Two-photon absorption and optical storage in a polythiophene functionalized with azodye pendants

D. S. Correa*, M. R. Cardoso, V. C Gonçalves, D. T. Balogh, L. de Boni and C. R. Mendonça

Instituto de Física de São Carlos - USP - São Carlos, SP, Brazil,

***e-mail: daniel@ursa.ifsc.usp.br**

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- Z-scan technique
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- Conclusions

Motivation

Two-photon absorption (2PA) occurs when two photons are simultaneously absorbed by the material in a single event, which causes the light to penetrate deeper, providing higher spatial resolution and decreasing light scattering.

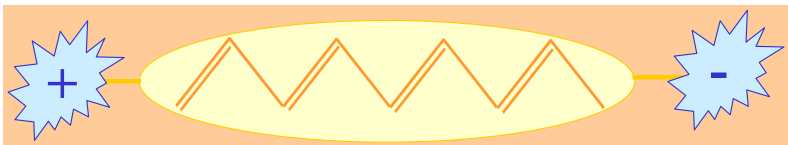
The large interest in 2PA process is due to its versatility, which allows to manufacture photonics crystals and structures of micro and sub-micro dimensions, 3D optical data storage, optical limiting, photodynamic therapy and fluorescence imaging. Particurlarly, 3D optical storage achieved by 2PA increases the storage capability by several orders of magnitude owing the possibility of 3D recording in the medium.

Here we study the 2PA birefringence caused by photoisomerization of Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate], PazT, in spincoated films. The process was induced by 2PA of the azomoieties attached to the backbone, using as excitation femtosecond laser pulses at 680nm and 775 nm. We also determined the 2PA cross-section spectrum of PAzT to obtain an overview of its nonlinear optical properties, which can be useful to select the optimized wavelength for 2PA birefringence experiments.

PAzT

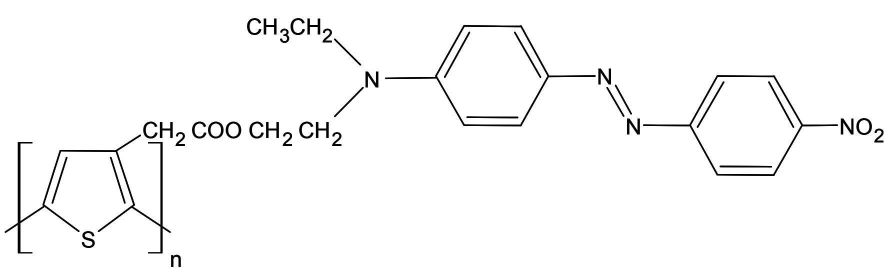
Why conjugated materials, such as PAzT, present high nonlinear optical processes?

Delocalization of π-electrons along the polymer backbone

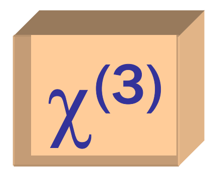


PAzT

Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate]

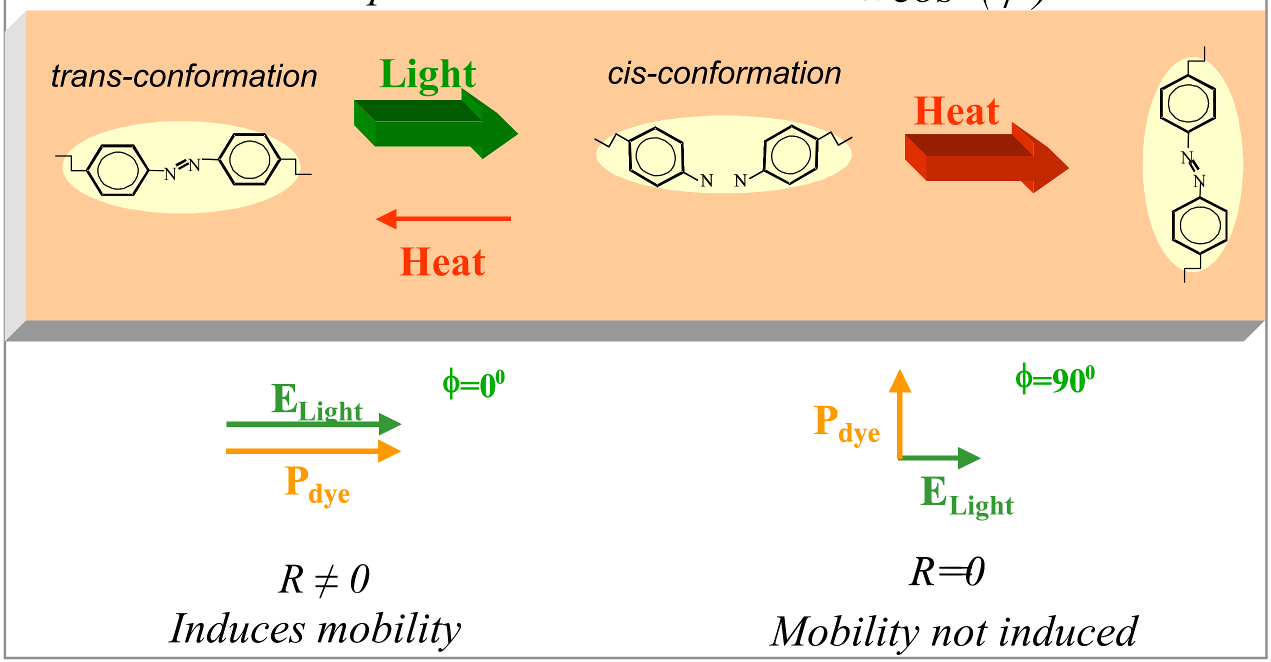


High optical nonlinearities

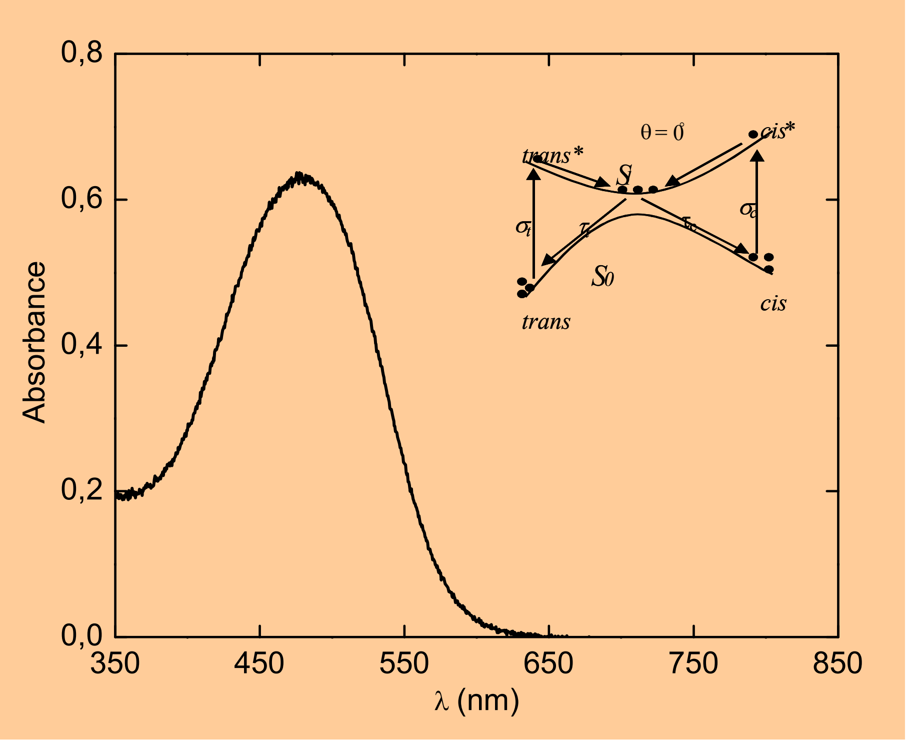


Azochromophores undergo *trans–cis* isomerization when exposed to light

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



Linear spectrum

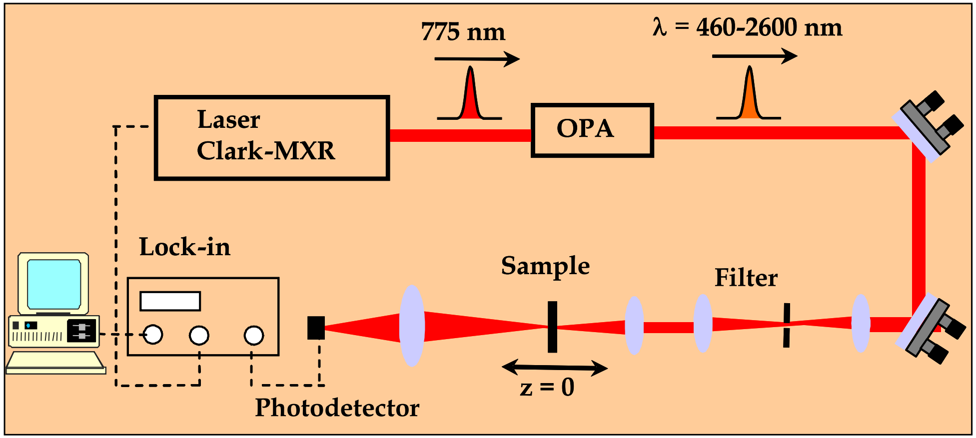


•PAzT presents a π-π* absorption peak around 480 nm.

•Completely transparent in the red spectral region for wavelength > 640 nm

Z-scan technique

Experimental setup



Laser system

λ= 1400 nm m;

τ= 150 f;

F= 1 KHz

OPA

Tunable λ -460 - 2600 nm

$\approx$ 120 fs

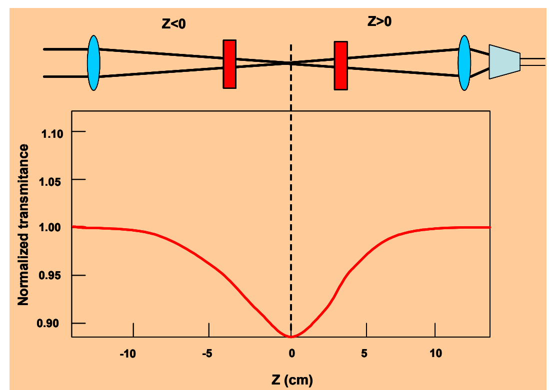
20-60 μJ

Typical Z-scan signature

$$TN(z) = \frac{T(z)}{TL} = \frac{1}{\sqrt{\pi}\, q_0(z,0)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z,0) e^{-\tau^2}\right] d\tau$$

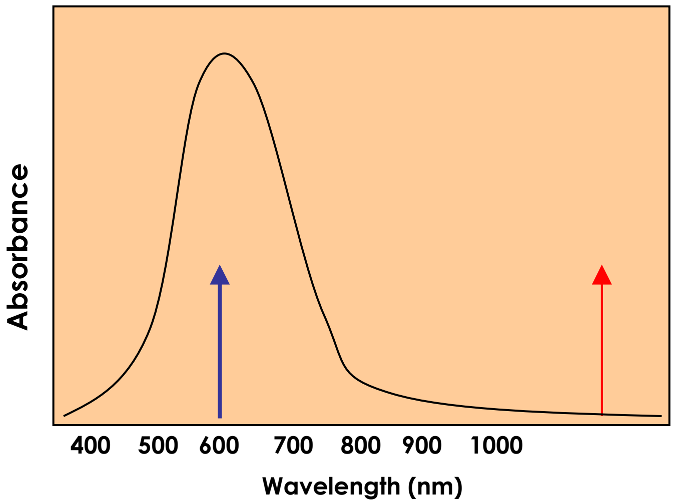
Where:

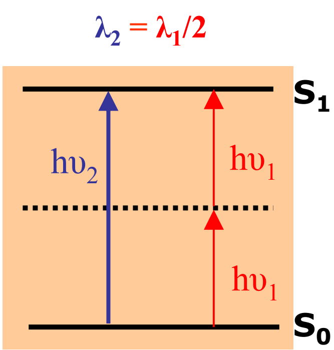
$q_0(z,t) = \beta I_0(t) L \left(1 + z^2 / z_0^2\right)^{-1}$ and $\delta = h\nu\beta / N$



Two-photon absorption

In the presence of intense laser pulses, molecules can instantaneously absorb two or more photons, being promoted to an excited state. These multi-photon absorption processes exhibits transition probabilities proportional to I^n , where I is the intensity of the laser pulse and n is the number of photons absorbed in the event. This implies in chromophore excitation with high degree of spatial selectivity

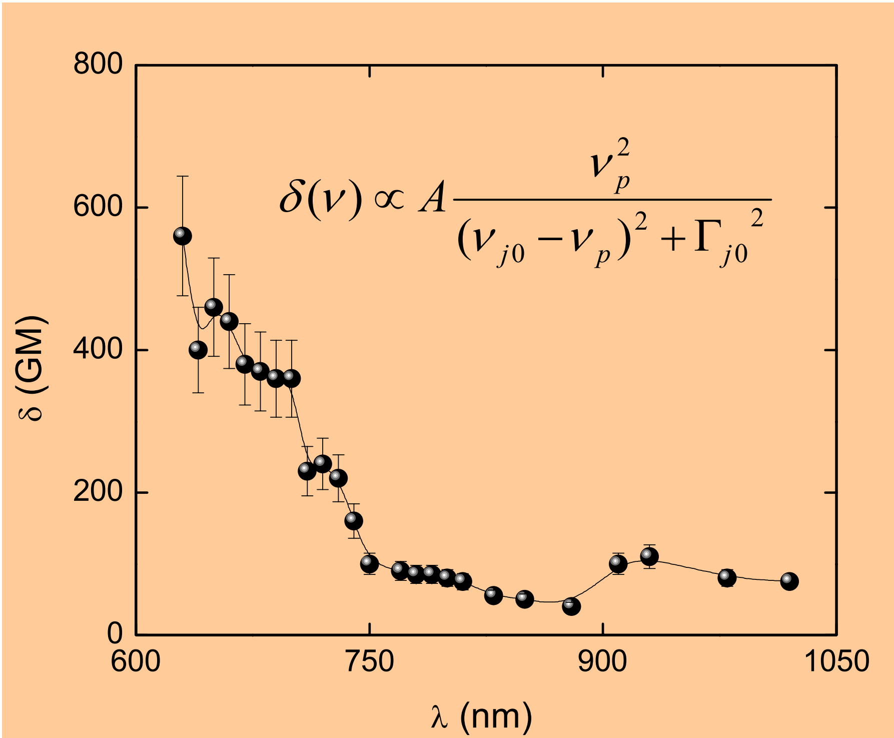




$$\alpha = \alpha_0 + \beta I$$

β : 2PA coefficient

2PA absorption spectrum



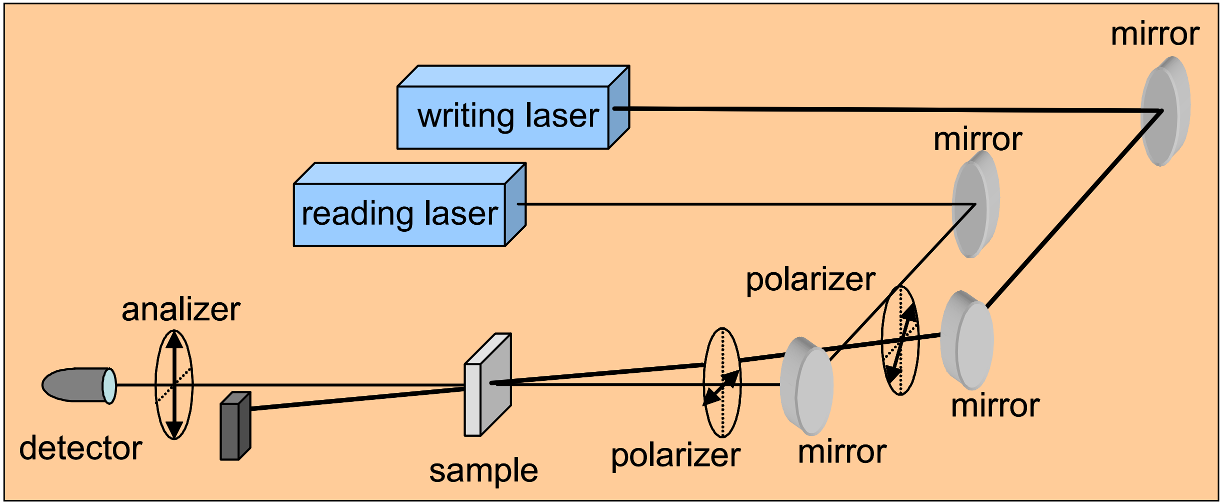
ν_{j0} First real state's central frequency

Γ_{j0} Linewidth of the first real state

A Transition dipole moment

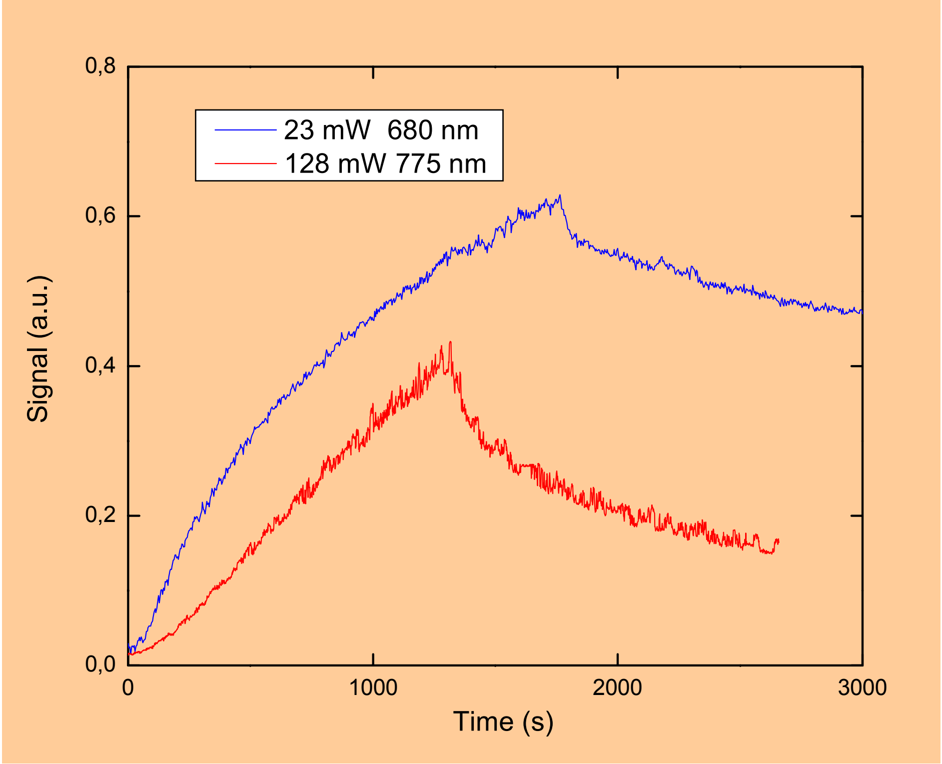
The increase observed in the 2PA cross-section spectra → resonance enhancement of the nonlinearity, is given by the sum-over states (SOS) model assuming that the $\pi \to \pi^*$ transition gives the major contribution.

Birrefringence experimental setup



The 2PA birefringence was induced in the spincoated films using the linearly polarized 150 fs pulses at 680 and 775 nm (writing beam), delivered by the laser system used in the Z-scan measurements. The polarization angle of the writing beam was set at 45° with respect to the linear polarization orientation of the probe beam (reading beam). As the reading beam we used a low-power He-Ne laser at 632.8 nm passing through crossed polarizers.

2PA Induced birrefringence



$$\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{\frac{I}{I_0}}$$

where:

$T = I/I_0$

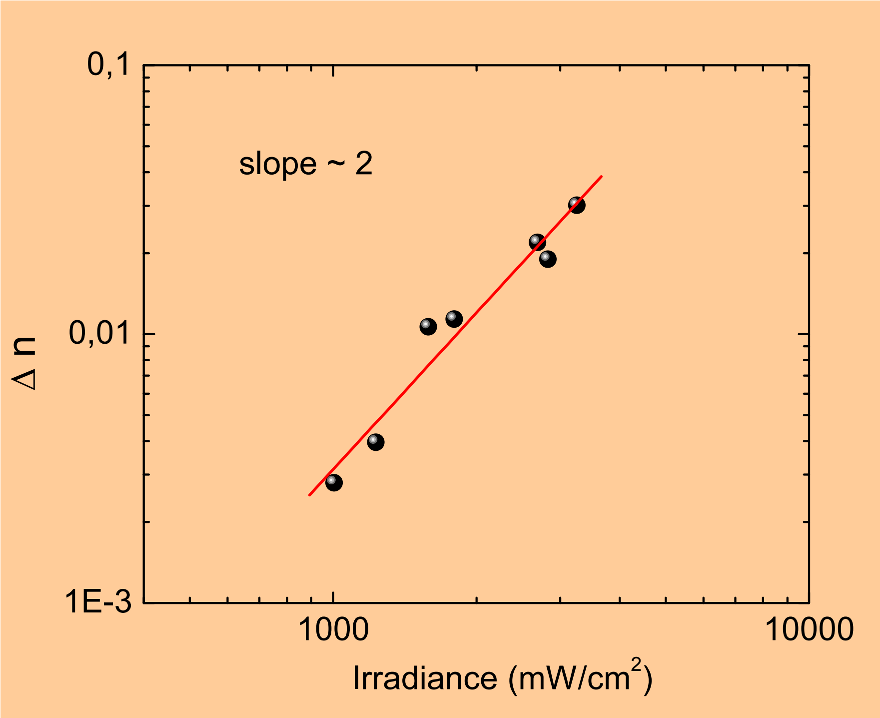
$\lambda =$ Excitation wavelength

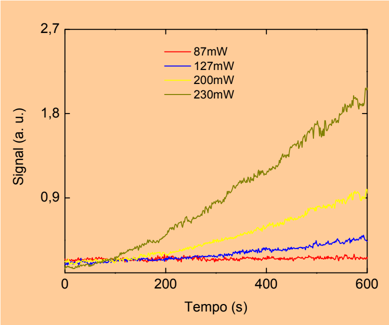
$d =$ film thickness

For 3000 s, we observed a residual fraction of about 20 % at 775 nm and around 50 % at 680 nm. At 775 nm, the input power used was 5.5 higher than that used at 680 nm, because of its smaller 2PA cross-section

2PA Induced birrefringence

Experiment performed at 775 nm, in order to check the order of the nonlinear process





The quadratic dependence of Δn as a function of Irradiance corroborates the 2PA origin of the process.

Conclusion

The 2PA cross-section spectrum of PAzT was determined through the open aperture Z-scan technique, which values increase near the UV-Vis absorption edge due to nonlinear resonance enhancement. In order to test an application using the 2PA properties of PAzT, optically induced birefringence experiments were carried out for distinct excitation wavelengths. This 2PA birefringence arises from the molecular orientation after several cycles of light absorption/isomerization/relaxation by the azo chromophore attached at the polymer backbone. The birefringence achieved is confined into the focal volume of the pump beam, which allows 3D data recording. This feature combined to its intrinsic conductivity makes this material a promising candidate to be used in photonics applications, such as 3D optical memory devices.

This work was carried out with the financial support from FAPESP, CNPQ and CePOF from Brazil