High-order photobleaching of pyrylium salts under two-photon excitation

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Abstract. Pyrylium salts were found to be attractive candidates for applications based on two-photon absorption effect. Especially, they have been used for three-dimensional data storage through photobleaching process. In the present work the photobleaching, under two-photon excitation, is investigated for a representative pyrylium salt hosted in a polymethylmethacrylate film. The photobleaching dependence on time, power and wavelength irradiation as well as on the film concentration is presented. Our results reveal the existence of two photobleaching mechanisms and indicate the presence of high-order interactions in these processes.

1. Introduction
Two-photon absorption (TPA) is a third order nonlinear process in which two photons are absorbed simultaneously to excite a molecule [1]. It is one of the first nonlinear phenomena that were observed experimentally [2]. However, this phenomenon attracted considerable attention after the invention of ultrafast lasers during the last decade [3]. Two-photon microscopy, photodynamic therapy, optical power limiting, upconverted lasing, single molecule detection, microfabrication and 3-dimensional data storage are significant applications of two-photon technology [4].

Two-photon absorption probability depends quadratically on intensity, so under tight focusing conditions the absorption is confined to a small volume. This fact provides a means of activating chemical or physical processes with high spatial resolution in three dimensions [5]. Photobleaching is one of these processes. It is defined here as the irreversible light induced change in the chemical structure or even the destruction of a molecule that causes a decrease of its fluorescence.

In a previous work of our group photobleaching was used as the recording mechanism for permanent 3-D data storage in a dye doped polymer matrix [5]. The bleached dye was a representative pyrylium salt, 4-phenyl-2,6-bis (4-methoxyphenyl) pyrylium tetrafluorobate (abbreviated as P), which has shown both large TPA cross-section and high quantum yield. In the present work we examine the photobleaching of this dye regarding concentration and different irradiation parameters as time, power and wavelength.
2. Experimental

The synthesis of pyrylium salts, as well as, their one- and two-photon absorption spectra were reported elsewhere [5,6]. The pyrylium salt (P) that is investigated is shown in figure 1. Polymethylmethacrylate (PMMA) was selected as the polymer host because of its good optical behavior. To prepare the dye-doped polymer films, purified P (99%) and PMMA (Aldrich) were mixed together with weight ratios from 1 to 3%. The mixture was diluted in Tetrahydrofuran (THF) and casted over a microscope slide glass to form the film. The evaporation of the solvent was made in the ambient air and room-temperature (25 °C).

The films were continuously irradiated with short laser pulses (~100 fs). The laser source was a mode-locked Ti:Sapphire laser, tunable from 740-850 nm (Tsunami, Spectra-Physics). The beam was focused into the samples with an oil immersion objective lens (100X, N.A.: 1.2). The power was controlled with a motorized λ/2 plate and a femtosecond polarizer (Melles Griot, 16PPB200). The fluorescence signal was collected with the same lens and separated from the input beam with a cold mirror reflecting from 400 to 600nm (Thor-Labs FM03). A photomultiplier tube (PMH-100-4) and a single photon counting system (Becker&Hickl, PMS300) were used for the measurement of this signal. In order to record the sharp decay in the fluorescence caused by photobleaching, a fast shutter system (rise time 5 ms, Newport 845HP) was synchronized with the single-photon counting electronics.

3. Results and discussion

A very important parameter involved in the photobleaching process is the irradiation time of the sample. It is known that an increase of the irradiation time causes a decrease of fluorescence. The exact relation that describes the above general finding depends on the molecular structure. The experimental definition of this relation for the pyrylium salt P was made by photobleaching the films at different power levels and for a certain time-period. The results are shown in figure 1. In all cases, the best-fitting function of the fluorescence signal versus irradiation time was a double-exponential decay:

\[ F(t) = F_0 + A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \]

where \( F \) is the fluorescence photon flux, \( k_1 \) and \( k_2 \) are the photobleaching rates, \( A_1 \) and \( A_2 \) are the weight constants for each decay and \( F_0 \) is a noise constant. From simple molecule kinetics it is evident that, under two-photon excitation, there are two distinct photobleaching mechanisms for the pyrylium salt. The contribution of each mechanism to the photobleaching process differs significantly. As shown in figure 2a the weight ratio \( A_1/A_2 \) ranges from 7.5 to 145 for irradiation power levels from 5 to 18 mW respectively. Furthermore, the photobleaching rate \( k_1 \) is much greater than \( k_2 \). For instance, at a power level of 7.5 mW these rates are 11s\(^{-1}\) and 0.16 s\(^{-1}\) respectively. According to the previous remarks we conclude that the first mechanism is responsible for the steep decrease of fluorescence at the first few ms of irradiation. The second mechanism causes a much slower bleaching and becomes

![Figure 1. a) The pyrylium salt P b) Fluorescence signal versus irradiation time for 5 different irradiation power values. (The concentration of the film C=1% wt, \( \lambda_{exc}=755nm, \tau=80\) fs)](image)
important at very low power levels and long irradiation times (which is not our case). Thus, for three-dimensional data storage only the first photobleaching mechanism is vital and will be studied in more detail afterwards.

The fluorescence that is induced by TPA depends on the square of the incident power. It is expected that the photobleaching rate should depend on power with the same manner. Figure 2b shows the photobleaching rate $k_1$ versus irradiation power at a particular wavelength. The slope of this log-log plot is $-3$, indicating that photobleaching is a process in which more than two-photons are involved ($k_1 \propto P^3$). Similar results have been reported in the recent literature for other dye classes [7,8,9]. The high order photobleaching explains, in a very persuasive way, the very fast and efficient 3-D recording in pyrylium-doped matrices demonstrated in our previous work.

The dependence of $A_1$ and $k_1$ on the wavelength is shown in figure 3. It is observed that the spectrum of $A_1$ is similar to the TPA one, namely $A_1(\lambda) \propto \delta(\lambda)$, where $\delta$ is the TPA cross section. The physical meaning of this observation is that the molecule absorbs simultaneously two photons to reach the first excited state and then absorbs one more photon to reach the bleaching state. Thus, photobleaching occurs with an excited state absorption and not with the simultaneous absorption of three photons from the fundamental state.

The spectrum of the photobleaching rate $k_1$ deviates significantly from the TPA spectrum. Hence, the electronic states involved in the two-photon absorption are not the same with those involved in the photobleaching process. This result is in agreement with the conclusion that photobleaching is a three- and not a two-photon process incorporating more electronic states.

**Figure 2.** a) Weight constant ratio versus irradiation power b) log-log plot of the photobleaching rate $k_1$ versus irradiation power. The slope of the linear fit is $3.04 \pm 0.02$ (concentration=1% wt, $\lambda_{exc}=755$nm, $\tau=80$ fs)

**Figure 3.** Normalized Weight constant $A_1$ and photobleaching rate $k_1$ spectra compared with the TP excitation spectrum of pyrylium salt [5] (concentration=1% wt. Irradiation power $P=7.5$ mW, $\tau=80$fs)
In order to examine the dependence of $k_1$ on the dye concentration, five samples at different concentrations were photobleached. The irradiation power, wavelength and pulse duration were kept constant. The results are shown in figure 4. It is not clear if the photobleaching rate depends on the concentration, at least for the range of concentrations used in our experiment.

![Figure 4. Photobleaching rate $k_1$ versus concentration of the pyrylium salt in the polymer matrix. (Irradiation power=7,5 mW, $\tau$=80 fs . $\lambda_{exc}$=755 nm)](image)

4. Conclusion
In conclusion, the photobleaching properties of a pyrylium salt doped in PMMA were investigated. It was found that there are two bleaching mechanisms. The first one is dominant and causes a very fast bleaching whereas the second one is less important and causes a slow bleaching. The first mechanism, which is essential for the 3-D data storage, is a three-photon process. This means that the photobleaching is restricted to an even smaller volume compared with TPA, increasing significantly the spatial resolution of recording. The last finding might constitute a guide for the selection of the materials that can be used in 3-D memories based on photobleaching.

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6. References
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