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Measurement of two-photon absorption coefficient of dye molecules doped in polymer thin films based on ultrafast laser ablation

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Abstract

Two-photon absorption cross-section of a series of dyes (**1a**–**3a**) in polymer thin films was determined by measuring the femtosecond laser ablation threshold. The ablation threshold decreased gradually when the dopant increased. The two-photon absorption cross-section of the dye molecules dispersed in the polymer film was estimated by using the theoretical relationship between the ablation threshold of the blended polymeric thin films and the dye concentration. The relative values of two-photon absorption cross-section are in good agreement with those measured in solution. On the other hand, the absolute values are smaller than the latter.

1. Introduction

Two-photon absorption (TPA) is one of the most fundamental processes in nonlinear optical phenomena. There is much interest in this area for possible applications in biological and materials sciences. For example, two-photon microscopy (TPM) has become a vital tool for live-tissue imaging due to the enhanced spatial resolution and long-term applicability [1,2]. Also, TPA dyes with large cross-section and high emission quantum efficiency in visible region may find application as diode pumped upconversion light source [3–5]. Such materials are also useful in material processing because blending a dye with large TPA cross-section into the target materials can dramatically reduce the ablation threshold. To develop an efficient TPA material, it is essential to measure the TPA cross-sections of newly synthesized materials. Several methods including nonlinear transmittance measurement [6], Z-scan technique [7], and two-photon fluorescence measurement [8] have been employed for this purpose. Although these methods have certain drawbacks such as excited state excitation and photo-thermal effects, they are widely used in the field related on the two-photon absorption process [6–8]. A few studies have been reported on the two-photon absorption coefficient of dye molecules by fs-laser processing of polymer system doped with two-photon absorption dye [9,10]. Furthermore, the two-photon absorption coefficient for bulk InP was reported by analyzing the cross section profiles of the ablated region by irradiating fs-laser pulses [11]. However, there does not exist any universal method for the measurement of two-photon absorption cross-section in the solid state. There has been no precedent study with a purpose of TPA cross-section measurement of a dye molecule doped in polymer matrix based on the fs-laser ablation. In this work, we have developed a new method for measuring the TPA cross-section of a dye in a transparent polymer thin film based on the laser ablation phenomena. We have measured the TPA cross-section of a series of two-photon materials (**1a**–**3a** [12]) in PMMA films. The results are compared with those in solution measured by the fluorescence method.

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2. Theory

Whereas the exact mechanism of ablation dynamics is not known, it is well accepted that the ablation threshold is determined by the total energy absorbed by the materials. For ablation to occur by photoexcitation, the total absorbed energy should exceed an ablation work-energy of the sample that is needed to change the materials from the solid to the gas phase. We suppose that the changes in beam-intensity $I(\mathrm{W/cm^2})$ along the propagation direction (z axis) is used to the work-energy to ablate material. If we neglect the higher-order absorption process of the thin films, the ablation work-energy, $\varepsilon_{\mathrm{abl}}(\mathrm{W/cm^3})$, can be described by the absorption of photons by the films with one- and two-photon absorption coefficients, $\alpha(\mathrm{cm^{-1}}) = \sigma^{(1)}(\mathrm{cm^2})N_0$ and $\beta(\mathrm{cm/GW}) = \sigma^{(2)}(\mathrm{cm^4/GW})N_0$, respectively,

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -\alpha I - \beta I^2 \rightarrow \varepsilon_{\mathrm{abl(polymer)}} = -\frac{\mathrm{d}I}{\mathrm{d}z}$$
$$\varepsilon_{\mathrm{abl(polymer)}} = \beta I^2 + \alpha I = \sigma_{\mathrm{p}}^{(2)} N_0 I_{\mathrm{th}}^2 + \sigma_{\mathrm{p}}^{(1)} N_0 I_{\mathrm{th}} \tag{1}$$

where $N_0(1/\mathrm{cm^3})$ is number density; $\sigma_{\mathrm{p}}^{(1)}(\mathrm{cm^2})$, $\sigma_{\mathrm{p}}^{(2)}(\mathrm{cm^4/GW})$ are the one-photon absorption cross-section, TPA cross-section, respectively. The ablation processes occur mainly at focus of laser beam. The on-axis fluence $F(\mathrm{J/cm^2})$ in free space of Gaussian beam is given by [13]

$$F = \int_{-\infty}^{\infty} I \exp\left[-\left(\frac{t}{\tau}\right)^2\right] \mathrm{d}t = \pi^{1/2}\tau I \tag{2}$$

where τ is the laser pulse duration. Equivalently, Eq. (1) can be written in terms of fluence $F\,(\mathrm{J/cm^2})$

$$\varepsilon_{\mathrm{abl(polymer)}} = \frac{\sigma_{\mathrm{p}}^{(2)} N_0}{\pi\tau^2} F_{\mathrm{th}}^2 + \frac{\sigma_{\mathrm{p}}^{(1)} N_0}{\pi^{1/2}\tau} F_{\mathrm{th}} = \varepsilon_0 \tag{3}$$

where ε_0 is the ablation threshold work-energy of the pure thin films, if the material is ablated at the ablation work-energy.

For a polymer film doped with a dye, the total absorbance can be described as follows:

$$\begin{aligned}\varepsilon_{\mathrm{abl(total)}} &= \left(\frac{\sigma_{\mathrm{p}}^{(2)} N_0}{\pi\tau^2} F_{\mathrm{th}}^2 + \frac{\sigma_{\mathrm{p}}^{(1)} N_0}{\pi^{1/2}\tau} F_{\mathrm{th}}\right)_{\mathrm{polymer}} \\ &\quad + \left(\frac{\sigma_{\mathrm{d}}^{(2)} N_{\mathrm{A}} c_{\mathrm{d}} \times 10^{-3}}{\pi\tau^2} F_{\mathrm{th}}^2 + \frac{\sigma_{\mathrm{d}}^{(1)} N_{\mathrm{A}} c_{\mathrm{d}} \times 10^{-3}}{\pi^{1/2}\tau} F_{\mathrm{th}}\right)_{\mathrm{dye}} \\ &= \left(B\sigma_{\mathrm{p}}^{(2)} F_{\mathrm{th}}^2 + \frac{\sigma_{\mathrm{p}}^{(1)} N_0}{\pi^{1/2}\tau} F_{\mathrm{th}}\right)_{\mathrm{polymer}} \\ &\quad + \left(A\sigma_{\mathrm{d}}^{(2)} c_{\mathrm{d}} F_{\mathrm{th}}^2 + \frac{\sigma_{\mathrm{d}}^{(1)} N_{\mathrm{A}} c_{\mathrm{d}} \times 10^{-3}}{\pi^{1/2}\tau} F_{\mathrm{th}}\right)_{\mathrm{dye}}\end{aligned} \tag{4}$$

where N_{A} is the Avogadro's number, $(\sigma_{\mathrm{d}} N_0)_{\mathrm{dye}} = \sigma_{\mathrm{d}} N_{\mathrm{A}} c_{\mathrm{d}} \times 10^{-3}$, $A = \frac{N_{\mathrm{A}} \times 10^{-3}}{\pi\tau^2}$ and $B = \left(\frac{N_0}{\pi\tau^2}\right)_{\mathrm{polymer}}$; $\sigma_{\mathrm{d}}^{(1)}$, $\sigma_{\mathrm{d}}^{(2)}$ and c_{d} (mol/L) are the one-photon absorption cross-section, TPA cross-section, and molar concentration of doped dyes, respectively. Assuming that the one-photon absorption cross-section is negligible compared to the two-photon absorption process at the interested wavelength, the Eq. (4) can be approximated as Eq. (5).

$$\varepsilon_{\mathrm{abl(total)}} \approx A\sigma_{\mathrm{d}}^{(2)} c_{\mathrm{d}} F_{\mathrm{th}}^2 + B\sigma_{\mathrm{p}}^{(2)} F_{\mathrm{th}}^2 \tag{5}$$

If the dye concentration is very low so that the ablation energy for the doped film is very similar to that of the pure film, the ablation threshold of the two films should be almost the same ($\varepsilon_0 \approx \varepsilon_{\mathrm{abl(total)}}$). Under this condition, Eq. (5) can be written as follows:

$$\frac{1}{F_{\mathrm{th}}^2} = \frac{A\sigma_{\mathrm{d}}^{(2)}}{\varepsilon_0} c_{\mathrm{d}} + \frac{B\sigma_{\mathrm{p}}^{(2)}}{\varepsilon_0} \tag{6}$$

This predicts that the plots of $1/F_{\mathrm{th}}^2$ versus the dye concentration in the polymer films should give straight lines with the same intercepts, because $\frac{B\sigma_{\mathrm{p}}^{(2)}}{\varepsilon_0}$ is assumed to be a constant under this condition. The two-photon cross-section ($\sigma^{(2)}$) can be estimated from the slope/intercept ratio as shown in Eq. (7) (*vide infra*).

3. Experimental

TPA cross-section was determined based on a femtosecond laser ablation system, which was fully described elsewhere [14]. Briefly, Ti: sapphire laser system (Quantronix, pulse duration 150 fs, wavelength 800 nm, repetition rate 1 kHz) was used as a light source. The output of laser was delivered to galvanometer scanner (Scanlab AG, Germany), which is digitally controlled by an interface board (Scanlab AG, Germany) and IBM compatible PC. To avoid the accumulated effects due to the multiple pulses in ablation process, we have modulated the laser beam direction with high scanning speed of 43 mm/s. The variable neutral density filter (Sigma Koich, Japan) is used for controlling the laser power. A telecentric lens (Sill Optics, Germany), of which focal length is 130 mm, was employed to focus the laser beam on the thin film surface. The diameter of laser beam was about 6 mm. Experiment was performed by the ablation method by varying the laser power and dye concentration in the film. The irradiated areas were inspected with an optical microscope (Nikon ECLIPSE E400) and an atomic force microscope (PSIA, Korea) in contact-mode to obtain information about the morphological changes.

The dye molecules, which are supplied by B.R. Cho are 2,5-dyciano-1,4-bis-(*p*-diphenylaminostyryl)benzene (**1a**), *N*,*N*-bis{*p*-[4-(p-diphenylaminostyryl)-2,5-dicyanostyryl] phenyl}aniline (**2a**), and *N*,*N*,*N*-tris{*p*-[4-(*p*-diphenylaminostyryl)-2,5- dicyanostyryl]phenyl}amine (**3a**) (Fig. 1) [12]. Their TPA cross-sections measured in solution are reported elsewhere [12,15]. These molecules are designed to show systematic increase in the TPA cross-section by varying the number of branches of unit chromophore. Samples were prepared by dissolving polymethylmethacry-

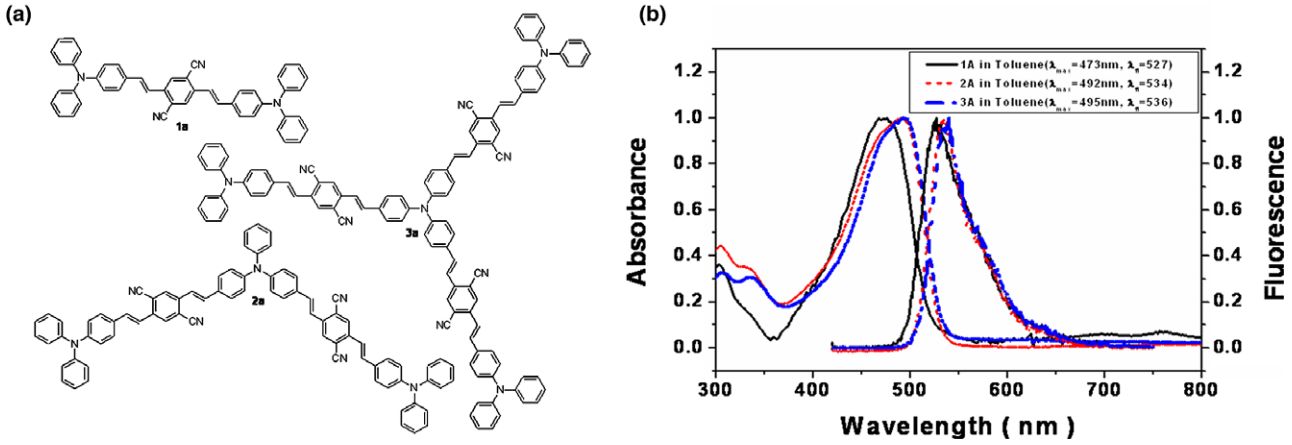

Fig. 1. The chemical structures and optical properties of **1a-3a** [11]. (a) Structures of **1a**–**3a**. (b) Normalized one-photon absorption and emission spectra of **1a**–**3a** in toluene.

late (PMMA, $M_w = 120{,}000$, Aldrich) in toluene using a magnetic stirrer at about 190 rpm for 2 days to obtain a 5 wt% polymer solution. TPA dye was dispersed in the same polymer solution by stirring for 2 days. Both solutions were mixed to prepare sample solutions with various dye concentration ($0–4 \times 10^{-4}$ M). The glass substrate (76 mm × 26 mm, 1 mm thickness, Knittel Glaser, Germany) was cut into three equal parts for further processing, cleaned with acetone and methanol, sonicated in distilled water, and then dried at 80 °C in the air oven. The solution was spin coated on a slide glass substrate by using a spin coater at a spinning speed of 2000 rpm for 4 s and dried at 80 °C for 2 h in the air oven. The thickness of thin films determined by AFM was approximately 250 nm.

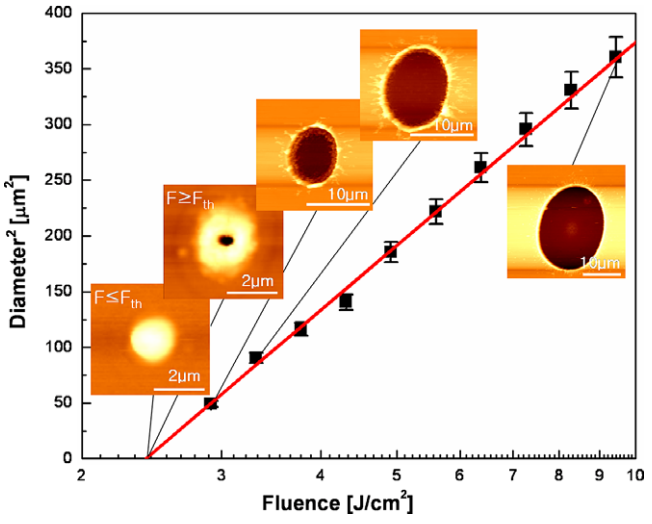

Fig. 2. Squared diameter D^2 of the ablated area of pure PMMA thin films as a function of laser fluence. The insets show the changes in the morphology of the film surface at five different laser fluences. The film thickness is 250 nm.

4. Results and discussion

Fig. 2 shows the ablated area of pure PMMA films as a function of laser fluence between 2.4 and 9.4 J/cm^2. The changes in the morphology of the polymer film surface were characterized by AFM. Below the ablation threshold, the polymer film swells gradually up to the height of about 260 nm from the plain of intact polymer thin film. At the threshold, a small hole appeared on the top of the swelling [16]. Similar phenomena were reported in PMMA films with a pulse width of 20 ns at 308 nm [17] and gold thin films with a pulse width of 30 fs at 800 nm [18,19]. The results have been attributed to the effective volume increase due to the breaking of C-O bonds in PMMA [20], and the local detachments of the films from the substrate, producing a void at the interface between film and substrate [21], respectively. When the laser fluence was further increased above the threshold, the ablation process became more evident with gradual increase in the ablated region. On the other hand, the topography of the ablated region revealed no indication of ablation on the glass substrate when processed at moderately high fluence. This indicates that the ablation threshold of the substrate is much higher than that of the thin film, of which values was measured to be approximately 3.5 J/cm^2.

To determine the ablation threshold F_{th} of the thin films, we have used the relationship $D^2 = 2\omega_0^2 \ln\left(\frac{F_0}{F_{th}}\right)$ between the diameter D of the ablated area and the maximum laser fluence F_0 at the sample surface with a supposition of a Gaussian spatial beam profile and a $1/e^2$-beam radius ω_0 [20]. The ablation threshold F_{th} can be estimated by extrapolating the linear fit to $D^2 = 0$. The plot of D^2 against fluence for pure PMMA films is shown in Fig. 2. The value of F_{th} estimated from the plot is 2.4 J/cm^2, which is in good agreement with the reported value of 2.6 J/cm^2 [20].

As shown in Fig. 3, the plots of $1/F_{th}^2$ versus the dye concentration are linear for **1a**–**3a**. Note that the data are well fitted to the straight lines by assuming that the intercepts

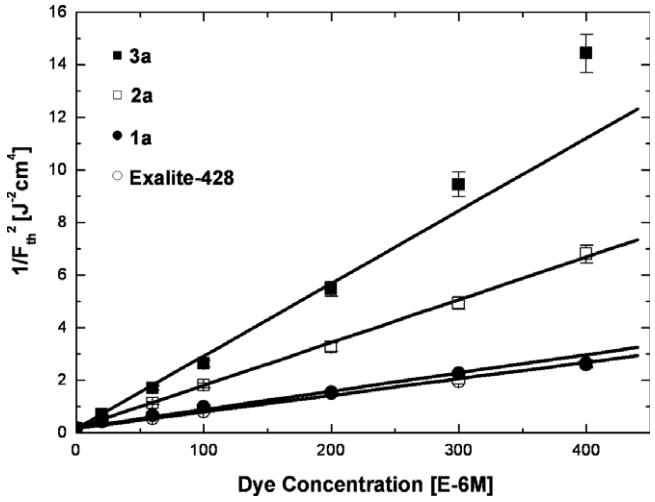

Fig. 3. Plots of $1/F_{th}$ against the dye concentration in PMMA thin films. Exalite-428 (open circles), **1a** (closed circles), **2a** (open square) and **3a** (closed square). The data are fitted to straight lines by the least sqaure method by assuming that the intercepts are constant. (see the text).

are the same for all dyes (*vide supra*). Hence, the slope is $A\sigma_d^{(2)}/\varepsilon_0$ and the intercept is $B\sigma_p^{(2)}/\varepsilon_0$. From the ratio of the slope to the intercept, R, TPA cross-section $\sigma_d^{(2)}$ can be expressed as follows:

$$\frac{A\sigma_d^{(2)}/\varepsilon_0}{B\sigma_p^{(2)}/\varepsilon_0} = \frac{N_A \times 10^{-3}\sigma_d^{(2)}}{N_0\sigma_p^{(2)}} = \frac{\sigma_d^{(2)}}{c_p\sigma_p^{(2)}} = R \quad (7)$$

$$\sigma_d^{(2)} = c_p\sigma_p^{(2)}R \quad (8)$$

where c_p and $\sigma_p^{(2)}$ are $\left(\frac{N_0}{N_A\times 10^{-3}}\right)_{polymer}$ (mol/L) and TPA cross-section of PMMA thin films, respectively. Since δ(cm^{4}sec/photon molecule) equal to $\sigma^{(2)}$(cm^4/GW)$h\nu$,

$$\delta_d = c_p\delta_p R. \quad (9)$$

To determine the TPA cross-sections of **1a**–**3a** in PMMA films, we have conducted the same experiments for Exalite-428 (Exciton Inc.). The literature value of TPA cross-section for Exalite-428 in PMMA matrix measured by comparing the fluorescence intensities pumped by one- and two-photon excitations is 1×10^{-49} cm^{4}s [9]. By using this value and slope/intercept ratio from the plot in Fig. 3, the $c_p\delta_p$ value has been calculated from Eq. (7). The value of $c_p\delta_p$ estimated by this method is 27.9×10^{-55}(cm^{4}s)·(mol/L). The TPA cross-sections of **1a**–**3a** have been calculated by substituting $c_p\delta_p$ and slope/intercept ratios R of the corresponding plots in Fig. 3 into Eq. (9). The calculated values of δ_d for **1a**, **2a** and **3a** are 10.0×10^{-50} cm^4 s, 25.2×10^{-50} cm^4 s, 45.4×10^{-50} cm^4 s, respectively (Table 1).

We note that PMMA thin films blended with **3a** show positive deviation from the expected straight line in Fig. 3 at the higher concentration range. Because the ablation work-energy of the thin films blended with **3a** is expected to be similar to those with **1a** and **2a** (*vide supra*), this result may be attributed to the additional nonlinear optical process such as higher order absorption process or photo-induced absorption of the excited state molecules. The existence of the additional photon absorption processes may eventually result in the decrease of the ablation threshold.

Table 1 shows that the relative TPA cross-section increases from 1.0 to 2.5 to 4.5 fold as the number of branching increases from 1(**1a**) to 2(**2a**) to 3(**3a**). This indicates a significant enhancement of the TPA cross-section in the multi-branched structure. Similar result was observed from solution measurements [12,15]. Moreover, the positive deviation noted for **3a** in Fig. 3 indicates additional advantage of the multi-branched structure. However, there is large discrepancy in the values measured in thin films and in solution. The values measured in thin films are smaller than those in solution by a factor of 30–90. Similar discrepancy was already noted in the TPA coefficients of AF-50 (*N*,*N*-diphenyl-7-[2-(4-piridinyl) ethenyl]-9,9-di-*n*-decylfluoren-2-amine) in solution and in the solid phase [9]. At present, the origin of this discrepancy is not clear. A possible explanation is that the TPA cross-section for Exalite-428 may have been underestimated. Alternatively, the different local environment of the dyes in solution and in the thin film may have played an important role in the nonlinear optical absorption process.

Table 1
Two-photon absorption cross-sections of **1a**–**3a** determined by various methods

Method		Dye concentration (M)	Excitation wavelength (nm)	$\sigma_{1a}^{(2)a}$	$\sigma_{2a}^{(2)a}$	$\sigma_{3a}^{(2)a}$
Laser ablation[b]	fs single pulse	$(0–4)\times10^{-4}$	800	10.0(1.0)	25.2(2.5)	45.4(4.5)
Absorption (THF)[c]	Z-scan	$(1–10)\times10^{-4}$	800	432(1.0)	708(2.6)	1020(4.7)
Fluorescence (Tol)	fs 76 Mhz[c,d]	1×10^{-5}	800	618(1.0)	1540(2.5)	1960(3.2)
	fs 1 kHz[c,e]	$(0.5–1)\times10^{-5}$	800	982(1.0)	2950(3.0)	4170(4.2)
	ns[f,g]	$(0.5–1)\times10^{-5}$	800	495(1.0)	1020(2.1)	1900(3.8)

[a] Two-photon cross-section in 1×10^{-50} cm^4 s.
[b] This work.
[c] Ref. [14].
[d] Repetition rate = 76 MHz, λ = 767–818 nm, τ = 180 fs.
[e] Repetition rate = 1 kHz, λ = 740–1020 nm, τ = 160–180 fs.
[f] Repetition rate = 10 Hz, τ = 5 ns.
[g] Ref. [11].

5. Conclusions

We have developed a new method to measuring TPA cross-section of a dye in polymer thin film based on fs-laser ablation process. For a given matrix, the ablation work-energy for fs-laser ablation at the threshold remains constant. The ablation threshold is significantly decreased by the TPA dye when doped into the polymer matrix even at a very low concentration ($<10^{-4}$ M). This result suggests that one can selectively process an area with high spatial resolution of multi layered thin films or plasma membranes without apparent damage in other region, by doping a dye with large TPA cross-section. Finally, the relative TPA cross-sections of the three dyes measured in solid film are in good agreement with those in solution, although the absolute values are much smaller than those in solution.

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