

Two-photon induced optical-power limiting in *N*-vinylcarbazole tricarbonyl chromium

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The nonlinear optical properties of a new organic material, *N*-vinylcarbazole tricarbonyl chromium, are reported. The large two-photon absorption (TPA) coefficient and nonlinear refraction index are measured by an open-aperture Z-scan technique and closed-aperture Z-scan technique, respectively. The sample solution shows excellent optical limiting response.

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Optical limiting (OL) effects and devices are of increasing interest in the areas of nonlinear optics and optoelectronics because of their special potential applications in protecting human eyes and sensors from intense light. Recently, a great deal of the effort has been devoted to the development of OL materials^[1–6]. It is well known that OL can be caused by several different mechanisms such as reverse saturable absorption (RSA), two-photon absorption (TPA), nonlinear diffraction, and optical induced scattering^[7,8]. In particular, RSA, which results from higher absorption from a photo-excited state than from the ground state, was observed in the samples such as fullerenes and their derivatives, as well as many polymer molecules^[9–11]. On the other hand, due to the relative low TPA coefficients^[2], TPA materials have not been widely used for OL^[2].

As we know, if adjusting organic macro-molecular properties by metal coordination or polymer, the novel macro-molecular materials with senior function can be attained with electronic mutual action^[12]. Recently, through reaction active intermediate (NH₃)₃Cr(CO)₃ and ligand substitution *N*-vinylcarbazole, a new coordinated material *N*-vinylcarbazole tricarbonyl chromium (VCzC) was synthesized successfully. In this paper, we study the nonlinear optical absorption and OL effects of VCzC. The large TPA coefficient was measured by an open-aperture Z-scan technique, and the sample solution shows excellent OL response.

Under the Schlenk, (NH₃)₃Cr(CO)₃ (20 g) and *N*-vinylcarbazole (6.4 g) were dissolved in dioxane (250 mL). The solution was heated to 70 °C for 2–3 h, then was cooled and distilled completely to subtract dioxane. The residue was dissolved in hexane and re-crystallized. The yield of VCzC yellow crystal was 81.6%. The chemical structure of VCzC is shown in the inset of Fig. 1.

The nonlinear optical absorption of the sample was measured by the Z-scan technique^[13]. A mode-locked Ti:sapphire laser (spectra-physics spitfire amplifier) is used as the excitation source with the pulse duration of about 50 fs, center wavelength of 800 nm, and repetition rate of 1 kHz. The laser beam was focused on

a narrow waist with a 15-cm lens. The sample is positioned near the beam waist, and is moved along the direction of the beam propagation, the *z*-direction. In the closed-aperture Z-scan technique the transmittance is measured with a detector behind an aperture. In the open-aperture Z-scan technique, a lens was placed before the detector so that all the transmitted energy could be collected. The transmittance versus sample position data gives information about the sample nonlinearities.

In the OL experiment, an attenuator was used to adjust the incident laser energy. The incident and transmitted laser energies were recorded simultaneously by two identical photodiodes. In addition, to avoid the thermal lens effect, slow-scanning speed is adopted. To avoid the nonlinear optical effects such as self-focusing, self-defocusing, and nonlinear scattering, a lens with focal length of 10 cm was used in front of the photodiode to collect all the transmitted energy and an appropriate neutral-density attenuator was placed in front of the photodiode to ensure working in the linear region.

Figure 1 shows the linear absorption spectrum of VCzC with a concentration of 1×10^{-3} mol/L in CH₂Cl₂, which was measured by a Hitachi U-3500 UV-VIS-IR recording spectrophotometer. The solution sample was filled

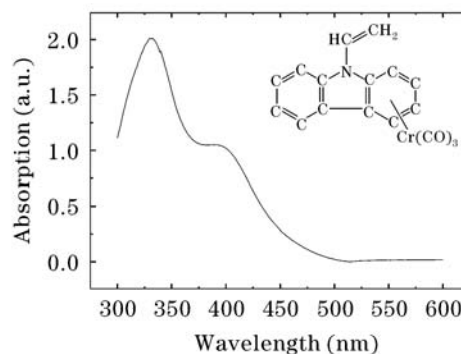


Fig. 1. Linear absorption spectrum of VCzC in CH₂Cl₂ with the concentration of 1×10^{-3} mol/L (inset: its chemical structure).

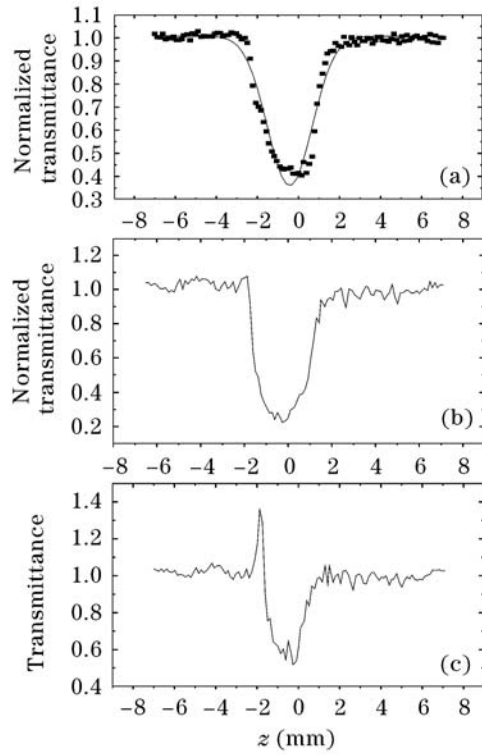


Fig. 2. Z-scan transmittance versus z . (a) Open-aperture (solid line: theoretical fit); (b) closed-aperture; (c) divided Z-scan data.

in a 0.5-cm-path quartz cuvette. The influences of the CH_2Cl_2 and quartz cuvette have been excluded. From Fig. 1 one can see that there is a strong linear absorption band at 332 nm and an observable absorption at 400 nm. There is no linear absorption in the range from 700 to 900 nm. Therefore the TPA is expected to occur at 800 nm.

The nonlinear optical absorption of the VCzC was measured by the Z-scan technique. As shown in Fig. 2, maximum absorption typically occurs when the sample is at the focal point of the lens, since the on-axis intensity of the beam is a maximum. The reduction of the transmittance measured with open aperture is independent of the nonlinear refraction (if nonlinear reflection from the sample surface is ignored), and thus can be used to determine TPA coefficient. Moreover, transmittance measurement with the closed aperture is given and the nonlinear refraction coefficient is obtained.

For TPA process, the normalized transmittance of open-aperture Z-scan signal can be given by^[14]

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z)} \int_{-\infty}^{+\infty} \text{Ln}[1 + q_0(z) \exp(-t^2)] dt, \quad (1)$$

where $q_0(z) = \beta I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$, $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, $I_0 = 2E/(\pi^{3/2}w_0^2\tau)$, E is the pulse energy, τ the pulse width, $z_0 = \pi w_0^2/\lambda$ the diffraction length of the beam, w_0 the beam radius at focus, L the sample length, and α linear absorption coefficient. Since there is no linear absorption at 800 nm (e.g., $\alpha \rightarrow 0$), L_{eff} equals L .

In the experiment, let $w_0 = 0.3$ mm, $\tau = 50$ fs, $\lambda = 800$ nm, $I_0 = 4.36 \times 10^8$ W/cm², and $L = 0.5$ cm. Figure 2(a) shows the simulation of open-aperture Z-scan

Table 1. TPA Coefficients β of Different Samples

Sample	β (cm/GW)
$\text{C}_{42}\text{H}_{62}\text{S}_2$	0.34 ^[15]
HEASPI	1.12 ^[2]
$\text{C}_{114}\text{H}_{174}\text{S}$	3.1 ^[15]
Poly Ruthenium	3.5 ^[16]
Dye	5.0 ^[17]
VCzC	9.15
DMA-HPV	14.7 ^[18]

curves. The experimental data agree well with the theoretical TPA fitting line and the TPA coefficient of 9.15 cm/GW. To compare with the other organic materials, we give the TPA coefficients of the different samples in Table 1, from which we can see that VCzC has relative high TPA coefficient.

The molecular TPA cross section σ'_2 (in units of cm⁴/GW) can be determined by^[5]

$$\beta = \sigma'_2 N_A d_0 \times 10^{-3}, \quad (2)$$

where $N_A = 6.02 \times 10^{23}$ is the Avogadro constant, $d_0 = 1.0 \times 10^{-3}$ mol/L, σ'_2 is calculated to be 1.52×10^{-17} cm⁴/GW.

To obtain the nonlinear refraction index γ , we divide the normalized data in Z-scan with closed aperture (Fig. 2(b)) by the one with open aperture (Fig. 2(a)), the result is shown in Fig. 2(c). The refraction index n can be expressed as^[13]

$$n - n_0 = \frac{\sqrt{2}\lambda}{2\pi L_{\text{eff}}} \frac{\Delta T_{\text{P-V}}}{0.406(1-S)^{1/4}}, \quad (3)$$

$$n = n_0 + \gamma I_0, \quad (4)$$

where n_0 is the linear refraction index, $\Delta T_{\text{P-V}} = 0.84$ is the difference between the peak and the valley in the closed-aperture Z-scan signal, $\lambda = 800$ nm is the laser wavelength, $S = 1 - \exp(-\frac{2r_a}{w_a}) = 0.02$, r_a is the radius of the aperture, w_a is the beam radius at the aperture, and the nonlinear refraction coefficient γ can be calculated as 2.37×10^{-7} cm²/GW.

The measured large TPA coefficient indicates that the new material may show OL response. Figure 3 shows the measured transmitted power as a function of the incident

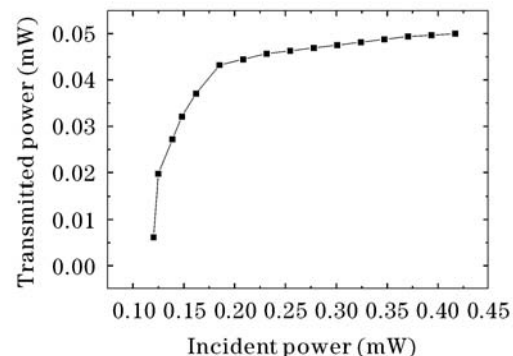


Fig. 3. Optical limiting response for VCzC in CH_2Cl_2 with the concentration of 1×10^{-3} mol/L.

power for the VCzC in CH_2Cl_2 with the concentration of 1.0×10^{-3} mol/L. There is a linear response of the transmitted energy for the very low incident laser intensity, and the obvious deviation from the linear response can be observed as incident power increasing. One can see that there is a clear optical power limiting effect. This effect might be used to protect the human eyes and sensors.

In this letter, we present the nonlinear optical properties of a new organic material VCzC. The nonlinear absorption and OL response of the sample are investigated, respectively, which show its possible to be used in optical limiters.

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References

1. Y. Zhang, Y. Zhang, P. Yuan, X. Sun, J. Xu, and J. Zhu, *Chin. Opt. Lett.* **3**, 292 (2005).
2. G. Zhuo, X. Wang, D. Wang, C. Wang, X. Zhao, Z. Shao, and M. Jiang, *Opt. Laser Technol.* **33**, 209 (2001).
3. R. Chari, S. R. Mishra, H. S. Rawat, and S. M. Oka, *Appl. Phys. B* **62**, 293 (1996).
4. J. S. Shirk, R. G. Pong, F. J. Bartoli, and A. W. Snow, *Appl. Phys. Lett.* **63**, 1880 (1993).
5. G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt, and A. G. Dillard, *Opt. Lett.* **20**, 435 (1995).
6. G. He, Q. Zheng, C. Lu, and N. Prasad, *IEEE J. Quantum Electron.* **41**, 1037 (2005).
7. W. S. Sun, C. C. Byeon, M. M. McKerns, C. M. Lawson, G. M. Gray, and D. Wang, *Appl. Phys. Lett.* **73**, 1167 (1998).
8. D. G. McLean, R. L. Sutherland, M. C. Brant, D. M. Brandelik, P. A. Fleitz, and T. Pottenger, *Opt. Lett.* **18**, 858 (1993).
9. S. Hughes, G. Spruce, B. S. Wherrett, and T. Kobayashi, *J. Appl. Phys.* **81**, 5905 (1997).
10. M. Pittman, P. Plaza, M. M. Martin, and Y. H. Meyer, *Opt. Commun.* **158**, 201 (1998).
11. B. Ma, J. E. Riggs, and Y.-P. Sun, *J. Phys. Chem. B* **102**, 5999 (1998).
12. X. Tian, J. Liu, and Z. Xu, *Chem. J. Chin. Univ.* (in Chinese) **22**, 1045 (2001).
13. J. E. Ehrlich, X. L. Wu, I. Y. S. Lee, Z. Y. Hu, H. Rockel, S. R. Marder, and J. W. Perry, *Opt. Lett.* **22**, 1843 (1997).
14. M. S. Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Van Stryland, *IEEE J. Quantum Electron.* **26**, 760 (1990).
15. I. Fuks-Janczarek, J. M. Nunzi, B. Sahraoui, I. V. Kityk, J. Berdowski, A. M. Caminade, J. P. Majoral, A. C. Martineau, P. Frere, and J. Roncali, *Opt. Commun.* **209**, 461 (2002).
16. C. Y. Liu, H. P. Zeng, Y. Segawa, and M. Kira, *Opt. Commun.* **162**, 53 (1999).
17. G. R. Kumar, F. A. Rajgara, and S. A. Rangwala, *Chem. Phys. Lett.* **245**, 287 (1995).
18. C. Li, C. L. Liu, Q. S. Li, and Q. H. Gong, *Chem. Phys. Lett.* **400**, 569 (2004).