

Nonlinear fluorescence modulation of an organic dye for optical data storage

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Most approaches to high-capacity 3D optical data storage (ODS) require confinement of the writing action to a specified depth in the writing medium. This is achieved by a nonlinear photoresponse, usually two-photon absorption, which requires a pulsed long-wavelength source. Fluorescence photobleaching of a dye/polymer composite can be used at a short wavelength to store data at the diffraction limit in a layered storage medium. In this work, the writing response of a bleachable dye/polymer system illuminated with single pulses of various duration obtained from a modulated 405 nm wavelength CW laser was studied. A transition from a linear to nonlinear writing mechanism was observed near the microsecond time scale. Concentration-dependent measurements indicate that a photothermal mechanism accounts for the nonlinear response in the short pulse, higher power regime. This nonlinear response may be useful for realizing terabyte scale ODS in multilayered polymer media. © 2014 Optical Society of America

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1. INTRODUCTION

Commercial optical data storage (ODS) technologies such as Blu-ray (BR) offer a low-cost, long-term solution to data-storage needs, but their adoption has mainly been limited to multimedia and small-scale personal archiving due to limited capacity. Efforts to increase the capacity of BR media by stacking more data layers have been slow because the phase-change writing scheme employed leads to beam attenuation and interference from multiple reflections [1], and the cost of fabricating additional data layers is high [2].

Many alternative methods have been proposed to increase ODS capacity, such as holographic storage [3,4], polarization [5], spatial [6] multiplexing, and nanostructured DNA-based storage [7]. 3D storage has also been extensively explored in organic materials using two-photon absorption to localize the bits during reading and writing [8,9]. This requires a long-wavelength, pulsed laser with attendant cost, size, and safety drawbacks. Although CW lasers have also been utilized, large writing and reading cross talk is observed due to the linear response. We have shown that these effects can be mitigated by physically layering the medium, which greatly improves the data-layer axial confinement and allows for increased storage density [10]. While layer cross talk is reduced, it is still large enough to limit the number of writable layers and number of reading cycles.

To address this, we demonstrate here a new method for generating a nonlinear fluorescence (FL) modulation in dye/polymer systems using a CW laser. We show that by exciting the samples at 405 nm from a pulse-modulated CW laser on the sub-microsecond and nanosecond time scales, a nonlinear dependence of the photobleaching is observed. The dye employed in this study exhibits reverse saturable absorption (RSA) at the laser wavelength [11], which

promotes multistep excitation into higher excited states. These states increase the nonradiative decay channels at high power, contributing to a nonlinear photoresponse through direct bleaching from these states [12], deposition of thermal energy, or other effects. In addition, the sub-microsecond exposures are used to reduce the lowest lying triplet population. This suppresses the bleaching at low power, further enhancing the nonlinearity.

The method demonstrated here will have a significant impact on ODS. Using a wavelength in the linear absorption regime, but still essentially off-resonance, allows for less power, smaller spot sizes, and the ability to read and write with the same source, compared to IR illumination. There are also low-cost, high-power laser diodes available at this wavelength. Furthermore, the nanosecond response times lead to higher bit rates for ODS applications. The nonlinear mechanism is efficient enough to obtain good contrast with sub-microsecond pulses with less than 100 mW of CW power. Fluence, concentration, and power-dependence measurements were carried out in order to determine the photophysical mechanism.

2. EXPERIMENT

Films consist of poly(styrene-*co*-acrylonitrile) (SAN25) doped with the FL dye Rhodamine 6G (R6G). SAN25 was dissolved in γ -butyrolactone at a concentration 10 wt. %, and films of between 0.1 and 2.0 wt. % of R6G to SAN25 were prepared by addition of an appropriate amount of the dye to the solution and spin coating on glass slides at 1000 rpm for 60 s. The films were then left to dry at 80°C for 1 h, with additional drying at room temperature for several hours. This yielded films between 500 and 700 nm thick. SAN25 was chosen for its exceptional dye solubility.

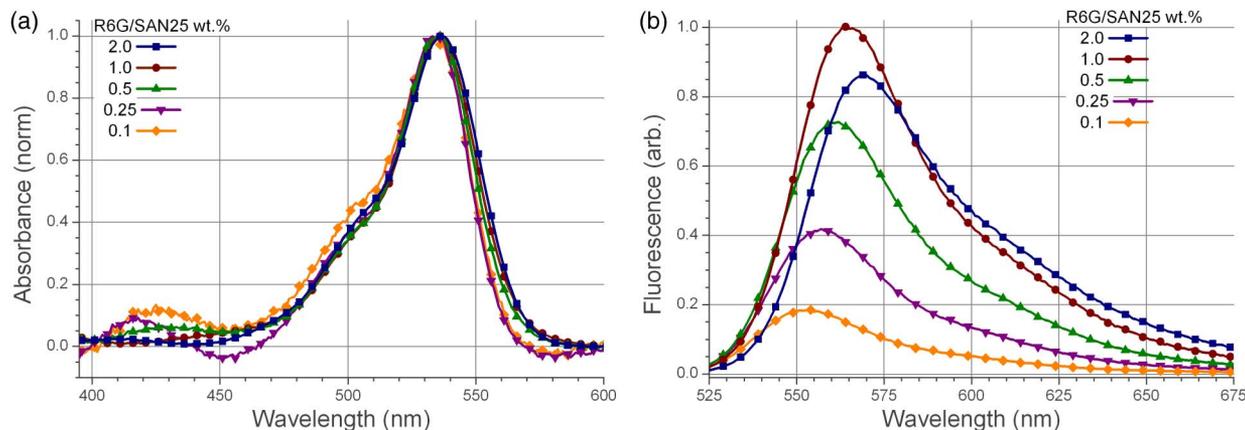


Fig. 1. (a) Absorption spectra of films with varying dye concentrations, normalized to the peak values, showing no significant dimer formation. (b) FL spectra of same films, normalized only to thickness and beam intensity. There is a large bathochromic shift indicative of FL absorption and re-emission.

The absorption spectra of films with varying concentration are shown in Fig. 1(a). Each curve is normalized by its peak absorbance, and the absorption coefficient for the 1.0 wt. % sample at 405 nm is approximately $0.015 \mu\text{m}^{-1}$. Based on the extinction coefficient for R6G and the measured absorbance of the film, the actual concentration in the films is as expected: 1.0 wt. % gives a nominal concentration of 20 mM. Besides a very slight shift of the peak wavelength, there is no significant change in the shape, indicating limited aggregate formation. This is likely due to the good dye solubility in the polymer.

The FL spectra of the same films are shown in Fig. 1(b). An observed bathochromic shift in the FL peak of more than 15 nm from 0.1 to 2.0 wt. % is indicative of FL absorption and re-emission rather than aggregation, as concluded in concert with the absorption spectra. This is expected based on previous work on R6G FL quantum yield in polymer films at similar concentrations [13]. The presence of FL absorption and re-emission is also indicated from the integrated absorbance and FL shown in Fig. 2. The magnitude of the FL is sublinear with concentration, and, given that the absorption is linear, this implies that the relative quantum yield decreases at higher concentrations. This is calculated and included as an inset to Fig. 2.

Spots in the sample were bleached by single pulses from a 405 nm, 300 mW CW laser (Omicron PhoxX) externally modulated with a National Instruments DAQ card while simultaneously translating the sample. A modulation bandwidth of 50 MHz is possible with this system. The laser was focused for writing using a Leica HCX Plan Fluotar, 100 \times , 0.90NA objective. The FWHM of the writing spot was measured to be 580 nm in the radial direction and 1.9 μm in the axial direction using a knife-edge technique, though this has been known to overestimate the actual spot size by around 35% [14]. The spots were read in a Leica SPE scanning confocal microscope using a 488 nm laser and an ACS apochromatic 1.4NA oil-immersed objective, which improved the resolution and number of spots that could be read at once. The bleaching magnitude and width of a single spot are obtained by fitting the spot profile to a Gaussian. The results from 10–20 spots, written using the same pulse duration and power but in different areas and/or different samples, are then averaged, which is plotted in the figures. For individual spots with the same exposure

parameters, the absolute uncertainty in the bleaching (on a scale of 0%–100%) is a few percent.

3. RESULTS AND DISCUSSION

A. Bleaching at Equal Fluences

The nature of the bleaching process for the range of writing parameters used is examined first in Fig. 3 for the 1.0 wt. % sample. For these measurements, the incident power and exposure are simultaneously adjusted to maintain equal fluence for each data point. As the exposure time is shortened and the power increased, the total bleaching increases. The trend of this graph can help to elucidate the pathways involved.

Bleaching mechanisms in organic dyes have been reported to be due to the lowest lying triplet state (T_1), which reacts with oxygen to produce a permanent, dark photoproduct [15]. Higher excited states (S_n and T_n) have also been shown to be an efficient pathway to bleaching through formation of an intermediate radical by interaction with the polymer or solvent [16]. If the bleaching were linearly dependent on the intensity, then one would expect the response to be the same for all exposure times used in Fig. 3. This is because as pulse length is decreased, the increased intensity would

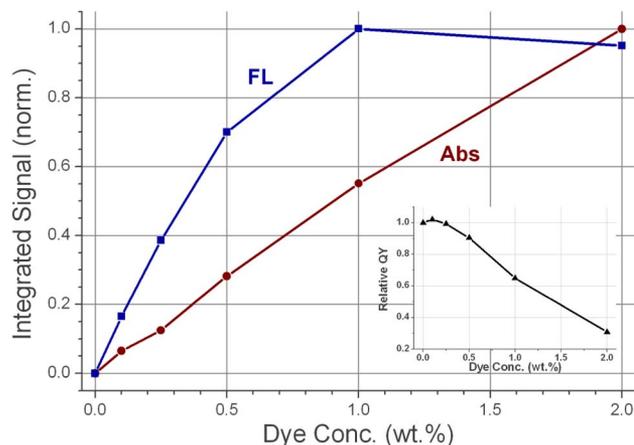


Fig. 2. Integrated FL and absorption from spectra in Fig. 1. Absorption increases linearly with concentration but FL saturates, indicating a reduction in FL QY expected from the FL absorption and re-emission. Inset: calculated relative QY versus concentration.

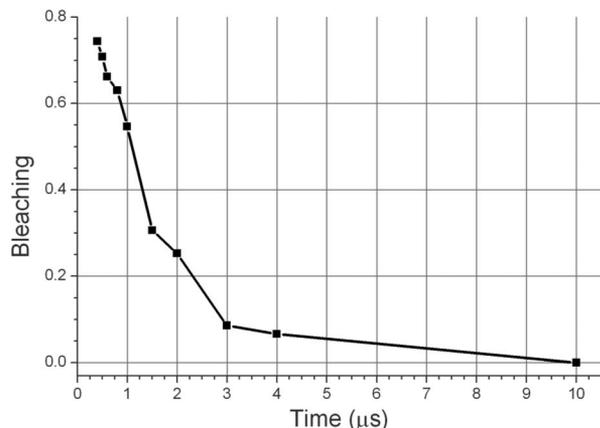


Fig. 3. Bleaching for different exposure times in the 1.0 wt. % sample. The excitation power is altered to keep the fluence constant. This shows that there are bleaching pathways being activated at higher powers that dominate a linear response from S_1/T_1 states.

allow the bleaching rate to compensate. Such a behavior would be expected for bleaching occurring from S_1 and/or T_1 at low intensities. However, at the higher intensities we would expect a negative trend for decreasing exposure since these states would begin to saturate.

Thus the positive trend with decreasing time observed here is an indication of bleaching that is nonlinearly dependent on the intensity; that is, there are additional states or pathways, which become active at higher powers, allowing the bleaching rate to increase with the decreased time. This could be due to bleaching from the higher excited states or photothermal heating and temperature-dependent rates. This behavior can be exploited for low crosstalk ODS and is explored in more detail below.

B. Bleaching Power Dependence of Single Nanosecond Pulses

The amount of bleaching achieved for different incident powers is shown in Fig. 4 for the 1.0 wt. % sample and exposure times of 2 μ s, 400 ns, and 200 ns. These are much shorter time scales than those that have previously been used to explore bleaching in these organic dyes. For bleaching above about 85%, the spot profile becomes flattened at the peak indicating maximal bleaching, given the dark counts in the system. For these parameters, all the spots maintain a circular shape, indicating that no ablation is occurring. Exposure times larger than about 10 μ s are required to observe ablation in these samples.

Below this saturation for all exposure times, there is a marked increase in the slope of the bleaching curve as the power is increased. For 2 μ s, the power at which this occurs is relatively low. The nonlinear behavior is more obvious for the 400 and 200 ns exposures, with the onset occurring around 18 MW/cm^2 irradiance for 400 ns and 42 MW/cm^2 for 200 ns. For the 400 ns exposure series, there is also a saturation trend when the bleaching approaches 60%. Interestingly, this occurs at a lower bleaching than for 2 μ s, indicating that it is possibly not due to depletion of photoactive chromophores but to a decrease in the reaction rate itself.

This data demonstrate that a nanosecond scale response is possible in this system, which is required to achieve high data throughput for ODS. The nonlinear nature of the bleaching

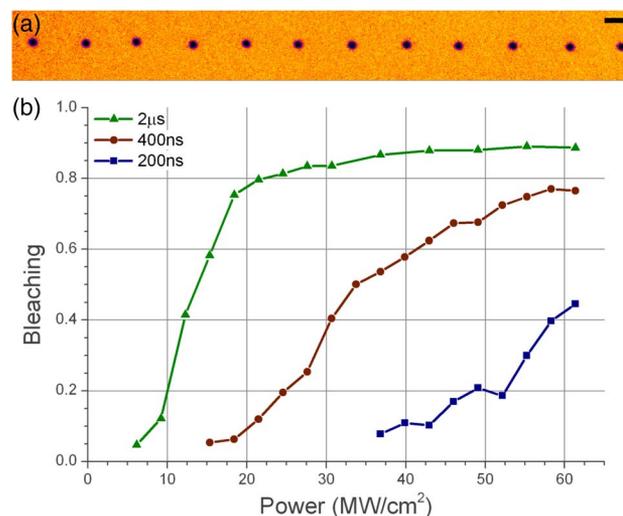


Fig. 4. (a) (False color online) confocal FL image of spots written in the 1.0 wt. % sample at 400 ns and 36 MW/cm^2 . Scale bar is 2 μ m. (b) Bleaching versus power in the 1.0 wt. % sample at various exposure times demonstrating ability to write for short times and with a nonlinear response.

response also allows for limited cross talk during writing of multiple layers and increases the number of writable layers and the contrast in such 3D systems. Note that the dye used in this study was chosen for its ready availability and extensive previous studies, so that an even faster response and larger bleaching may be possible by selecting a chromophore with more favorable QY and excited and ground state cross sections.

The nonlinear intensity dependence is evidence for a bleaching either from S_n/T_n or thermal mechanisms. Molecular models involving the former effect have been well studied, and the transition rates and cross sections for R6G characterized [12,14,15]. These higher states would be particularly active at this wavelength where R6G exhibits RSA. However, the threshold for onset of these effects is typically much lower than the 10 s of MW/cm^2 observed here [12], suggesting that photochemical bleaching from the S_n/T_n states is likely not a dominant contributor in this regime.

The FWHM of the bleached spots resulting from the fits are plotted in Fig. 5 versus the magnitude of the bleaching. This data has not been corrected for the convolution with the reading beam diameter, which is around 300 nm. Most of the widths are smaller than those measured for the writing beam, but this is likely due to the overestimate of the knife-edge measurement. The width is constant up to the point where the bleaching starts to saturate, though more precise measurements are required to measure this behavior accurately. Significantly, the spots are written at the diffraction limit of the writing beam, allowing areal bit densities commensurate with BR.

C. Bleaching Versus Time and Concentration

The bleaching dependence on pulse duration for multiple concentrations is shown in Fig. 6. The 1.0 wt. % at 80 mW (red circles) yields significantly more bleaching than the 0.1 wt. % at the same power (blue squares). Only the higher concentrations yield measurable bleaching for sub-microsecond times, and a more than one order of magnitude increase in the pulse length is required to achieve bleaching for the 0.1 wt.

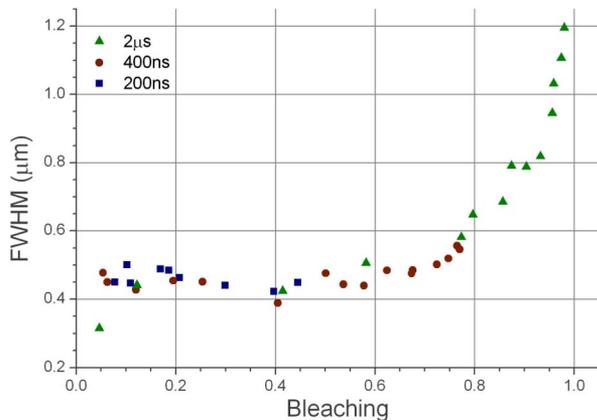


Fig. 5. FWHM of the bleached spots, obtained from Gaussian fits, versus bleaching. FWHM of the writing beam was measured to be 580 nm, and accounting for diffraction, written spots are no larger than the writing beam.

% sample. The absorption increases linearly with concentration, so the cross section for each dye molecule is the same in both samples. However, the relative QY decreases for the higher concentration due to emission and reabsorption.

This is further evidence against a bleaching reaction from the higher excited states, since this model would be independent of concentration for the same molar extinction coefficient. Bleaching reactions under different concentrations have been studied, though with much lower powers and exposure times, and found relevant for the comparable dyes at similar concentrations [17,18]. However, these typically involve energy-transfer reactions between different molecules in the S_1/T_1 states. Similar reactions could be occurring from the higher excited states, but given the fast internal conversion and limited dye mobility, this is unlikely to be a dominant process.

It is also apparent from Fig. 6 that the rate of energy deposited in the medium is more important than the total energy absorbed. For 1.0 wt. % at 80 mW, a 1 μ s exposure time (enclosed red circle) yields more than 70% bleaching, and for 0.1 wt. % at the same power, the 10 μ s exposure (enclosed blue

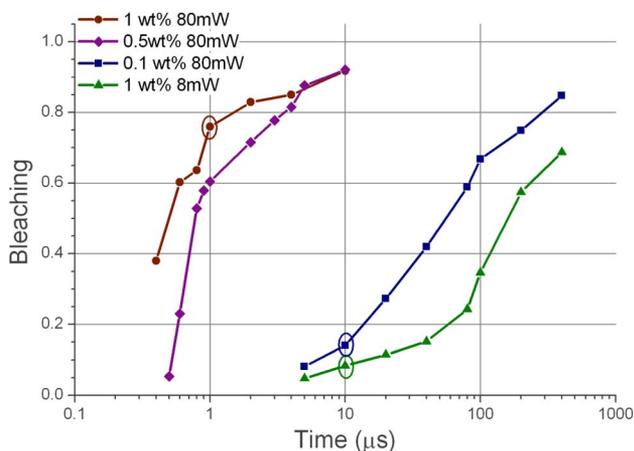


Fig. 6. Bleaching versus exposure time for multiple concentrations and power. Only high concentrations and large absorbed powers will yield measurable response for sub-microsecond times. Circled points are discussed explicitly in the manuscript. An incident power of 80 mW gives an intensity of 30 MW/cm².

square) yields less than 20%. These two points have the same total absorbed energy, but this energy is deposited in a shorter time for the 1.0 wt. % sample, suggesting that the rate of energy deposition is a crucial factor in the bleaching. When the incident power for 1.0 wt. % is decreased to 8 mW (enclosed green triangle), so the total absorbed energy and the rate of energy deposition is the same as the 0.1 wt. % sample, the amounts of bleaching are now more similar. This suggests that the bleaching is not necessarily activated at higher intensity but higher rate of energy deposition. This is highly suggestive of a photothermal mechanism.

D. Photophysical Mechanisms

For laser heating, decreasing the power and increasing the exposure time to deposit the same energy will lead to a smaller temperature rise, since there is a characteristic diffusion time that will balance the heating source. Thus one would expect a larger temperature rise for the 1 wt. %/80 mW/1 μ s exposure than the 1 wt. %/8 mW/10 μ s exposure. One would also expect a similar temperature rise for the 1 wt. %/8 mW/10 μ s and 0.1 wt. %/80 mW/10 μ s exposures, and, indeed, the bleaching magnitudes follow the same trend.

The temperature rise is facilitated by the increased dye concentration and proximity, but also by the large absorption cross section of higher excited states at this wavelength, which decay nonradiatively by internal conversion. This process has been suggested to be an efficient heating mechanism [19]. The close proximity of the molecules and the reabsorption of FL photons also contribute to the heating. The actual molecular FL quenching reaction could then proceed via a number of possible channels, such as a thermally activated chemical reaction, increased T-T, or S-S annihilation reactions through polymer softening, or direct thermal degradation.

The fact that the QY for the 1.0 wt. %/8 mW curve in Fig. 6 is lower than for the 0.1 wt. %/80 mW and that bleaching is actually slightly smaller indicates there is probably a limited charge transfer among dye molecules, or that any interactions act to depopulate the excited states back to the ground state rather than dark states.

The same experiment has been performed with the 0.5 wt. % at the 80 mW incident power (purple diamonds). This bleaching is less than the 1.0 wt. % sample, but not as significantly as the 0.1 wt. % sample. The 0.5 wt. % sample displays only a slightly reduced relative QY compared to the much larger reduction for the 1.0 wt. %. Thus it is likely that dye proximity and absolute number of dye molecules in the beam are more important than the FL reabsorption.

The theoretical temperature rise of a solid film due to laser heating has been considered in the literature [20]. Ignoring the effects of the glass substrate and radiation from the surface for a CW beam with a Gaussian profile, the temperature rise at the center of the beam near the surface can be solved exactly:

$$\Delta T(r = 0, t) = (1 - QY) \frac{I_0 \alpha d^2}{K} \ln \left(1 + \frac{4\kappa t}{d^2} \right), \quad (1)$$

where QY is the FL quantum yield, I_0 is the peak intensity, α is the absorption coefficient, d is the FWHM divided by 1.67, K is the thermal conductivity of the polymer (0.19 μ W/ μ m K at

room temperature from the manufacturer), and κ is the thermal diffusivity of the polymer ($0.086 \mu\text{m}^2/\mu\text{s}$ at room temperature).

It can be seen here that the time scale of thermal degradation can be estimated to be $d^2/4\kappa$, which is essentially the time it takes heat to diffuse across the beam size. From the knife-edge measurement, d is approximately 260–350 nm. This time constant is then in the range of 190–360 ns. It is thus reasonable that heating effects could occur for these exposure times.

It should be clear that the above oversimplified model cannot accurately predict the value of ΔT , but nevertheless can be used to guide the comparison of different writing conditions. Using the measured value of the absorption coefficient for the 1.0 wt. % sample, conservative estimates for QY and d of 0.8 and 350 nm, respectively, then a $40 \text{ MW}/\text{cm}^2$ exposure for 200 ns will give a peak temperature of approximately 1400 K. In comparison, reducing the absorption coefficient by a factor of 10 and increasing the exposure time by the same factor yields about half the peak temperature. It is thus not unreasonable that high temperatures can be achieved by laser heating on the time scales observed and that the short exposure 1.0 wt. % samples yield much larger temperature than the longer exposure 0.1 wt. % samples.

An exact determination of the reactions leading to irreversible bleaching requires more experiments. Exploring polymers with different thermal properties and functional groups, as well as samples of different thicknesses and larger writing spot sizes, would allow for testing thermal properties of the host without affecting the chemical ones. In addition, local temperature can be probed directly by incorporation of thermometers dyes and examinations of morphological changes.

Finally, the nonlinear behavior is beneficial to writing, but low power exposures might still lead to destructive reading via standard photochemical processes. To minimize this, the use of a pulsed beam with subintersystem crossing pulse lengths can greatly reduce the T_1 state and suppress this effect [21]. Our results show that photothermal effects will still permit writing if the power and absorption are sufficiently large.

4. CONCLUSION

We have shown that it is possible to achieve a significant nonlinear FL modulation response using dye/polymer system by exploiting dye interactions and nanosecond-pulses from a low-cost CW laser. This will reduce writing cross talk for 3D ODS devices, and the short exposure times increase the bit rate. Current commercial materials are limited by their cost, scattering, and fabrication difficulties, and this result demonstrates that these issues can be overcome and still provide the required photoresponse. Dyes that exhibit improved stability at low powers are being explored, as well as the effect of the writing wavelength, which may allow for a larger bleaching magnitude without significantly sacrificing on the nonlinearity.

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