Eliminating thermal effects in z-scan measurements of thin PTCDA films

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Abstract: We investigate the two-photon absorption (TPA) and nonlinear refraction of a micrometer thick 3,4,9,10-perylentetracarboxyl–dianhydride (PTCDA) film using z-scans with tightly focused 100 fs laser pulses. The PTCDA film was grown by organic molecular beam deposition on a Pyrex substrate. To study the influence of sample heating, the pulse repetition rate was varied between 4 MHz and 50 kHz with an acousto-optic pulse selector. We find that thermal effects diminish for pulse repetition times longer than 5 and 0.75 μs when using a 10x or 20x microscope lens, respectively, resulting in a TPA coefficient of 6 cm/GW and a nonlinear refractive index of 1.2 x 10^{-13} cm^2/W at a wavelength of 820 nm.

OCIS codes: (190.4870) Photothermal effects; (320.7110) Ultrafast nonlinear optics; (190.4710) Optical nonlinearities in organic materials.

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1. Introduction

The z-scan technique is a highly sensitive optical method that allows measuring both the two photon absorption (TPA) coefficient and the nonlinear refractive index [1,2]. Due to this advantage the z-scan technique has been widely used to study the nonlinear optical properties of semiconductors [3,4], nanoparticles [5,6], hybrid structures [7–9] and organic materials [10–14]. Depending on the damage threshold of the material and on the size of the investigated samples different lasers are applied. For large crystal lengths (1 mm or more) [15,16] or molecules in solution in a cuvette [5,12,14] low-repetition, high pulse fluence lasers with focus diameters of several 100 micrometers are used. In order to avoid structural changes of materials with low damage threshold high repetition 100 fs pulses with low energy fluence per pulse are applied [4]. The small fluence also allows for tighter focusing of the incident beam without damaging the material enabling the z-scan technique for thin solid films [17,18]. However, due to the high pulse repetition rate the nonlinear signal is often modified by accumulated thermal effects [9,19–22] since the sample has not reached the ambient temperature before the next pulse arrives [23]. Various approaches have been reported to manage accumulated heating [19–21,23] considering that thermal effects can be reduced if the pulse repetition time exceeds the heat diffusion time from the optically excited sample area [23]. In most of these investigations, a mechanical chopper has been used to control the exposure time of the sample by setting a chopping frequency and a chopper opening rise time [19–21]. Since the sample is excited by a train of pulses during the chopper opening time, this technique has limitations for materials with fast thermal build-up time [19–23]. As an alternative approach to eliminate heat accumulation in thin, dielectric films we propose the application of low fluence 100 fs laser pulses at reduced repetition rates using an acousto-optic modulator (AOM) as pulse selector. In addition, the pulses are tightly focused to reduce the thermal diffusion time from the area of the laser excitation into the unexcited film area.

Using this modified z-scan technique we were able to determine the nonlinear optical constants at 820 nm of a 3,4,9,10-perylentetracarboxylic dianhydride (PTCDA) film which has been grown by organic molecular beam deposition (OMBD) on a Pyrex substrate. PTCDA molecules form polycrystalline films in the monoclinic space group $P2_1/c$ with two different modifications (the α- and β-phase [24]), both possessing two nearly coplanar molecules within the unit cell [25]. The molecules align parallel to the (102) lattice plane, which is equal to the substrate surface. The distance between consecutive molecular planes is shorter as in graphite resulting in a large overlap of molecular π-orbitals [26–28].

The reason for choosing a PTCDA film to examine the modified z-scan technique is two-fold: First, many of organic materials possess high nonlinearities [10–13] and are promising materials for nonlinear optical applications including optical power limiting [13,29–31] and two-photon 3D data storage [32,33]. In particular, various perylene derivatives have shown TPA cross sections up to 8000 GM at nearly resonant excitation [12,13]. Both these large nonlinearities and the ability to form composite and hybrid nanostructures with semiconductors or metals give organic materials an enormous potential to enhance the nonlinear response of photonic structures [7,34]. Second, the two-photon-absorption cross-section of a PTCDA colloidal solution at 820 nm [14] and the third order susceptibility $\chi^{(3)}$ of a vacuum deposited PTCDA film using degenerate four wave mixing experiments at 602 nm [35] have been previously reported. These values serve as reference to test our modified tightly focused z-scan technique using 100 fs pulses at reduced pulse repetition rate.

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2. Experimental details

PTCDA films were grown by OMBD at room temperature on amorphous Pyrex® substrates of 0.5 mm thickness and ~1x1 cm^2 area. The substrates were cleaned in an ultrasonic bath with acetone, methanol and ultrapure water. Then it was transferred into the high vacuum OMBD chamber with a base pressure of 10^{-8} mbar. The deposition rate was measured using a quartz crystal thickness monitor which has been calibrated by film thickness measurements and by reflection measurements. Typical deposition rates from the effusion cells are 0.1 Å/s at a temperature of 330°C. X-ray diffraction measurements in θ-2θ scan mode at room temperature reveal a predominant α-PTCDA crystalline structure [26]. An approximately 0.9 μm thick film was used in our modified z-scan measurements. Thickness variations of ~ ± 0.2 μm due to oblique growth across the sample area were determined with a profilometer and have been considered in the evaluations of the z-scan data.

In the z-scan set up [1], the transmittance of the PTCDA film was measured as a function of sample position (z-axis) with respect to the focal plane (at z = 0). A Ti:Sapphire laser tuned to 820 nm was the excitation source providing ultrashort pulses of ~100 fs temporal width at a pulse repetition rate of 80 MHz (corresponding to a pulse repetition time of 12.5 ns).

In order to avoid heat accumulation or even structural damage in the PTCDA film, the pulse repetition rate is reduced by diffracting the pulses with an acousto-optic pulse selector at a variable division ratio (DR) ranging from 60 to 1600. Accordingly, the first-order diffracted pulses, which are used for the z-scan measurements, have a pulse repetition time ranging from 0.75 to 20 μs. The first- to (not diffracted) zero-order pulse intensity ratio was monitored with an oscilloscope using a fast photodiode. The ratio had a value of more than 1000 independent of the used DR. This zero-order background was further reduced by inserting a diaphragm in front of the z-scan setup. The remaining zero-order pulse intensity contributes to a constant transmission background. While this contribution is negligible at low DR it becomes important for long repetition times (> 1.25 μs) where several hundreds of weak zero-order pulses pass the PTCDA sample between each of the strong first-order diffracted pulses. To correct for this background, the average power of the laser beam was measured after the diaphragm with the AOM being switched on or off at each DR prior to each z-scan measurement, revealing the constant zero-order pulse power. The resulting zero-order background was subtracted from the experimentally obtained z-scan transmission signal. Likewise, the peak power P_0 of the exciting pulses was determined resulting in nearly constant peak intensity I_0 independent of the DR.

After the diaphragm the first-order diffracted laser beam was divided by a beam splitter (with 90% transmssion) directing the reflected beam onto a fast Si photodiode for reference. The transmitted beam (~2mm diameter) was directed towards a microscope objective which focussed the laser pulses tightly onto the PTCDA film. Measurements were made with a high-aperture 10x long working distance microscope objective (focal length ~20 mm) and then repeated with a high-aperture 20x microscope objective (focal length ~10 mm). The temporal width of the 100 fs pulses broadens when they pass the glass elements of the microscope objective lenses due to group-velocity-dispersion which affects the peak intensity I_0. The pulse widths after the 10x or the 20x microscope objective were measured to be 175 fs and 180 fs, respectively, by second-harmonic-generation autocorrelation in a BBO crystal. The PTCDA film on the Pyrex substrate was mounted on a piezo-translational stage, which was moved in step sizes ranging from 20 to 40 μm. The transmitted light (the z-scan signal) was collected by a fast Si photodiode. In addition, an optical long pass filter was placed in front of the photodiode to block any photoluminescence from the excited PTCDA film. The reference and z-scan signals were recorded simultaneously by two identical Agilent digital multimeters while moving the film from its negative to its positive z position (with respect to the focal plane, z = 0). Subsequently, the z-scan transmittance was divided by the reference signal to

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eliminate laser intensity fluctuations or changes of the spatial laser profile during the data acquisition.

In a ~1μm thick PTCDA film the change in transmittance due to two photon absorption (TPA) and nonlinear refraction is very small (in the 0.6% range) when using low energy fluence pulses. Therefore, multiple z-scans were recorded and averaged at both high and very low (attenuated by a factor of ~100) pulse intensity to improve the signal-to-noise ratio in these experiments. The transmittance at very low excitation intensity which does not lead to a z-scan signal serves as a reference of the linear transmittance during the movement of the sample along the z-axis. It allows to eliminate changes in transmittance with z due to surface imperfections of the sample [1].

3. Experimental results and discussion

3.1 Open aperture z-scan measurements

In order to study the accumulation of heat in the PTCDA film and its influence on the z-scan measurements we used a 10x microscope objective lens and varied the laser repetition time of incident laser pulses from 1.25 to 20 μs at a beam irradiance of 37 GW/cm^2. The background subtracted normalized transmittance for various pulse repetition times (as labeled) is shown in Fig. 1.

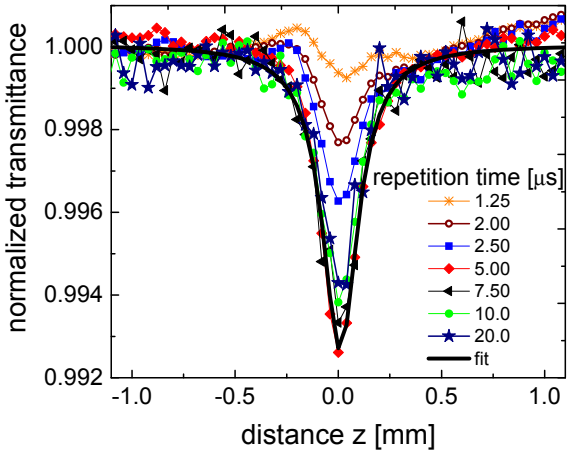

Fig. 1. Normalized open aperture transmittance of a PTCDA film as a function of z-axis displacement using a 10x microscope objective lens at different repetition times as labeled. The incident laser intensity was 37 GW/cm^2. The solid line represents the theoretical fit using Eq. (1) as described in the text.

In these measurements the aperture after the sample was completely open resulting in a transmittance dip in the vicinity of z = 0 due to TPA. While the transmittance dip is constant for repetition times ranging from 5 to 20 μs the dip steadily decreases for repetition time smaller than 5 μs. The corresponding two-photon-absorption coefficient β of the PTCDA film is determined by fitting the experimental data according to

$$T(z) = \sum_{0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}} \qquad (1)$$

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where $q_0(z,t) = \dfrac{\beta I_0(t) L_{eff}}{\left(1 + z^2/z_0^2\right)}$ and $I_0(t) = \dfrac{P_{av}}{\pi\left(\omega_0^2/2\right)\gamma_{rep}\Delta t}$ [1]. Here $I_0(t)$ is the pulse irradiance at the focal plane, γ_{rep} is the pulse repetition rate (80 MHz/), $z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh length of the beam, z is the sample position and ω_0 is the radius of the focused Gaussian (electric-field) beam waist which was determined by fitting the transmittance dips with Eq. (1). The average value of all beam waists ω_0 at different DRs was found to be 5.2 ± 0.3 and 2.6 ± 0.3 µm for the 10x or 20x lens, respectively. The effective film thickness L_{eff} is given by $L_{eff} = \left(1 - e^{-\alpha L}\right)/\alpha$ with L being the sample thickness and $\alpha = 1.5\times10^4$ m^{-1} being the linear absorption coefficient of PTCDA at 820 nm [36]. The thick solid line in Fig. 1 exemplarily represents the theoretical fit of the transmittance for a repetition time of 5.0 µs resulting in a TPA coefficient of 6.0 ± 0.6 cm/GW. The extracted TPA coefficients for all repetition times are shown in Fig. 2 as red squares. The vertical error bar in Fig. 2 represents the ~10% experimental error of these values. The error is attributed to laser intensity instabilities and to long-term temperature fluctuations which cause slight changes in the laser pulse energy and in the pulse width.

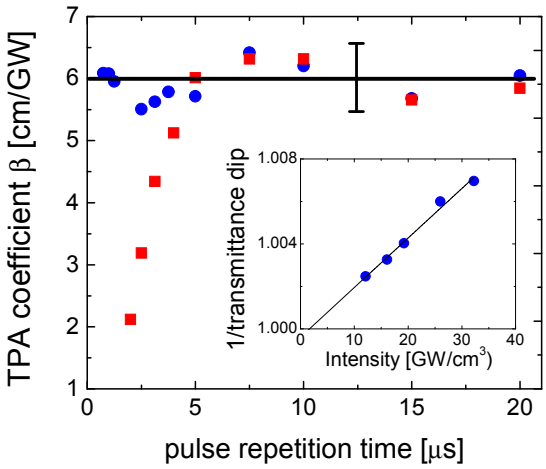

Fig. 2. Experimentally determined TPA coefficient β for a PTCDA film using a 10x (red squares) and 20x (blue circles) microscope objective lens as a function of different repetition times as labeled. Inset: Invers of the transmittance dip as a function of incident intensity using a 20x objective lens at a pulse repetition time of 3.125 µs.

As mentioned before, we attribute the reduction of the TPA coefficients for repetition times shorter than 5 µs to the accumulation of heat in the PTCDA film which is predominantly caused by the non-radiative recombination of Frenkel excitons, excimers and charge transfer excitons [26–28,37,38]. Our interpretation is supported by comparing the onset of the heating effect for repetition times smaller than 5 µs with the thermal diffusion time t_d of the accumulated heat within the laser focus area into the adjacent unexcited sample region in the PTCDA film. The thermal diffusion time t_d is given by the relation [20,23];

$$t_d = \frac{\omega_0^2}{4D} \tag{2}$$

Here, D = 0.05 cm^2 s^{-1} is the heat diffusion constant for PTCDA [39]. The derived thermal diffusion time using the 10x microscope lens amounts to 1.35 µs. This time is close to the

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repetition time of 1.25 µs, where heat accumulation drastically affects the z scan measurement (see Fig. 1) resulting in a very low TPA coefficient due to filling of excited states and the formation of a thermal lens as discussed in section 3.2. For repetition times between 1.35 and 5.0 µs, the nonlinear transmission is gradually less affected by accumulated thermal effects.

To further support this interpretation we repeated the z-scan measurements with a 20x microscope objective lens resulting in a tighter focus. For better comparison, we excited the PTCDA film with a similar energy flux as in the measurements with the 10x microscope objective lens by introducing attenuators into the beam path. Using Eq. (2) and a focus radius of ω_0 = 2.6 µm we obtain a heat-diffusion time of t_d = 0.34 µs. Accordingly, we expect a faster heat diffusion from the heated focus area into the unexcited film area and hence no or a less significant reduction of the TPA coefficient at laser repetition times below 5.0 µs. Figure 3 shows the normalized transmittance with the background subtracted as a function of the laser repetition time using the 20x lens at a beam irradiance of 26 GW/cm^2 for various repetition times as labeled. As before, the solid line represents the theoretical fit using Eq. (1) at a repetition time of 10.0 µs which results in a TPA coefficient of 6.2 ± 0.6 cm/GW. The extracted TPA coefficients are plotted in Fig. 2 as blue circles as a function of the pulse repetition time. For repetition times longer than 0.75 µs no reduction of the transmission dip or of the value of the TPA coefficient due to accumulated heating was observed. The inset of Fig. 2 shows the linear increase of the inverse of the transmission dip as a function of the pulse intensity at a repetition time of 3.125 µs using the 20x lens, confirming that the observed nonlinear process is due to TPA.

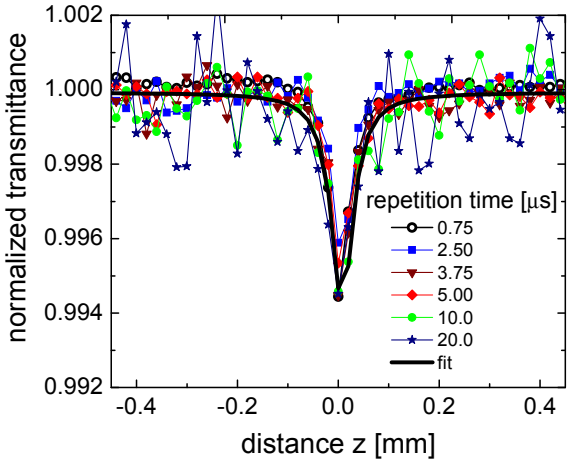

Fig. 3. Normalized open aperture transmittance of a PTCDA film as a function of the z-axis displacement using a 20x microscope objective lens at different repetition times as labeled. The incident laser intensity was 26 GW/cm^2. The solid line represents the theoretical fit using Eq. (1) as described in the text.

Within the experimental error the measured TPA value of β = 6.0 ± 0.6 cm/GW is the same for both the 10x and 20x microscope objective lens. When considering the reflection loss of the incident laser beam at the entrance surface of the PTCDA film (refractive index of 2.22 at 820 nm [40]), the TPA coefficient increases by ~16% resulting in a value of β = 7.0 ± 0.7 cm/GW. This value is higher than the TPA coefficient of β = 4.3 ± 0.5 cm/GW for colloidal PTCDA nanocrystals in solution at 820 nm [14]. The TPA coefficient has been calculated from the two-photon-absorption-cross-section σ = 40 GM using the expression $\sigma = h\nu\beta/N$ [12], where N is the number of molecules (2) per unit volume of 766.5 × 10^{-24} cm^{-3} for α-PTCDA [24], $h\nu$ is the photon energy. Due to its crystalline structure, PTCDA

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nanocrystals and films show a strong optical anisotropy for electric fields polarized within the molecular plane or along the molecular stacking direction (which is nearly normal to the molecular plane). Due to the higher electron density within the molecular plane, PTCDA films exhibit significantly higher in-plane linear absorption values and refractive index values as compared to out-of-plane values [41,42]. We therefore expect higher TPA values for in-plane polarized electric fields in α-PTCDA films than from randomly orientated PTCDA nanocrystals in colloidal solution which may explain the discrepancy between our TPA coefficient and the reported TPA from PTCDA nanocrystals. Z-scan experiments on α-PTCDA crystals [28] with the light polarization oriented along different crystal axes, similar as in [43], would provide information to clarify the anisotropy of the nonlinear response.

With the nonlinear absorption coefficient β the imaginary part of the third order nonlinear susceptibility $\chi_I^{(3)}(\mathrm{SI})$ for PTCDA can be calculated according to the relation $\chi_I^{(3)}(\mathrm{SI}) = n_0^2 \varepsilon_0 c \lambda \beta / 3\pi = 2 n_0^2 \varepsilon_0 c^2 \beta / 3\omega$ [8], which leads to $\chi_I^{(3)}(\mathrm{SI}) = 6.8 \times 10^{-20}\ \mathrm{m^2/V^2}$ using the linear refractive index $n_0 = 2.22$ at the wavelength of 820 nm [40]. The $\chi_I^{(3)}(\mathrm{SI})$ value is equivalent to $\chi_I^{(3)}(\mathrm{cgs}) = 4.8 \times 10^{-11}$ *esu* in cgs units using the conversion [44];

$$\chi^{(n)}(\mathrm{SI}) / \chi^{(n)}(\mathrm{cgs}) = 4\pi / \left(3 \times 10^4\right)^{n-1} \tag{3}$$

3.2 Closed aperture z-scan measurements

Closed aperture z-scan measurements, which are sensitive to both nonlinear refraction and nonlinear absorption, were performed at a repetition time of 0.75 μs with the 20x lens. The small (closed) aperture transmits 10% of the light of the open aperture z-scan measurements. Dividing the normalized closed aperture transmittance by the normalized open aperture transmittance extracts the contribution of the nonlinear refraction. Figure 4 shows the normalized closed/open z-scan signals for the PTCDA film at an intensity I_0 = 22 GW/cm^2. The valley-to peak profile of the closed aperture z-scan trace indicates that the nonlinear refractive index for the PTCDA thin film is positive (self-focusing). The phase shift $\Delta\phi_0$ of the transmitted light due to the nonlinear refractive index can be deduced by fitting the normalized closed/open transmittance with the following equation [1];

$$T(z, \Delta\varphi_0) = 1 + \frac{4\Delta\phi_0 x}{\left(x^2 + 9\right)\left(x^2 + 1\right)} \tag{4}$$

where $x = z / z_0$. Hence the nonlinear refractive index n_2 can be calculated using the relation:

$$\Delta\phi_0 = k I_0 n_2 L_{eff}. \tag{5}$$

The solid line in Fig. 4 shows the theoretical fit using Eq. (4) with ω_0 = 2.6 μm providing a nonlinear phase shift of $\Delta\phi_0$ = 0.022. The resulting nonlinear refractive index n_2 amounts to (1.2 ± 0.3) × 10^{-13} cm^2/W using Eq. (5), which is equivalent to 6.4 × 10^{-11} *esu* using the relation $n_2(esu) = c n_0 n_2 \left(\mathrm{m^2/V^2}\right) / 40\pi$ [1]. Considering the reflection losses at the entrance surface of the PTCDA further enhances the nonlinear refractive index value by ~16% to (1.4 ± 0.3) × 10^{-13} cm^2/W. The experimental error is mainly attributed to the dark current noise of the photodiodes. The signal-to-noise ratio could be improved by longer time-integration at each sampling step or by averaging more z-scans.

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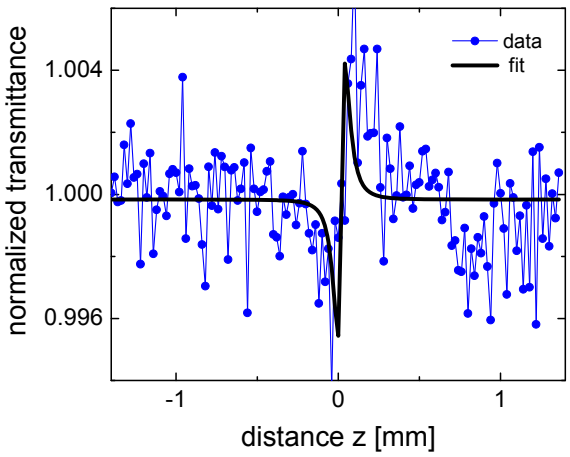

Fig. 4. Normalized closed/open z-scans at the repetition time of 0.75 μs using a 20x microscope objective lens. The incident laser intensity was 22 GW/cm^2. The solid line represents the theoretical fit using Eq. (4) as described in the text.

We also performed closed aperture z-scan measurements with the 10x lens at the repetition time 2.5 μs, where slight heat accumulation has been observed in open aperture z-scan measurements as described earlier. Figure 5 shows the normalized closed/open z-scan at an intensity of I_0 = 37 GW/cm^2. The solid line represents the theoretical fit according to Eq. (4) (using a beam waist of ω_0 = 5.2 μm), which renders a nonlinear phase shift of $\Delta\phi_0$ = 0.028 and results in a nonlinear refraction coefficient of (9.5 ± 0.3) × 10^{-14} cm^2/W. This value is by ~25% lower compared to the n_2 coefficient measured with the 20x microscope objective lens. We attribute this reduction to the formation of a thermal lens which causes a counteracting negative refraction [19–23].

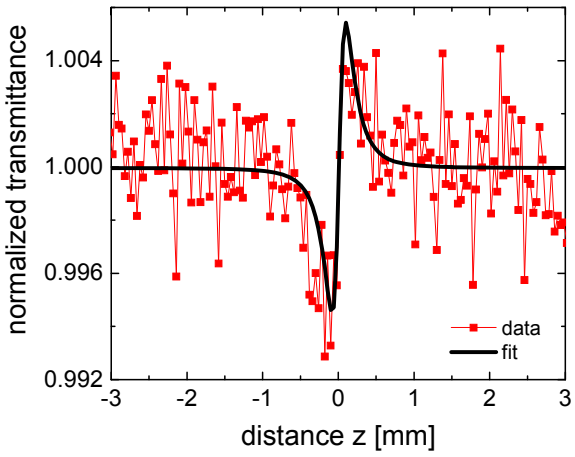

Fig. 5. Normalized closed/open z-scans at the repetition time of 2.5 μs with 10x microscope objective lens. The incident laser intensity was 37 GW/cm^2. The solid line represents the theoretical fit using Eq. (4) as described in the text.

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From the nonlinear refractive index value n_2 for the 20x lens the real part of the third order nonlinear susceptibilty $\chi_R^{(3)}$ for PTCDA is found to be $\chi_R^{(3)}(\mathrm{SI}) = 2.1\times10^{-19}\ \mathrm{m}^2/\mathrm{V}^2$ using the relationship $\chi_R^{(3)}(\mathrm{SI}) = 4n_0^2\varepsilon_0 c\gamma/3$ [8]. This value leads to $\chi_R^{(3)}(\mathrm{cgs}) = 1.5\times10^{-10}$ *esu* using Eq. (3). This value is in good agreement with the reported value of $\chi_R^{(3)}(\mathrm{cgs}) = 2.0\times10^{-10}$ *esu* which was measured with degenerate four wave mixing at an excitation wavelength of 602 nm.

4. Summary

We performed z-scan measurements on an OMBD grown PTCDA thin film with tightly focused 100 fs laser pulses at a wavelength of 820 nm. Cumulative thermal effects due to sample heating in the focus area were investigated by varying the laser repetition time using an acousto-optic pulse selector and by applying different focus diameters on the sample. Our results show that z-scan measurements using a 10x microscope objective lens at repetition times shorter than 5.0 μs are modified by accumulated heat within the optically excited area. For repetition times longer than 5.0 μs we observe a constant transmittance dip indicating that thermal effects can be neglected. Thermal effects at higher repetition times are diminished by a smaller focus area created by a 20x microscope objective lens leading to a faster heat diffusion from the excited focus area into the unexcited film. The measured TPA coefficient β, the nonlinear refractive index value n_2 and the third-order susceptibilities $\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)}$ of the PTCDA films at a wavelength 820 nm are summarized in Table 1. (Reflection losses at the entrance surface of the films have not been considered.)

Table 1. Measured two-photon absorption coefficient β, nonlinear refractive index n_2 and third order susceptibility values $\chi_I^{(3)}$ and $\chi_R^{(3)}$ of the PTCDA films at a wavelength of 820 nm.

β	n_2	n_2	$\chi_I^{(3)}$	$\chi_I^{(3)}$	$\chi_R^{(3)}$	$\chi_R^{(3)}$
cm/GW	cm^2/W	esu	$\mathrm{m}^2/\mathrm{V}^2$	esu	$\mathrm{m}^2/\mathrm{V}^2$	esu
6.0	1.2×10^{-13}	6.4×10^{-11}	6.8×10^{-20}	4.8×10^{-11}	2.1×10^{-19}	1.5×10^{-10}

Our experiments demonstrate that a modified z-scan technique which uses tightly focused 100 fs pulses at reduced repetition rates opens new prospects to measure the nonlinear optical properties of soft organic films. These soft films usually suffer from thermal effects or from structural damage in the standard z-scan setup. The modified z-scan technique can also be applied to plasmonic organic/metal films and nanostructures where thermal accumulation effects are severe limiting factors.

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