. With the excitation of laser pulses on the nanosecond scale, which is true in our case, triplet–triplet transitions are expected to make significant contribution to nonlinear absorption.

As shown in Figure 4, under the same incident laser power, the OL property of FePz is strong at relative high concentration, may be ascribed to the orbital forbidden, which partially released by the spin–orbit coupling effect of introduced central metal ions. Then the increasing strength of the spin–orbit coupling enhances the intersystem crossing rate, triplet population number and the excited-state absorption. Consequently, optical limiting properties are improved.

When the input power increases further and reaches a certain threshold, the relationship of the output and input power becomes nonlinear. The output is gradually moving to a stable state, the transmittance change is nonlinear. The OL properties of FePz have significant improved with the increase of the concentration of the solution (3.88×10^{-4} mol/L). The higher concentration of the FePz results the more molecules per unit volume. So the nonlinear effect occurs easily and the output of the laser power becomes smaller. As the curve of the transmittance shown, it the increase of the incident laser power. Therefore, the FePz investigated here will be a promising material for making optical power limiting devices.

Concentration dependence of nonlinear absorption coefficient is also studied. Figure 5 shows the plot of nonlinear absorption β vs. concentration. The measured value of nonlinear absorption coefficient β increases with the concentration of FePz in solution, indicating that the contribution to nonlinear absorptions arises due to the presence of the FePz. The β shows a saturating behavior to the concentration, further indicating that the nonlinearity includes is not only third-order but higher-order nonlinearity.

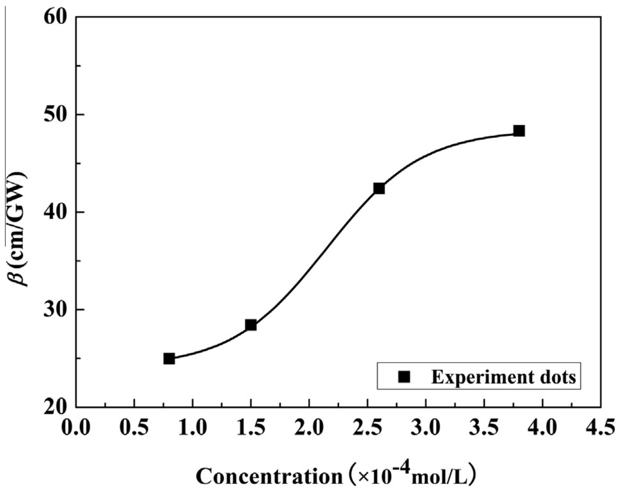

Figure 5. Concentration dependence of nonlinear absorption coefficient β.

In short, we should consider above various factors when we synthesize the optical limiting materials with high performance. With the increase of sample concentration, the optical limiting properties of the composite system will be improved. But it has also brought negative effect, namely, the reduced linear transmittance of the sample. In order to improve the optical limiting properties of the FePz solution, we can enhance the proportion of monomeric and decrease the proportion of the FePz molecules in polymer, on condition that its linear transmittance and concentration remains unchanged.

4. Conclusion

The nonlinear optical properties of FePz in DMF solution have been investigated by Z-scan technique. The experimental results show that the values of the nonlinear absorption coefficient and nonlinear refractive index of sample are 43.32 cm/GW and -1.65×10^{-10} esu, respectively. Optical limiting measurements indicate that the sample exhibits good optical limiting for 10 ns laser pulses at 532 nm wavelengths in solution. The optical limiting performance has demonstrated to be attributed to the OPA-induced RSA process. Hence, the samples are expected to be a potential candidate for optical applications.

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