



# Complex microstructures fabricated via two-photon absorption polymerization

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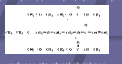


## Abstract

Two-photon absorption (2PA) processes have attracted much interest due to their potential applications in different fields of science. The quadratic dependence of the two-photon absorption rate on laser irradiance allows spatial confinement of the excitation, a feature that can be exploited in applications ranging from three-dimensional optical storage, two-photon fluorescence imaging, two-photon photodynamic therapy, and microfabrication via two-photon induced polymerization. Two-photon initiated polymerization allows the fabrication of sophisticated microstructures for optical circuitry, optical data storage, three-dimensional micromechanical actuators and photonic crystals. Typically, molecules of low molecular weight, called photoinitiators, are added to the monomer to start the photopolymerization process. Here we study the 2PA cross-section of Lucirin TPO-L, which has recently been shown to be a very efficient polymerization initiator under two-photon excitation. We fabricated complex microstructures using Lucirin TPO-L and acrylate resin. Finally, we performed molecular orbital calculations using semi-empirical methods to relate the nonlinear optical properties of this compound to its molecular structure.

## Resin composition for 2PA polymerization

SR499



• reduces structural shrinkage

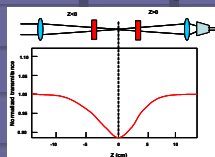
SR368



• confers hardness to the structure



## Z-scan technique for nonlinear optical characterization



Typical curve of 2PA. Curve is fitted by:

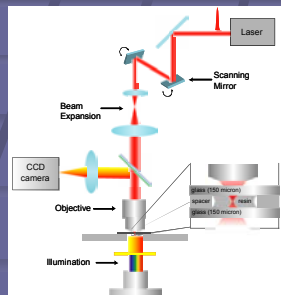
$$TN(z) = \frac{T(z)}{LT} = \frac{1}{\sqrt{q_0(z,0)}} \int_0^z \left[ 1 + q_0(z,0) e^{-z'} \right] dz'$$

Normalized Transmittance:

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

$$\delta = h \nu \beta / N$$

## Experimental setup for 2PP micro-fabrication

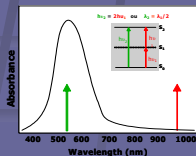


**Ti:sapphire laser oscillator**

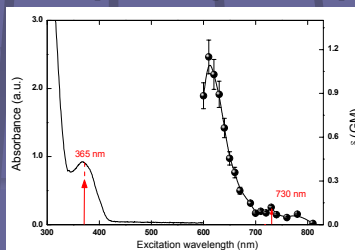
- 130 fs
- 800 nm
- 76 MHz
- 20 mW

**Objective**

40 x  
0.65 NA



## Two-photon absorption (2PA) spectrum of Lucirin T-POL at several $\lambda$ 's

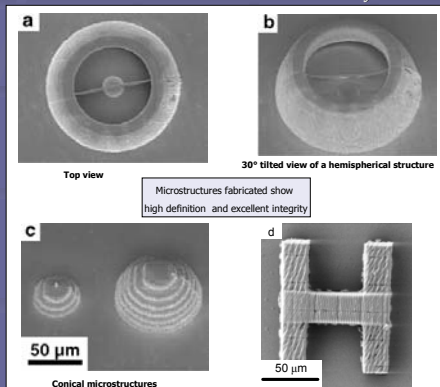


• Data obtained by plotting the NT of the Z-scan curves for the distinct excitation wavelengths.

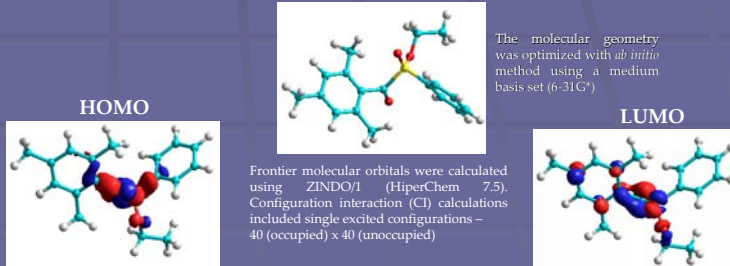
• Nonlinearity increases dramatically in regions closer to the linear absorption - Resonant Enhancement

• A subtle feature at 730 nm in the 2PA spectra can be observed, which is represents the same one observed in the linear absorption (given by selection rules).

## Microstructures fabricated by 2PP



## Molecular structure and Frontier Molecular Orbitals of Lucirin T-POL



## Conclusions

In conclusion, we measured the two-photon absorption cross-section of the photoinitiator Lucirin TPO-L and established a relation between the molecular structure of this photoinitiator and its nonlinear optical properties. We fabricated microstructures with excellent structural integrity and definition, demonstrating the potential of Lucirin TPO-L for two-photon polymerization microfabrication. This work was carried out with the financial support from FAPESP (Brazil), the National Science Foundation under contract DMI-0334984 and the Army Research Office under contract W911NF-05-1-0471.