

Nonlinear two-photon absorption properties induced by femtosecond laser with the films of two novel anthracene derivatives

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Two novel anthracene derivatives containing 4-vinylpyridine (FPEA) and 2-vinylpyridine (TPEA) poly(methyl methacrylate) films are prepared on quartz glass substrates. Their nonlinear absorption properties are investigated by using a 120-fs, 800-nm Ti:sapphire femtosecond pulsed laser operating at a 1-kHz repetition rate. The unique nonlinear absorption properties of these new compounds are observed by utilizing a *Z*-scan system. These two-photon absorption (TPA) properties are proven by the two-photon fluorescence excited at 800 nm. The FPEA and TPEA films have nonlinear TPA coefficients of 0.164 and 0.148 cm/GW and the TPA cross sections of 3.345×10^{-48} and 3.081×10^{-48} cm⁴·s/photon, respectively. The influence of the chemical structures on the nonlinear TPA properties of the compounds is also discussed. The highly nonlinear TPA activities of the films implied that the new anthracene derivatives are suitable materials with promising applications in super-high-density three-dimensional data storage and nano- or microstructure fabrication.

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Recently, organic two-photon absorption (TPA) materials have received considerable attention because of their potential applications in two-photon confocal microscopy^[1], photodynamic therapy^[2–5], three-dimensional (3D) microfabrication^[6,7], 3D data storage^[8–10], optical power limiting^[11], and up-converted lasing^[12]. TPA has two essential advantages. First is its ability to create excited states with photons having half of the normal excitation energy. This property can improve penetration in absorbing media. Second is the square dependence of the two-photon process on the input light intensity which allows for the 3D excitation of molecules with a high degree of spatial selectivity by using a tightly focused laser beam. To meet the requirements of these practical applications, many efforts have been made to develop molecules with large nonlinear TPA coefficient (β) and cross-section (σ) values. Numerous organic compounds, such as carbazoles^[13,14], triphenylamines^[15,16], porphyrins^[17–19], and fluorenes^[20–22], have been designed. The nonlinear two-photon activity was found to be highly dependent on the conjugated structure, to which the electron donors (D) or acceptors (A) from the D- π -D or D- π -A molecules, respectively, were attached symmetrically or asymmetrically. The TPA cross section was strongly influenced by the donor/acceptor strength, the conjugation length, the molecular dimensionality, and the planarity of the π center. Therefore, selecting a proper conjugated π center, introducing active groups at the ends to change the charge redistribution, and varying the effective conjugation length are necessary to produce structures with increased nonlinear two-photon activity.

As a potential conjugated π center, anthracene is a planar unit containing three π -conjugation benzene rings

that can highly delocalize the π orbital. The electronic and photonic properties of the anthracene-centered conjugated molecules can be adjusted effectively by the nature of their active groups and the way in which they are linked^[23,24]. However, only a few studies have focused on the relationship between the structure of the anthracene derivatives and their nonlinear two-photon properties. In this letter, two novel anthracene derivatives containing the active electron acceptors 4-vinylpyridine (FPEA) and 2-vinylpyridine (TPEA) were mixed in poly(methyl methacrylate) (PMMA) to fabricate the films of two compounds. The nonlinear absorption properties of the films were investigated by using a 120-fs, 800-nm Ti:sapphire femtosecond pulsed laser operating at a repetition rate of 1 kHz. The nonlinear absorption mechanism was studied by using two-photon fluorescence excited at 800-nm wavelength. The nonlinear absorption coefficients of the films were measured by using the *Z*-scan technology and an 800-nm, 120-fs pulsed laser. Then, the resulting TPA cross sections were obtained. The influences of the chemical structure of the compounds on the nonlinear TPA properties were also discussed.

The molecular constructions of the new anthracene derivatives, the FPEA, and the TPEA are shown in Fig. 1. The films consisted of the abovementioned derivative compounds and PMMA (TCI Tokyo Kasei Kogyo Co., Japan). The concentrations of the compounds in the polymer were 0.02 mol/L. The films were prepared on quartz glass substrates using a spin coater and dried in ambient air at room temperature. The film thickness was approximately 150 μ m. The FPEA and TPEA were obtained and synthesized. The linear absorption spectra of the films of the compounds were recorded by

using a spectrophotometer (Perkin Elmer Lambda 900 UV/Vis/NIR, USA).

The experimental setup for the open-aperture Z -scan system is shown in Fig. 2. The 120-fs, 800-nm pulsed laser was a Ti:sapphire femtosecond laser operating at a 1-kHz repetition rate. The samples were close to the focal point F of the 300-mm lens of the laser, which moved along the direction of beam propagation. The laser beam was divided by the beam splitter (BS) into two beams. The weaker beam detected by photodiode D_1 was used to monitor the incident laser energy. The stronger beam focused into the sample film by a 25-cm focal-length lens acted as the excitation beam. The overall intensities transmitted through the sample were collected into photodiode D_2 . These two photodiodes were connected to a two-channel energy meter (Moletron EPM 2000) that simultaneously records the input and output energies. A rotating half-wave plate between the two polarizers controlled the pump energy.

The two-photon-induced fluorescence method^[25,26] was used to explore the compounds' nonlinear absorption processes. The two-photon fluorescence spectra of the samples were investigated by using a 120-fs, 800-nm Ti:sapphire femtosecond pulsed laser operating at 1-kHz repetition rate. The pump light (with a beam diameter of 2 mm) was focused on the sample film by utilizing a convex lens with a focal length of 10 cm. The incident light power was adjusted through the attenuation slice. The fluorescence spectra were recorded by using a convex lens with a focal length of 5 cm and a 16-bit charge-coupled device (CCD, Jobin-Yvon, Horiba, France) mounted at the output of the monochromator, as shown in Fig. 3.

The one-photon absorption spectra of the FPEA and TPEA films are shown in Fig. 4. In our experiment, the influence from the quartz glass substrate has been subtracted. Figure 4 shows that the FPEA and TPEA films have strong linear absorption in the region from 300 to 420 nm, with maximum absorption peaks [$\lambda_{\text{abs(max)}}$] at 371 and 385 nm. These peaks can be attributed to the typical $n \rightarrow \pi^*$ transition^[13]. However, FPEA and TPEA had no linear absorption from 500 to 900 nm. Thus, the two- or multi-photon optical properties of these compound films were investigated.

The open-aperture Z -scan data obtained by the 120-fs, 800-nm laser and the theoretical fit line of the FPEA and TPEA films are shown in Figs. 5(a) and (b),

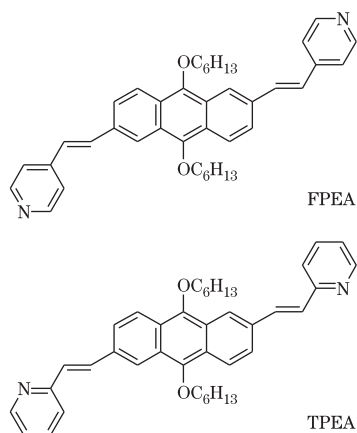


Fig. 1. Molecular constructions of FPEA and TPEA.

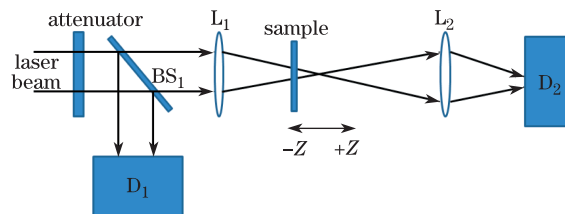


Fig. 2. Experimental setup for open-aperture Z -scan system.

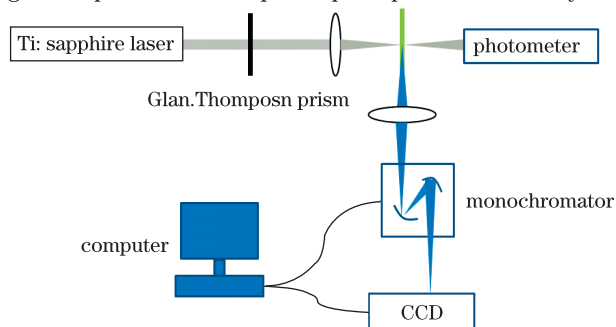


Fig. 3. Experimental setup for two-photon-induced fluorescence.

respectively. To avoid the influence of the pure PMMA film and the quartz glass, no nonlinear absorption from the substrate and the pure PMMA film was considered in the test process. The results show that nonlinear reverse saturation absorption is observed by the open-aperture Z -scan experiments for two organic compound films.

To understand the nonlinear absorption mechanism of the compound films, the two-photon-induced fluorescence method is utilized because of the absence of linear absorption at 800 nm, which is almost twice the wavelength at which the one-photon maximum absorption peaks are located. The intensity I_f of the fluorescence induced by the two-photon excitation was determined by the laser intensity I_0 and the total number of molecules N ^[27]

$$I_f = CI_0^2N, \quad (1)$$

where C is a constant. The pulsed intensities at the geometric focal point are calculated by

$$I_0(t) = \frac{\pi(\text{NA})^2}{\lambda^2}P(t), \quad (2)$$

where $\text{NA} = n\sin\theta$, θ is the half-angle of collection for the lens, I_0 is the intensity at the geometric focal point, and P is the incident power. Therefore, the linear relation between the logarithm of the fluorescence intensity and of input power can be attained using the formula $I_f = CI_0^2N$ for logarithms. The slope of the line should be 2 to verify whether the process has a TPA mechanism. The values of the FPEA and TPEA film fluorescences excited by a femtosecond pulsed laser at 800 nm were measured at different levels of input power. The results are shown in Figs. 6(a) and (c). The logarithms of the fluorescence intensity are plotted in the vertical axis and the logarithms of the input power are plotted in the abscissa, as shown in Figs. 6(b) and (d). According to Eq. (1), the slopes of the line are 1.97 and 2.14, respectively. These values ensure that the intense fluorescence emission is mainly induced by the TPA. The two-photon

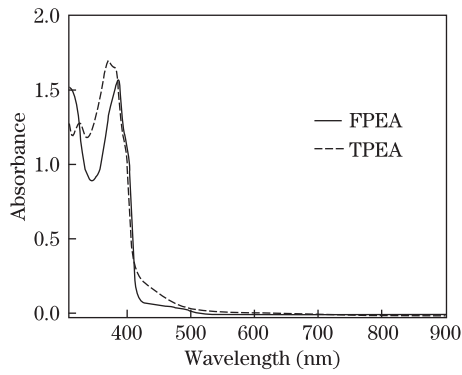


Fig. 4. Linear absorption spectra of FPEA and TPEA films.

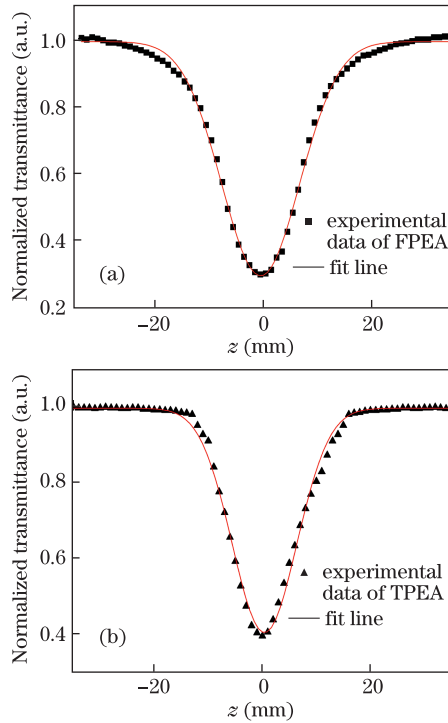


Fig. 5. Open-aperture, normalized Z-scan transmittances of (a) FPEA and (b) TPEA films measured by 120-fs, 800-nm pulsed lasers with different levels of input power.

fluorescence emission wavelengths of FPEA and TPEA had maximum wavelengths of 504 and 492 nm, respectively.

Based on the TPA process in this experiment, we considered a spatiotemporal Gaussian laser beam within the samples traveling in the $+z$ direction. Thus, the normalized energy transmittance $T(z)$ for TPA can be derived as^[28,29]

$$T(z) = \frac{1}{\pi^{1/2} q_0} \int_{-\infty}^{\infty} \ln [1 + q_0 \exp(-x^2)] dx, \quad (3)$$

where $q_0 = \beta I_0 L_{\text{eff}} / (1 + z^2/z_0^2)$, $L_{\text{eff}} = (1 - e^{-\alpha L}) / \alpha$, $z_0 = \pi \omega_0^2 / \lambda$ is the Rayleigh range, ω_0 is the minimum beam waist at the focal point ($z=0$), α is the linear absorption coefficient, λ is the laser free-space wavelength, and L is the sample thickness. For $|q_0| < 1$, the transmittance can be expressed in terms of the peak irradiance

through a summation from that is more suitable for numerical evaluation:

$$T(z, s = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}}, \quad (m = 0, 1, 2, 3, \dots). \quad (4)$$

The nonlinear TPA coefficient β can be extracted from the best fit between the above equation and the open-aperture Z-scan curve. After experimentally measuring the TPA coefficient, the two-photon cross-section of the film σ_{film} can be obtained as

$$\beta = \sigma_{\text{film}} N_0 = h\nu \sigma'_{\text{film}} N_A d_0 \times 10^{-3}, \quad (5)$$

where β is in units of cm^2/GW , $h\nu$ is the energy of the incident photon, N_A is the Avogadro constant, d_0 is the concentration of the TPA compound in the film (mol/L), and σ_{film} is in units of $\text{cm}^4 \cdot \text{s}/\text{photon}$. According to the above equation, the TPA coefficients (β values) of the FPEA and TPEA films are 0.164 and 0.148 cm^2/GW , respectively. Consequently, the TPA cross sections of 3.345×10^{-48} and 3.081×10^{-48} $\text{cm}^4 \cdot \text{s}/\text{photon}$ were obtained for the FPEA and TPEA films, respectively. The results indicate that the new anthracene derivatives, FPEA and TPEA, have high nonlinear absorption coefficients and TPA cross sections that are much larger than those of other organic compounds, such as carbazoles (1.2×10^{-48} or 1.23×10^{-48} $\text{cm}^4 \cdot \text{s}/\text{photon}$), triphenylamines (0.1×10^{-48} to 0.45×10^{-48} $\text{cm}^4 \cdot \text{s}/\text{photon}$), and fluorenes (0.25×10^{-48} $\text{cm}^4 \cdot \text{s}/\text{photon}$)^[13,30,31]. The significant nonlinear TPA mainly arises from the anthracene-conjugated central unit of the planar molecules containing three π -conjugation benzene rings that highly delocalized the π -conjugation structure. This delocalized anthracene structure is larger than those of carbazole, fluorene, and dioxin. The FPEA and TPEA groups, together with their strong electron-acceptor activity,

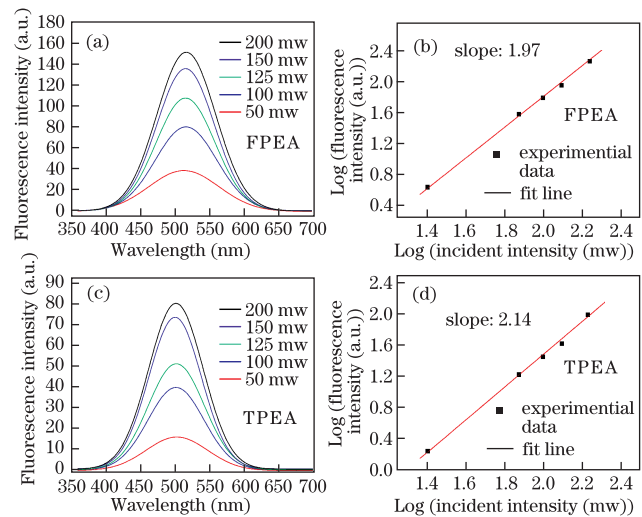


Fig. 6. (Color online) Two-photon-induced fluorescence values of the (a) FPEA and (c) TPEA films pumped by a 120-fs, 800-nm pulsed laser at different levels of input power. Logarithm of integrated fluorescence signals of (b) FPEA and (d) TPEA versus the logarithm of the input intensities.

also help in the adjustment of the molecules' charge redistributions. The results show that the anthracene-conjugated central unit and the strong electron-acceptor activity of the FPEA or TPEA end groups should be optimized to produce structures with enhanced nonlinear two-photon activity. The highly nonlinear TPA activities of the films imply that these new anthracene derivatives are suitable materials for super-high-density 3D data storage and 3D nano-/microstructure fabrication.

In conclusion, the PMMA films of two new organic compounds with anthracene-centered units containing FPEA and TPEA are prepared. The significant nonlinear reverse saturation absorption activities of the FPEA and TPEA films and nonlinear absorption coefficients of 0.164 and 0.148 cm/GW are obtained. The TPA absorption mechanization of these two materials are proved, and the TPA cross sections of FPEA and TPEA films are 3.345×10^{-48} and 3.081×10^{-48} cm⁴·s/photon, respectively. The results reveal that the anthracene-conjugated central unit and the strong electron-acceptor activity of the FPEA and TPEA end groups are necessary for producing structures with enhanced nonlinear two-photon activity. These new anthracene derivatives with highly nonlinear TPA activities are promising materials that can be applied to 3D data storage and nano-/microstructure fabrication.

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