Two-photon induced orientation in azoaromatic compounds: demonstration of three-dimensional optical storage.

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Abstract

The search for organic materials with high two-photon absorption process has increased because of the interest in photonic applications, some of which are related to the spatial resolution. This has motivated studies of two-photon induced birefringence via photoisomerization and subsequent molecular orientation in azoaromatic polymers, which have been used in surface-relief gratings and optical storage. Molecular orientation is usually a one photon-induced process, which does not allow three-dimensional storage. However, two-photon optically induced birefringence is attractive for recording data in an erasable medium, since it allows information to be written not only on the material surface but also within the volume. In this work it is showed two-photon induced birefringence associated with the molecular reorientation caused by two-photon induced isomerization using femtosecond pulses in azoaromatic polymers. This process allowed three-dimensional optical data storage.
**Optically induced birefringence**

Trans-cis photoisomerization rate: $R = I \cos^2(\phi)$

Information is stored in the form of optically induced anisotropy, i.e. dichroism or birefringence. Upon shining linearly polarized light of appropriate wavelength on an azopolymer film, the chromophore undergoes a *trans-cis* isomerization unless it is oriented perpendicular to the polarization direction. The *cis* form thermally relaxes to the more stable *trans* form, a process that is accompanied by a change in the chromophore orientation. The net result is an excess of molecules oriented perpendicularly to the laser polarization direction, thus inducing a birefringence that can be read with a probe beam in the transparent region.

The induced birefringence can be completely erased by overwriting the test spot with circularly polarized light or by heating the sample close to the glass-transition temperature of the polymer.
Usually, birefringence is achieved with a writing beam wavelength in the absorption region of the azo-chromophore (one-photon-induced processes), which does not allow data localization in a small volume within the sample.

Two-photon optically induced birefringence is attractive for recording data in an erasable medium, since it allows information to be written not on the material surface, but within the volume (3D), without erasing or overwriting the data already stored on neighboring positions. In this approach, the data density achievable by optical memory devices can be extremely increased.
Two-photon absorption

\[ \vec{P} = \chi^{(1)} \cdot \vec{E} + \chi^{(2)} : \vec{E} \vec{E} + \chi^{(3)} : \vec{E} \vec{E} \vec{E} + \ldots \]

\[ \text{Im}[\chi^{(3)}] \]

\[ \alpha = \alpha_0 + \beta I \]

\( \beta \): two-photon absorption coefficient

The rate of energy absorbed is proportional to the square of the excitation intensity, which allows for spatial resolution in applications such as microfabrication, two-photon fluorescence imaging, two-photon photodynamic cancer therapy and three-dimensional (3D) optical storage.
Z-scan experimental setup

**150 fs Laser**
Clark – MAXR CPA - 2001
\( \lambda = 775 \text{ nm} \); \( f = 1 \text{ KHz} \);
\( E_p = 800 \text{ } \mu\text{J} \)

**OPA**
Pump - Laser Clark
460 - 2600 nm
\( \approx 120 \text{ fs} \)
20-60 \( \mu\text{J} \)

\[ \alpha( I ) = \alpha_0 + \beta I \]
\[ \Delta T \propto \beta \]
Although the 2PA cross-section is not extremely high, it should be sufficient to induce the *trans-cis* isomerization. Due to the **accumulative nature of the molecular reorientation** process, an effective birefringence could be induced via 2PA.
Two-photon optical storage (2D)

Time evolution of the reading beam normalized transmission through the analyzer.

No probe beam transmission is observed while the writing beam is switched-off. When the writing beam is switched on at point A, transmission increases due to the induced molecular orientation. By switched off the writing beam at point B, transmission decreases sharply to a nearly constant value (point C), remaining stable for a relatively long period (≈ several weeks).

Guest host films – PMMA/DR13

λ = 532 nm I = 0.1 W/cm²
λ = 775 nm I = 25 GW/cm²
Two-photon optical storage (3D)

Birefringence was induced in the focal plane by focusing, with a 12 cm cylindrical lens, the writing beam that passes through a 1 mm aperture.

Three-dimensional birefringence was demonstrated through a volumetric optical storage experiment, performed in a bulk (1x2x0.5 cm³) PMMA/DR13 sample.

The sample was scanned which made it possible to draw a specific pattern inside the sample; in our case the acronym of the University of São Paulo (USP) was inscribed.
Two-photon optical storage (3D)

Figures (a) and (b) show the top view of the sample settled at 45° and parallel to the polarizer optical axis, respectively.

The pattern induced is located at 3 mm from the sample surface, demonstrating that the optically induced birefringence is confined in the bulk of the sample. Also, if polarizers were not used, no pattern could be seen. This two-photon induced pattern can be completely erased by heating or overwriting the test spot with circularly polarized light (erasing procedure).
Conclusions

In conclusion, we have obtained for the first time photoisomerization of azo-aromatic compounds (DR13) dispersed in poly(methyl-methacrylate) films, via two-photon absorption. This effect leads to an optically induced birefringence resulting from molecular reorientation in the photoisomerization process.

The optical storage for two-photon excitation is slower than that for resonant excitation for two possible reasons:

(i) a smaller isomerization rate at the nonresonant two-photon absorption and
(ii) smaller thermal effects induced in two-photon absorption process that decrease the molecular mobility. That is also the reason why the residual signal is higher.

This work was supported by the FAPESP, CNPq and Capes from Brazil.