The Abdus Salam International Centre for Theoretical Physics

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Winter College on Optics and Energy

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Optical nonlinearities in organic materials

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Optical nonlinearities in organic materials

Prof. Cleber R. Mendonca

Fotônica

http://www.photonics.ifsc.usp.br

University of Sao Paulo - Brazil

students 77.000
52.000 undergrad.
25.000 grad.
employers 15.000
professors 6.000

- Sao Paulo
- **Sao Carlos (9.000)**
- Ribeirao Preto

University of Sao Paulo – in Sao Carlos

University of Sao Paulo – in Sao Carlos

Instituto de Física de São Carlos

Professors: 80

Employers: 180
(technical and administration)

Students: 450 (undergrad)
100 (master)
140 (phD)

Several research areas in Physics and Material Sciences

Fotônica

Grupo de Fotonica
Photonics Groups

The purpose of the Photonics Group is to develop fundamental science and applied technology *in Optics and Photonics*

Some of the research areas

- Nonlinear optics
- Coherent control of light matter interaction
- fs-laser microfabrication and micromachining
- Optical spectroscopy
- Optical storage

Optical nonlinearities in organic materials

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Fotônica

http://www.photonics.ifsc.usp.br

Outline

introduction to nonlinear optics

nonlinear optics in organic materials

experimental methods

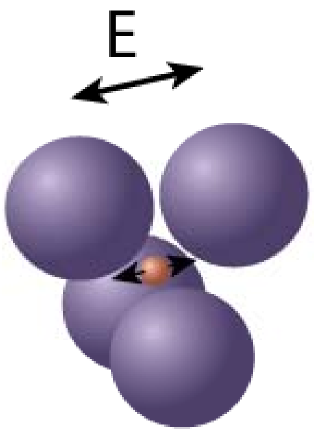
examples of some results

Nonlinear optics

Nonlinear Optics

The branch of optics that describes optical phenomena that occur when very intense light is used

Linear optics



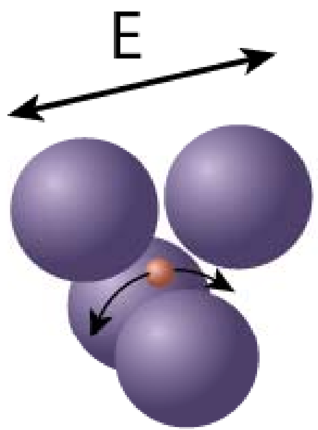
harmonic oscillator

$E_{rad.} << E_{inter.}$

linear response

$$P = \chi E$$

Nonlinear optics



anharmonic oscillator

high light intensity

$$E_{rad.} \sim E_{inter.}$$

nonlinear polarization response

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots$$

Nonlinear optics

nonlinear expansion of the polarization

$$\vec{P} = \chi^{(1)}.\vec{E} + \chi^{(2)} : \vec{E}\vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E} + \ldots$$

linear processes

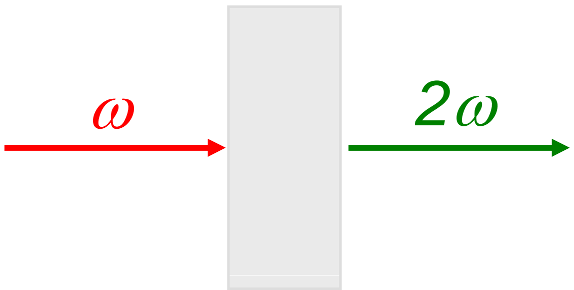
SHG

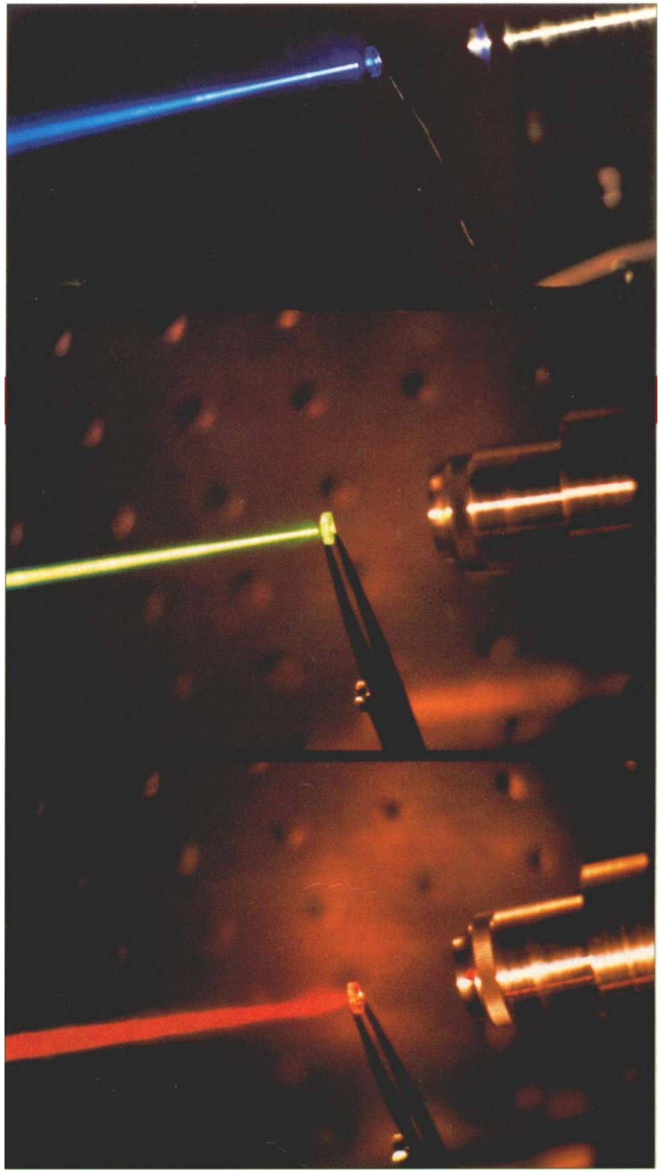
THG
Kerr effect

Nonlinear Optics

Second order processes $\chi^{(2)}$

Second Harmonic Generation





Nonlinear Optics

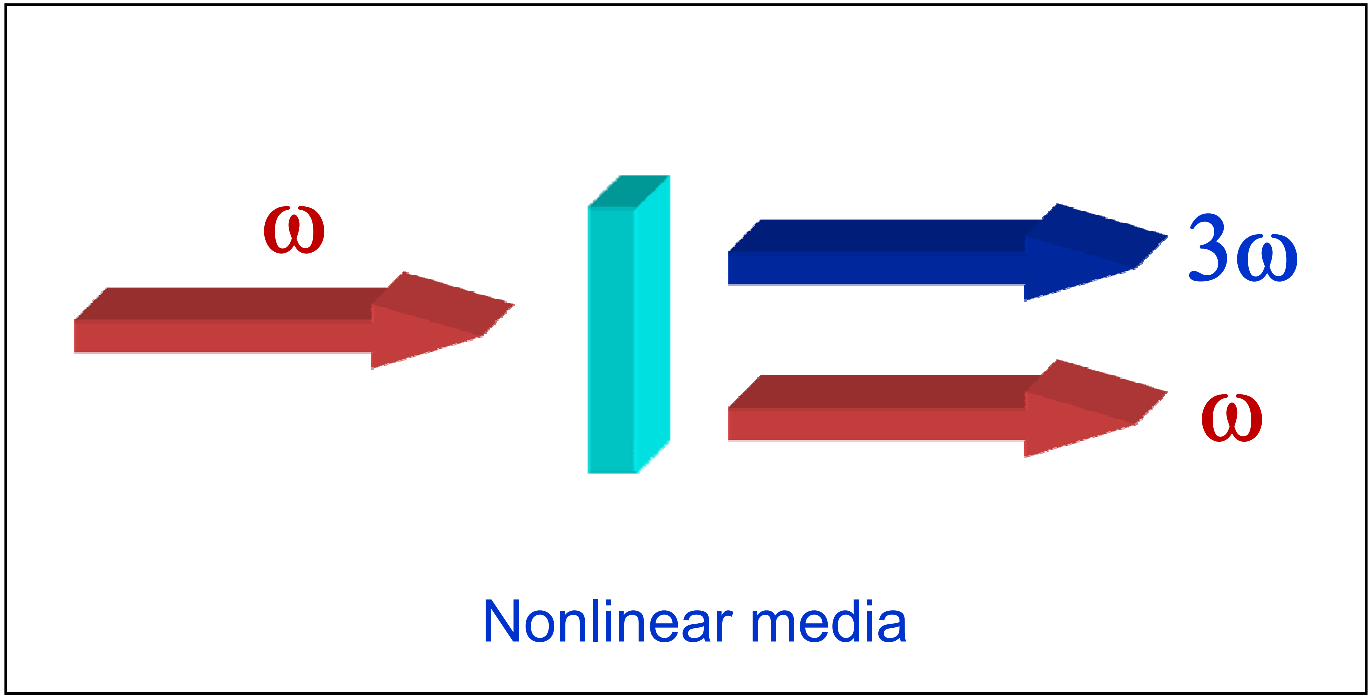
$\chi^{(2)} = 0$ → $\chi^{(3)}$ Third order processes

Nonlinear polarization

$$P = \chi^{(1)}E + \chi^{(3)}E^3 + \ldots$$

Nonlinear Optics

Third order processes $\chi^{(3)}$



Nonlinear Optics

Third order processes $\chi^{(3)}$

Kerr media:

$$n = n_0 + n_2 I \qquad n_2 \approx \chi^{(3)}$$

Index of refraction depends on the light intensity

Self phase modulation

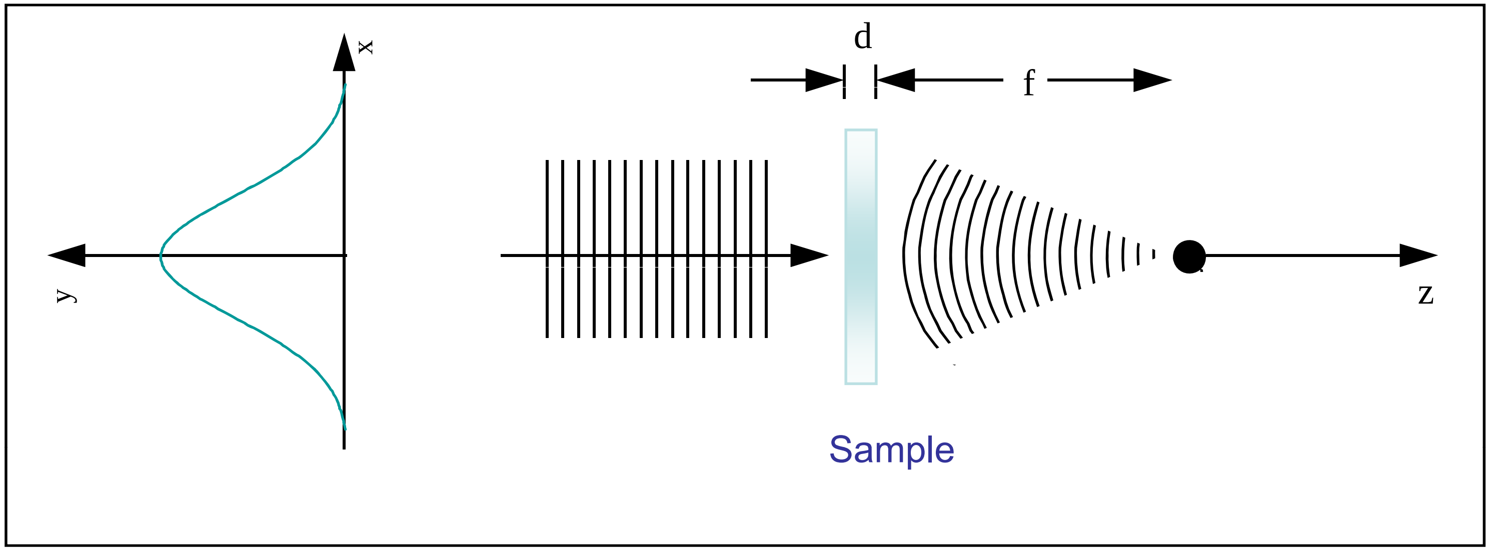
Kerr media:

$$n = n_0 + n_2 I$$

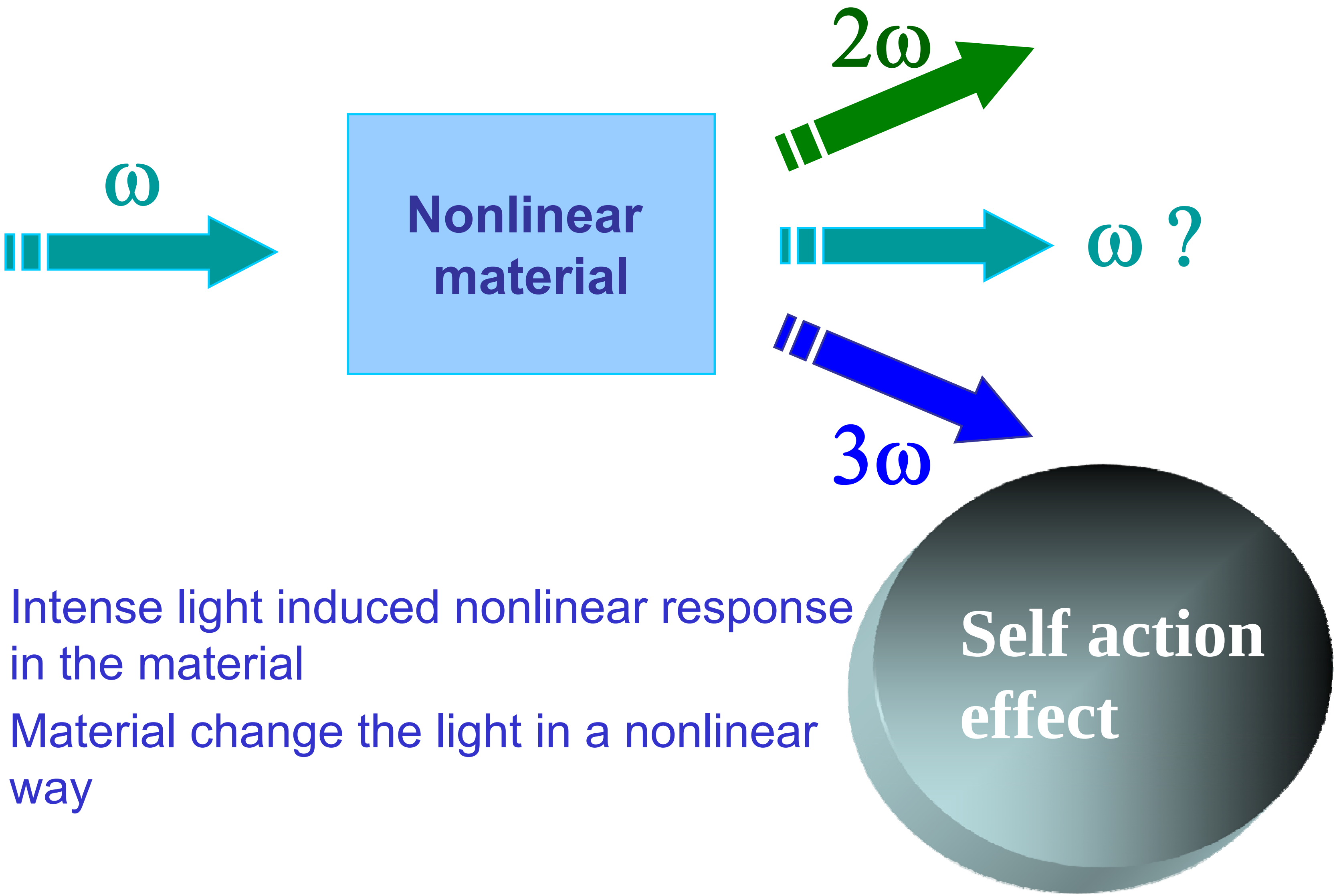
centre symmetric: $\chi^{(2)} = 0$

$$P_{NL} = \chi^{(3)} E^3$$

$n_2 > 0$ Material behaves as a convergent lens



Nonlinear optics



- Intense light induced nonlinear response in the material
- Material change the light in a nonlinear way

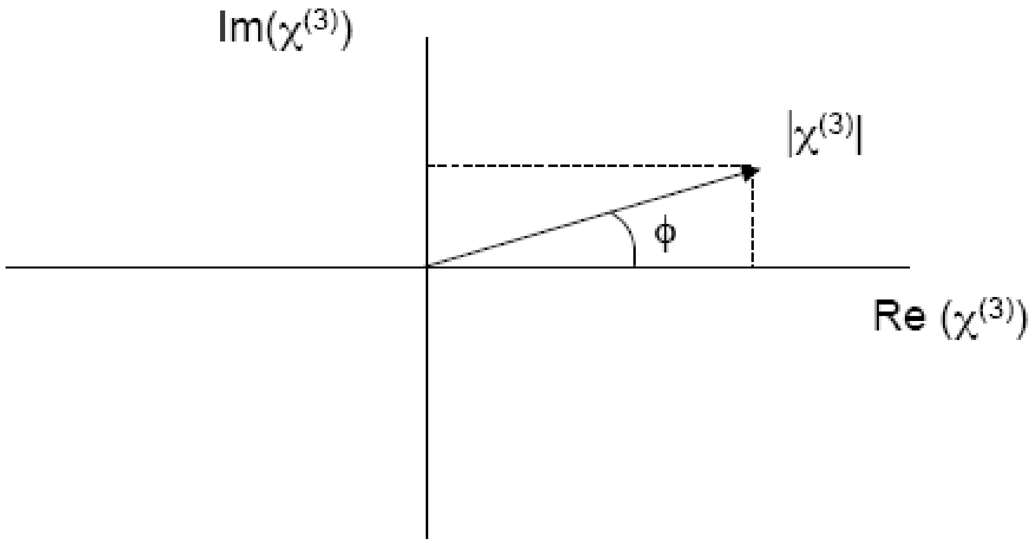
Nonlinear Optics

$\chi^{(3)}$ is a complex quantity

$$\chi^{(3)} = \mathrm{Re}\,(\chi^{(3)}) + i\,\mathrm{Im}(\chi^{(3)})$$

Related to intensity dependent refractive index

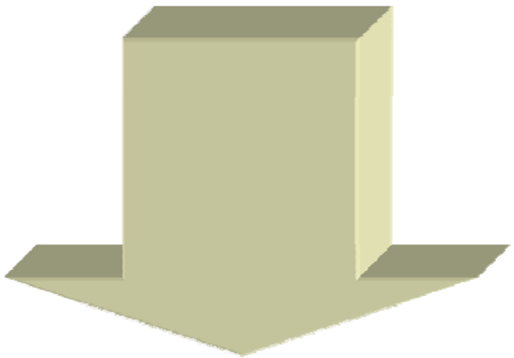
Related to two-photon absorption



Third order processes: $\chi^{(3)}$

Refractive process:

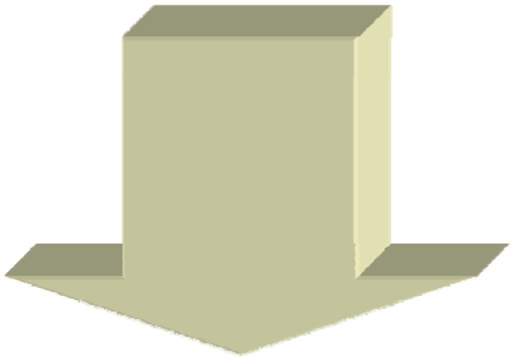
$$n = n_0 + n_2 I$$



- self-phase modulation
- lens-like effect

Absorptive process:

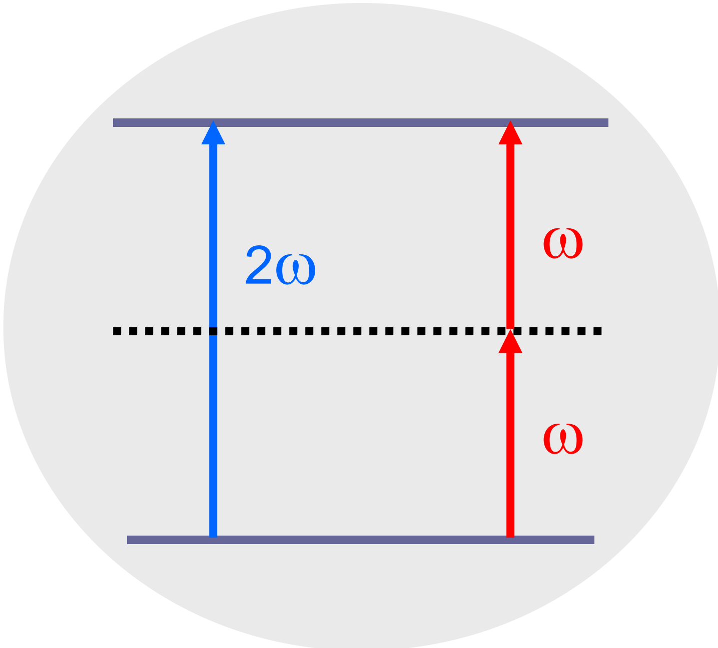
$$\alpha = \alpha_0 + \beta I$$



- nonlinear absorption
- two-photon absorption

Two-photon absorption (2PA) process

Phenomenon does not described for the Classical Physics and does not observed until the development of the Laser.



Theoretical model: Maria Göppert-Mayer, 1931

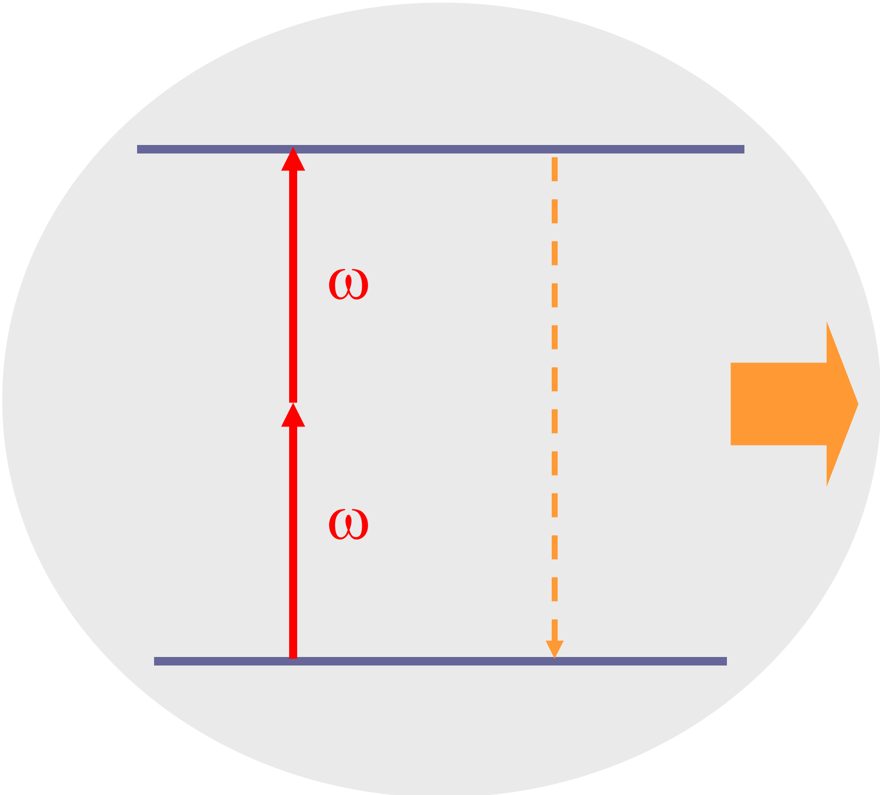
Two photons from an intense laser light beam are simultaneously absorbed in the same “quantum act”, leading the molecule to some excited state with energy equivalent to the absorbed two photons.

applications of 2PA - optical limiting

To protect eye and sensors from intense laser pulses

applications of 2PA - two-photon fluorescence

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

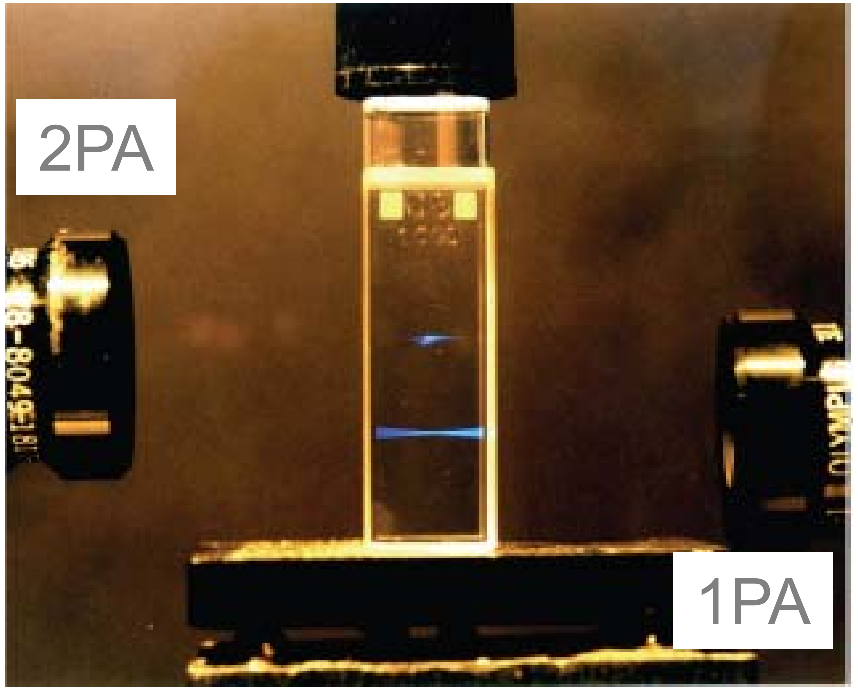


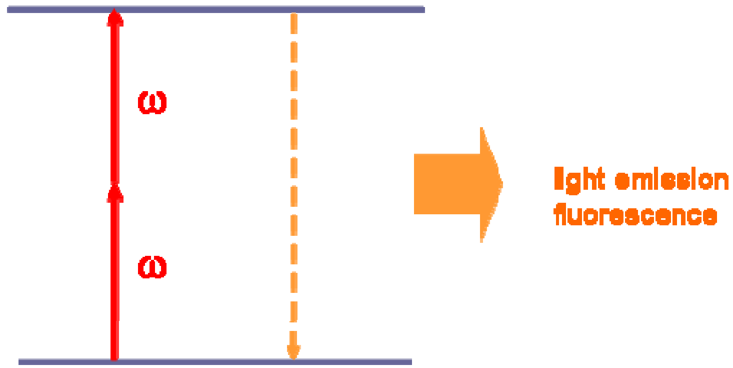
light emission
fluorescence

$$\text{TPA rate constant} \propto \delta I^2$$

localization of the excitation with 2PA

dilute solution of fluorescent dye





$$\mathrm{TPA} \propto \delta\, I^2$$

$$I \sim \frac{1}{z^2}$$

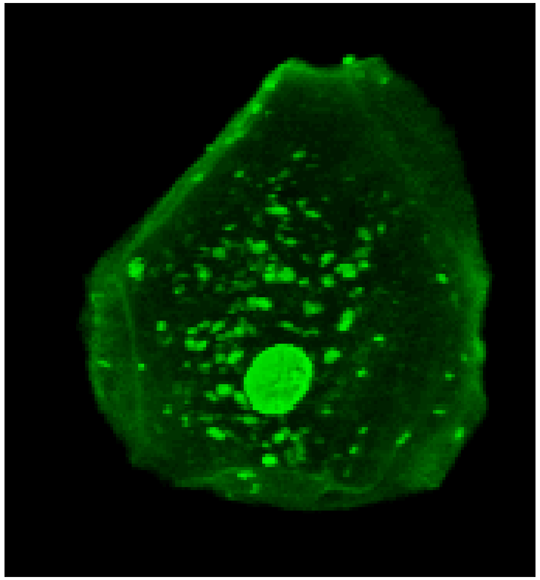
$$\Rightarrow TPA \sim \frac{1}{z^4}$$

spatial confinement of excitation

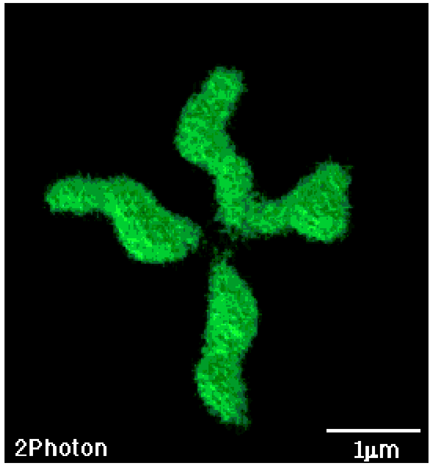
two-photon fluorescence microscopy

microscopy by two-photon fluorescence

3D image of a cell



Laboratory for Optics and Biosciences
Ecole polytechnique

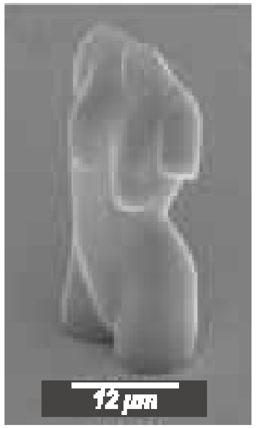


Human chromosome

Fluorescent marker ⇒ fluorophores

applications of 2PA - microfabrication

two-photon polymerization

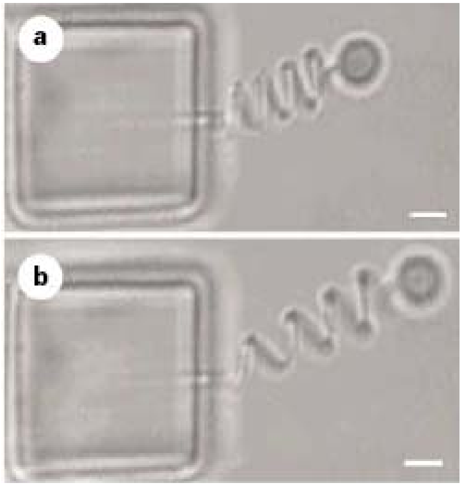


Venus statue

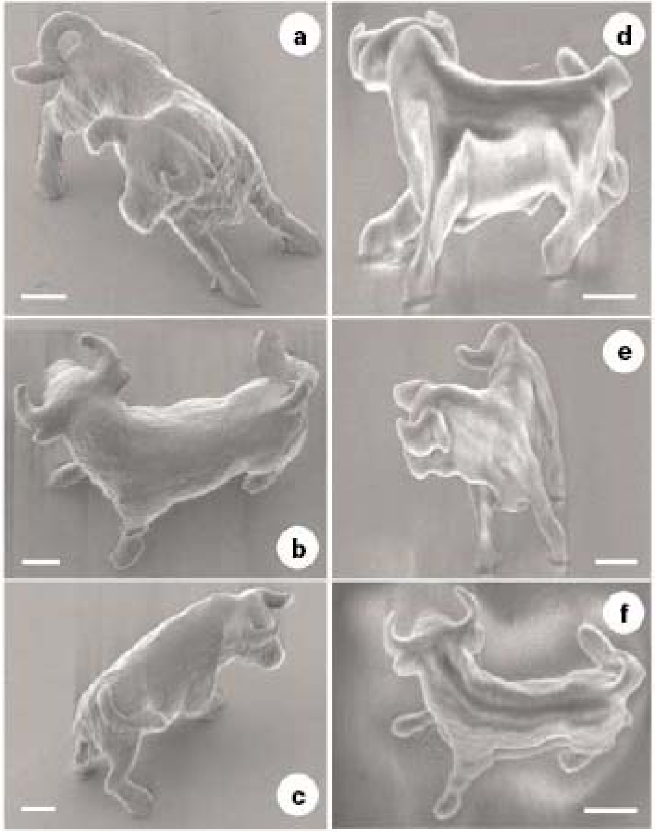
Two-photon polymerization

Opt. Exp. 12, 5521-5528 (2004)

Nature 412, 697-698 (2001)



oscillator

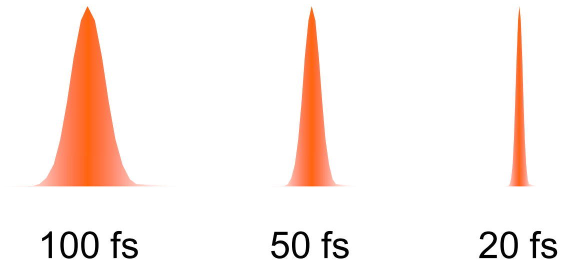


Bull

Real applications in nonlinear optics

Very intense light: femtosecond pulses

Ti:Sapphire lasers



1 fs = 10^{-15} s

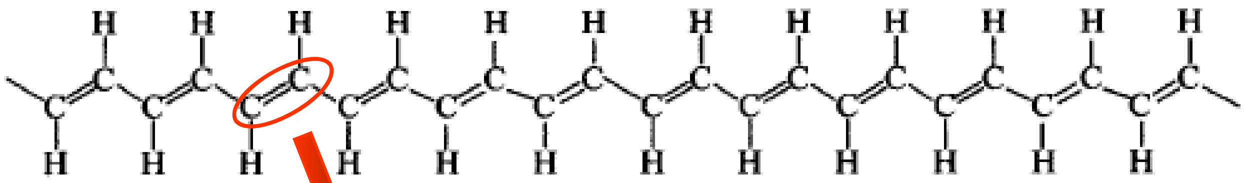
Laser intensities ~ *100 GW/cm^2*
1 x 10^{11}W/cm^2

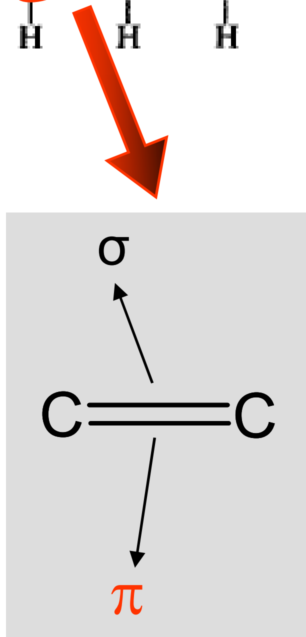
Laser pointer: 1 mW/cm^2 (1 x10^{-3} W/ cm^2)

Organic materials

- Flexibility to tune the nonlinear optical response by manipulating the molecular structure

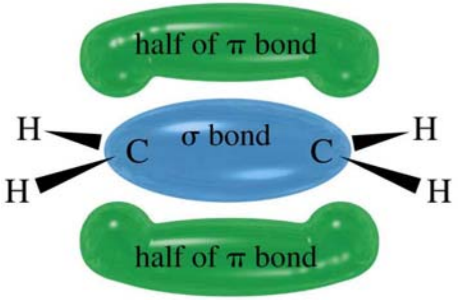
- π-conjugated structures





Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation



σ bond: forms a strong chemical bond; localized

π bond: weaker bond; out of the C atoms axis

π bond in conjugated system: delocalized electrons

high optical nonlinearities

$\chi^{(3)}$

Research

• study of optical nonlinearities in organic materials

• fs-laser microfabrication

• optical storage and surface relief gratings in azopolymers

• coherent control of light matter interaction

Optical nonlinearities in organic materials

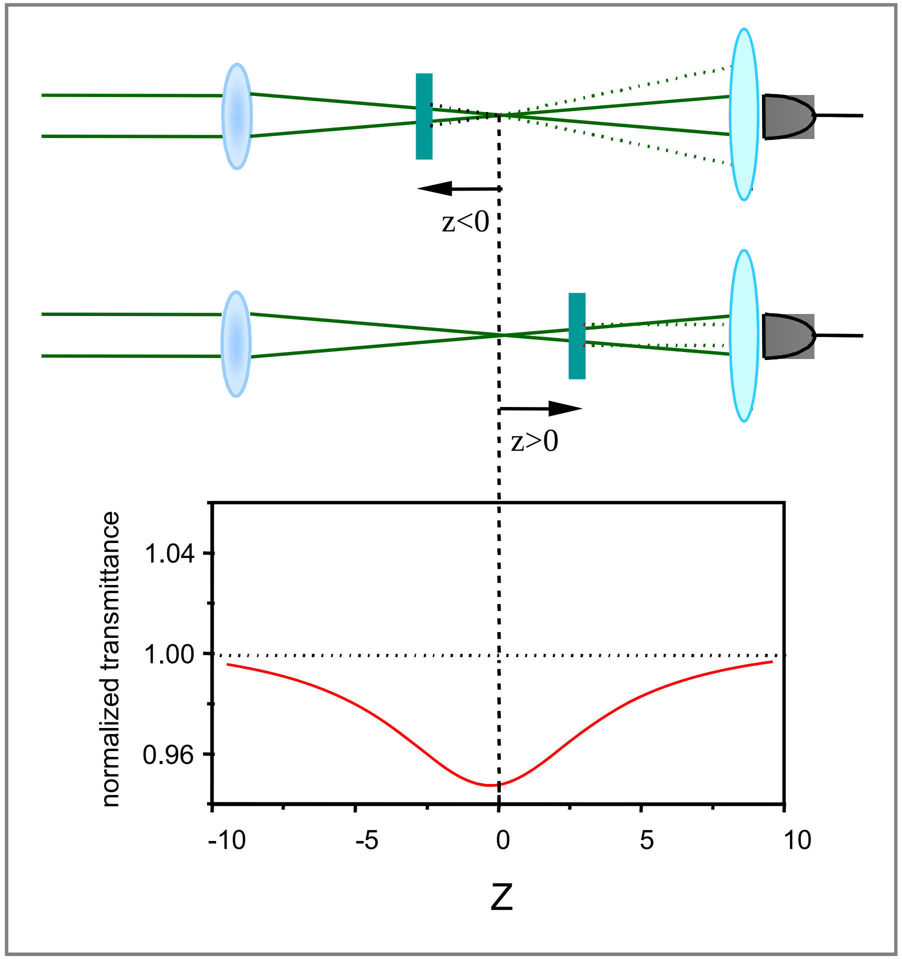
• Understanding the physical principles behind two-photon absorption

• Understanding the relationship between molecular structure and two-photon absorption

• Developing molecules with high optical nonlinearities that can be used for application

Z-scan (nonlinear absorption)

open aperture Z-scan



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

$$\Delta T \propto \beta I$$

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

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

150 fs laser system

Ti:Sapphire amplifier

775 nm

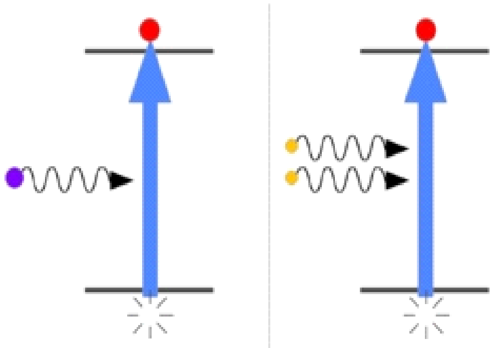
150 fs

800 μJ

Nonlinear spectrum

nonlinear absorption

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



nonlinear refraction

$$n = n_0 + n_2 I$$

intense laser (ultra short pulses)

discrete λ s

$\delta(\lambda)$ $n_2(\lambda)$

nonlinear spectrum ???

Nonlinear absorption spectrum

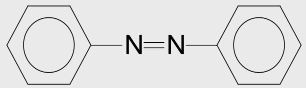
Optical parametric amplifier

460 - 2600 nm

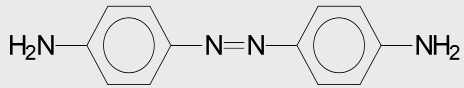
$\approx$ *120 fs*

20-60 μJ

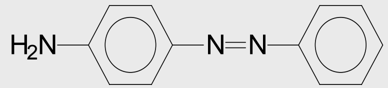
Azoaromatic samples



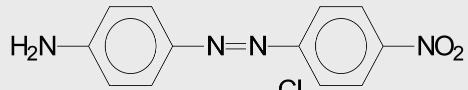
AZO



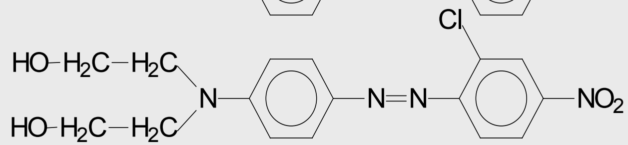
DIAMINO



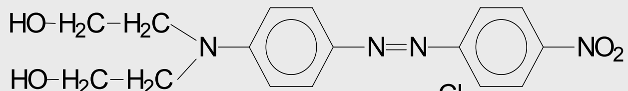
p-AMINO



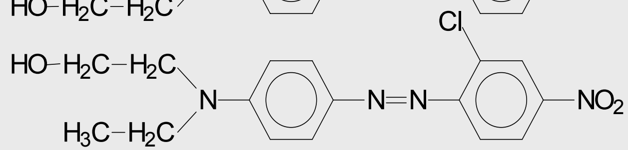
DO3



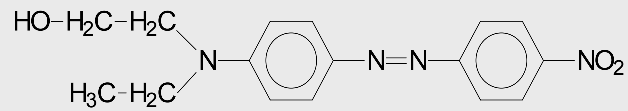
DR19Cl



DR19

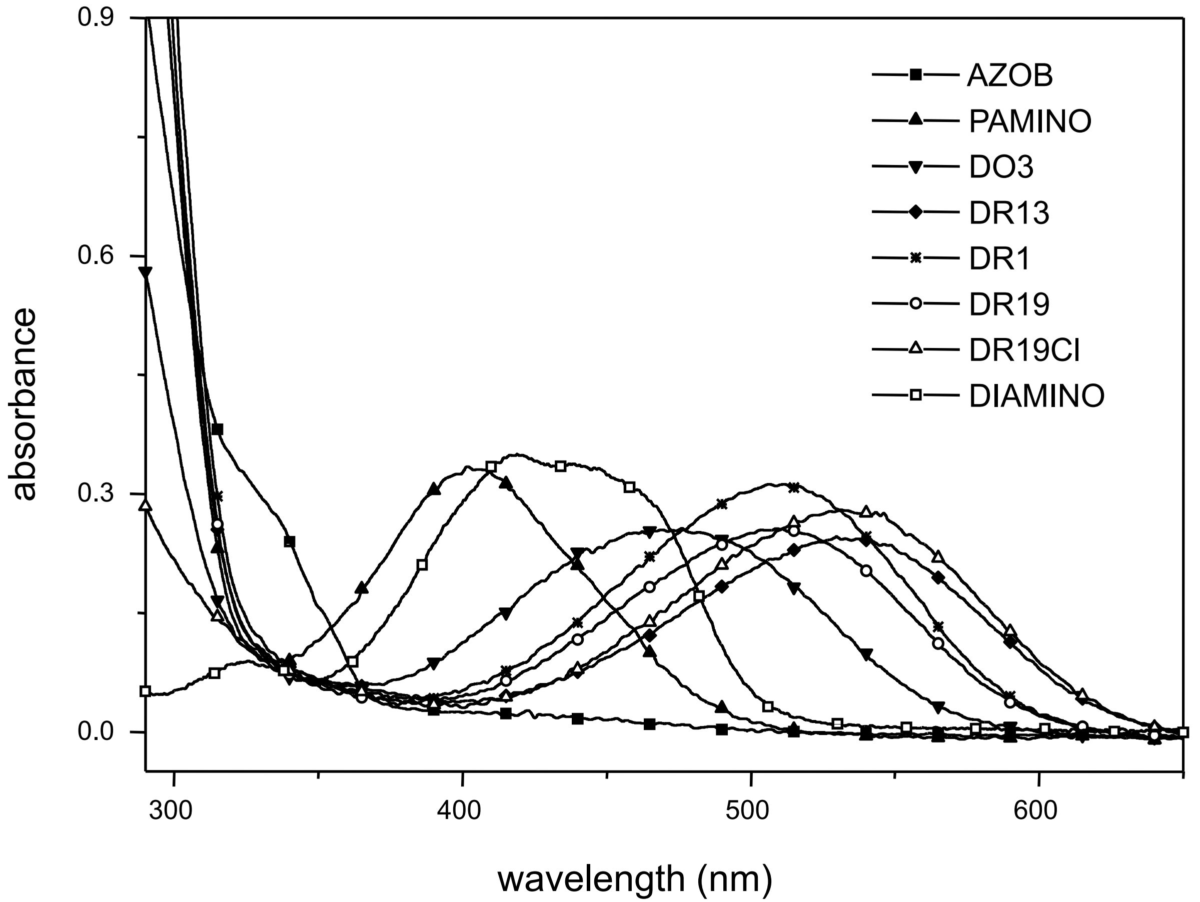


DR13

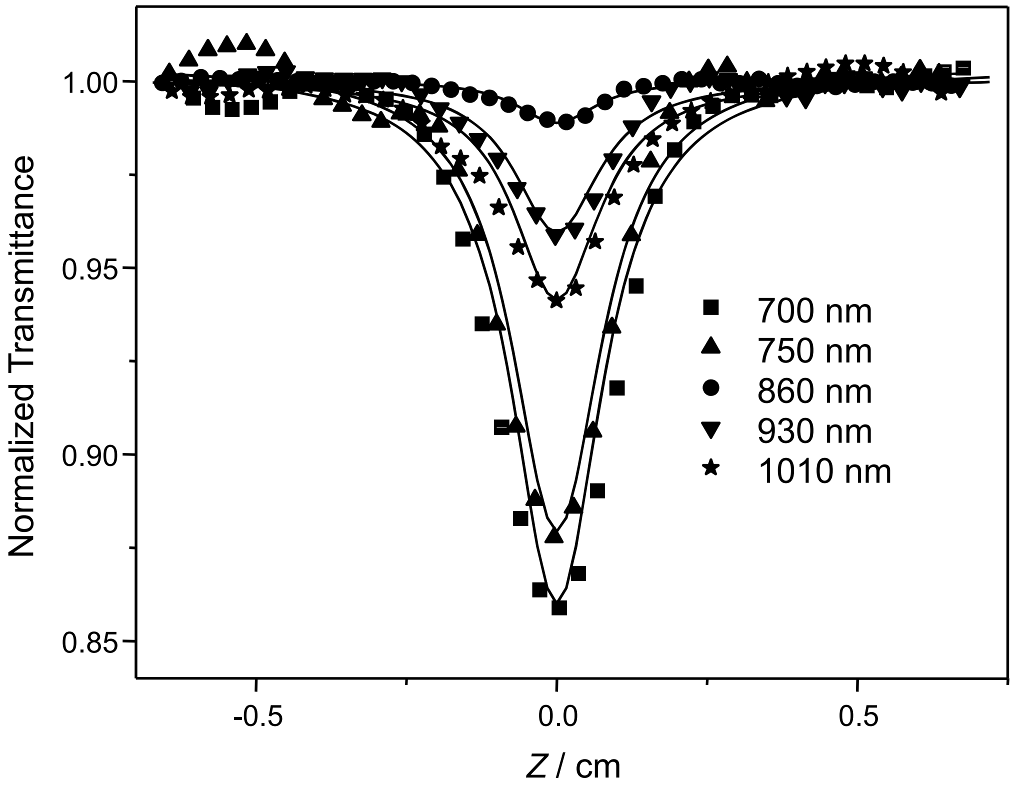


DR1

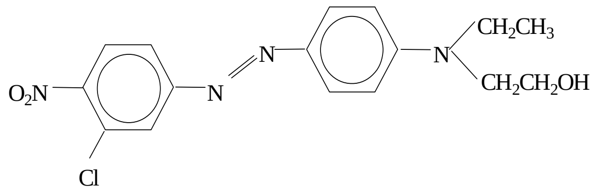
Linear absorption of azoaromatic compounds



Two-photon absorption



DR13

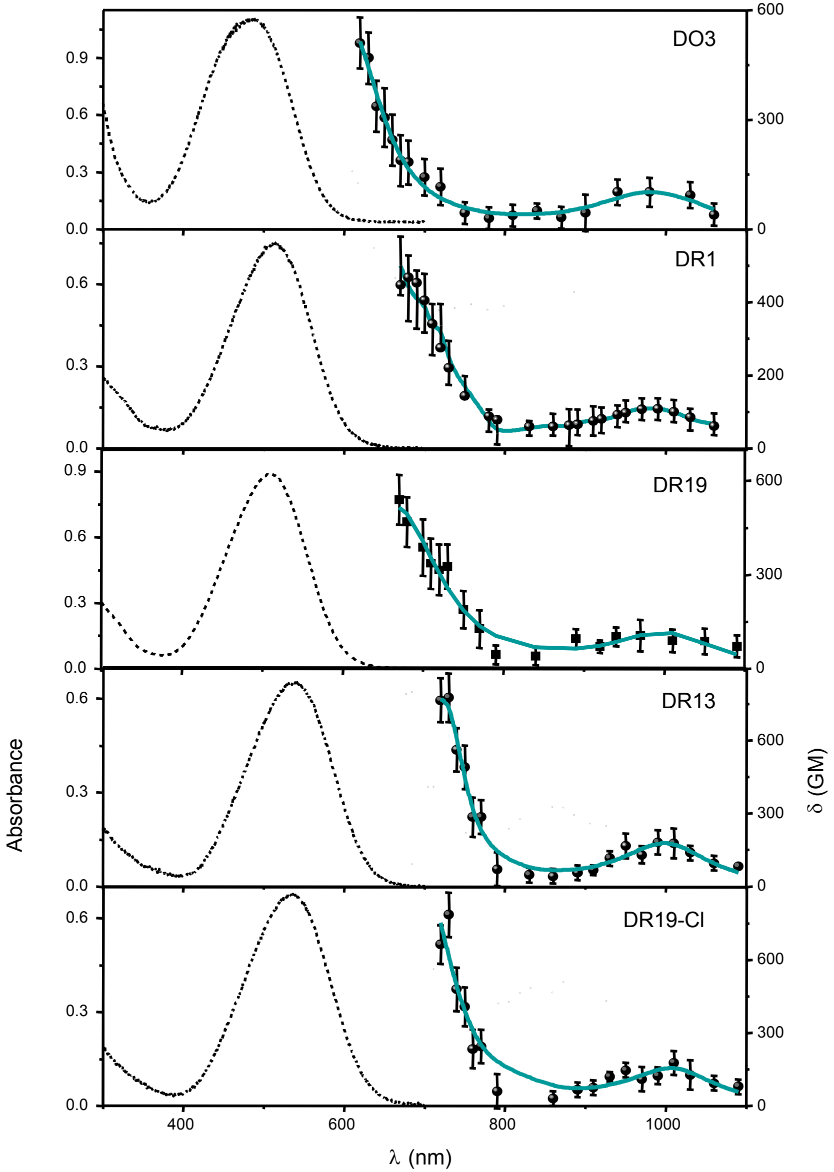


$$T(z) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}}$$

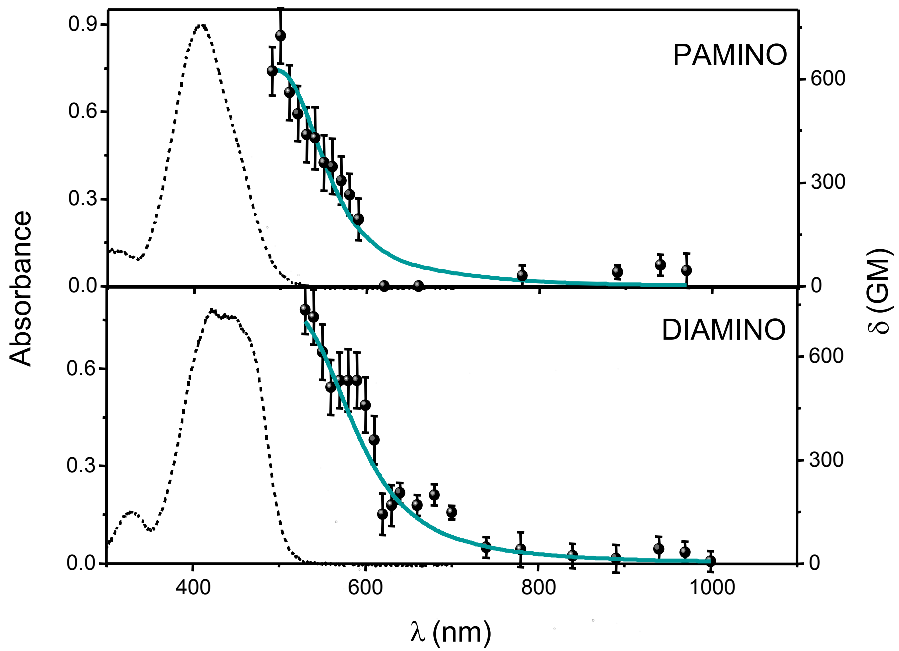
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

Pseudostilbenes

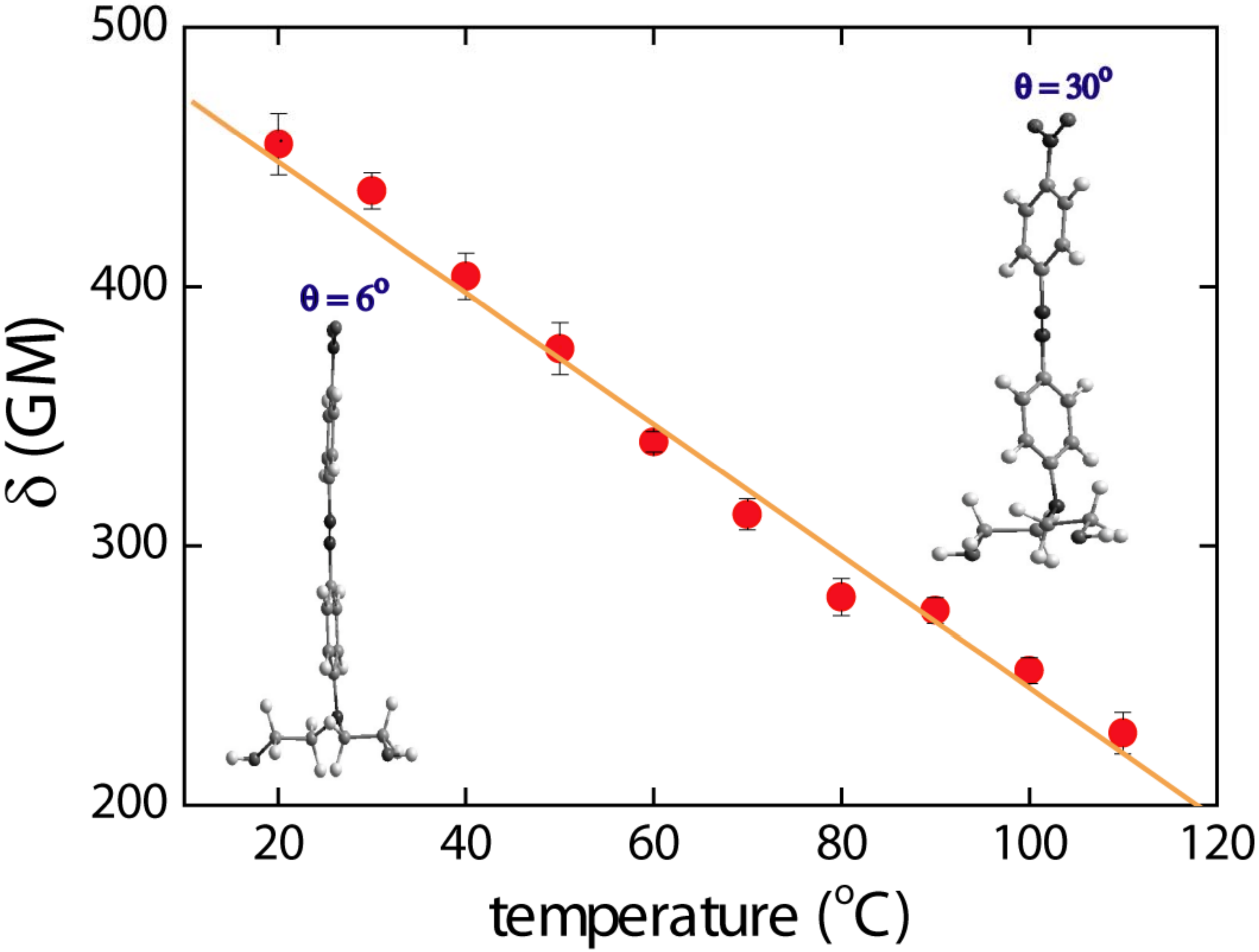


Aminoazobenzenes



$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0}-\nu)^2+\Gamma_{i0}^2}\left[\frac{A_1}{(\nu_{f_1 0}-2\nu)^2+\Gamma_{f_1 0}^2}+\frac{A_2}{(\nu_{f_2 0}-2\nu)^2+\Gamma_{f_2 0}^2}\right]$$

Planarity of the π-bridge

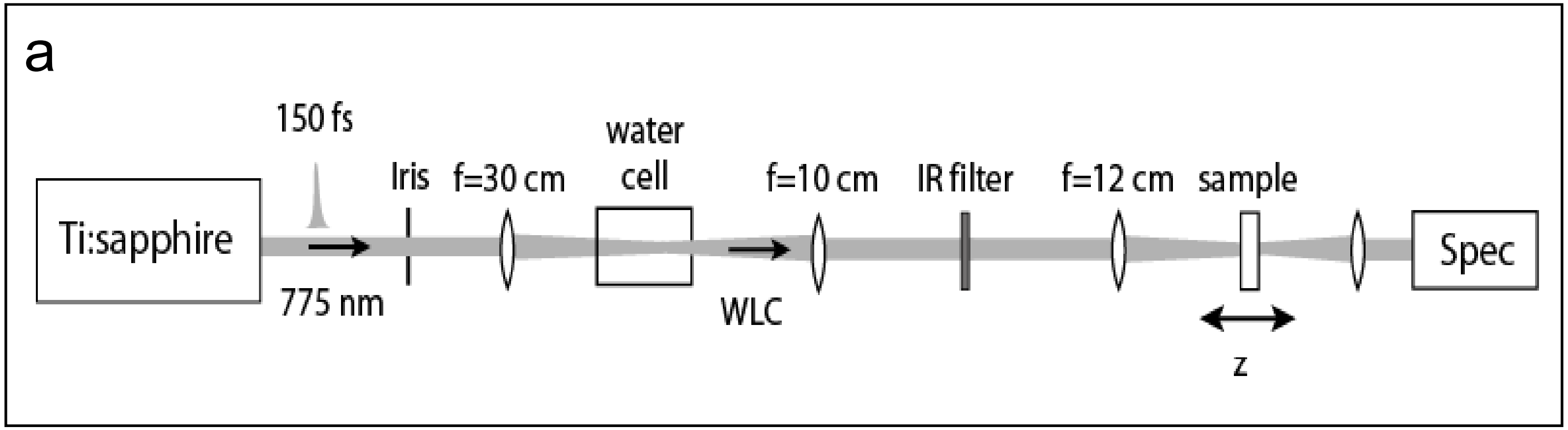


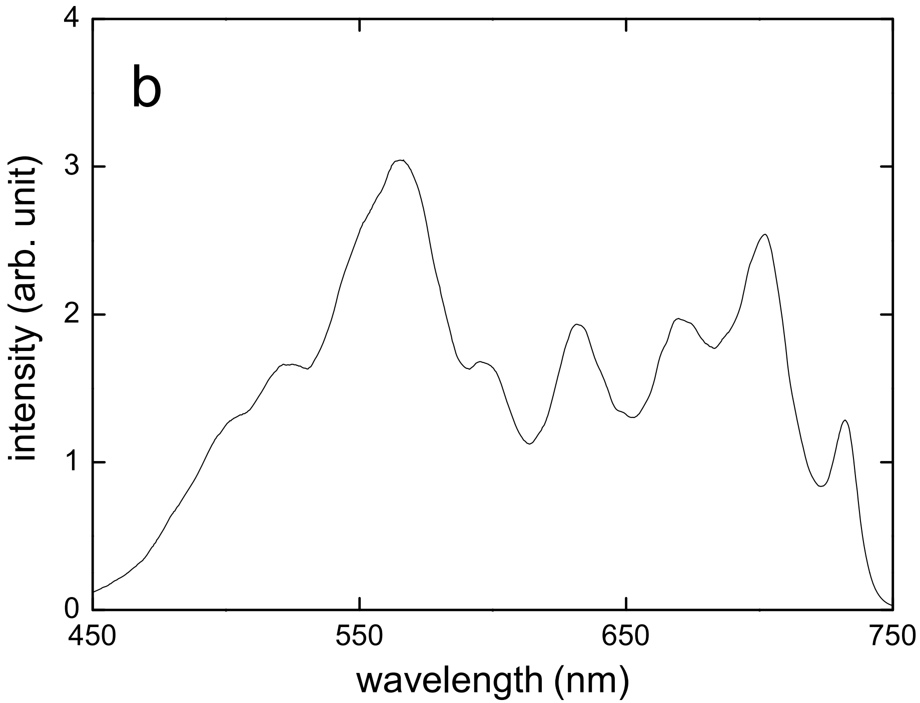
Thermally induced torsion in the molecular structure

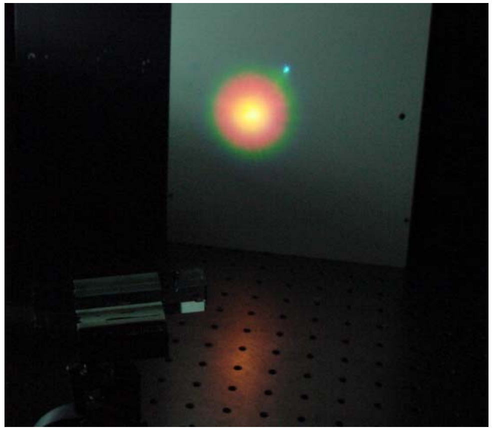
Molecular design strategy

- Increasing the molecular conjugation
- Adding charged groups to the molecule
- Keep molecular planarity

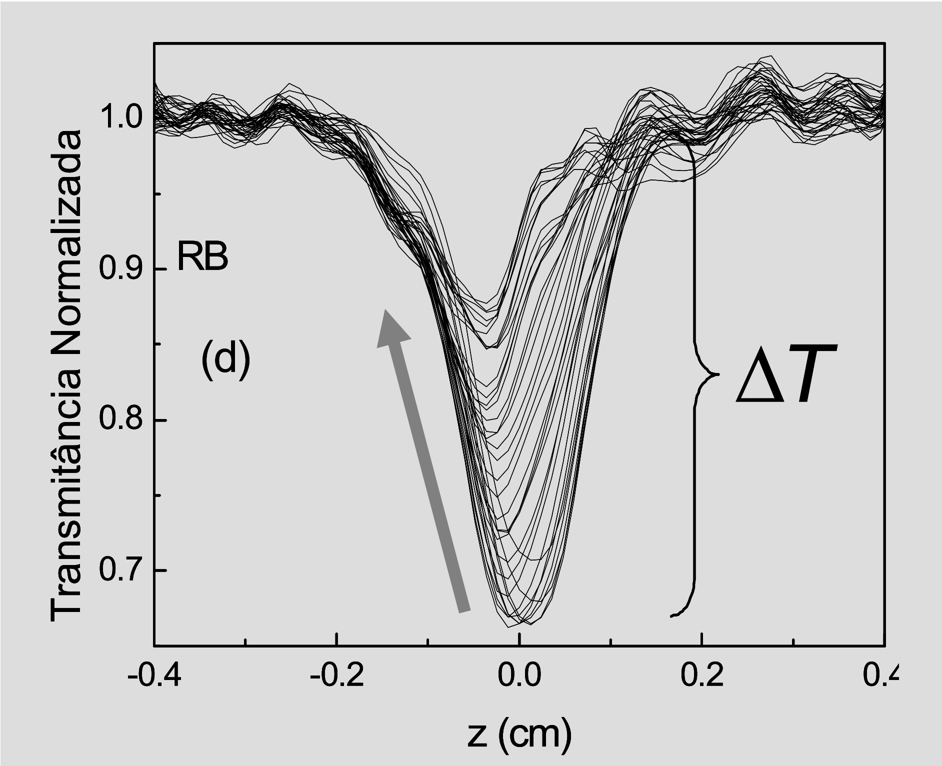
White light continuum Z-scan

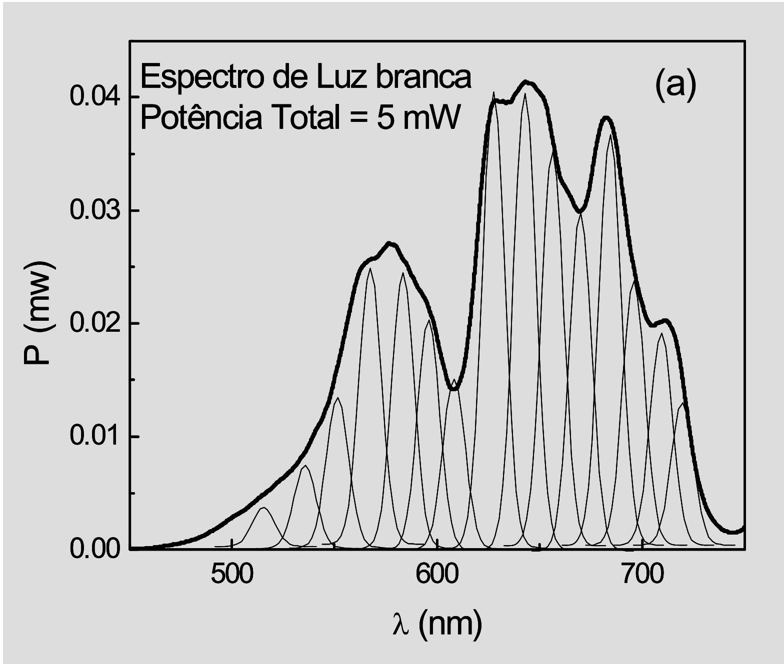






White light continuum Z-scan

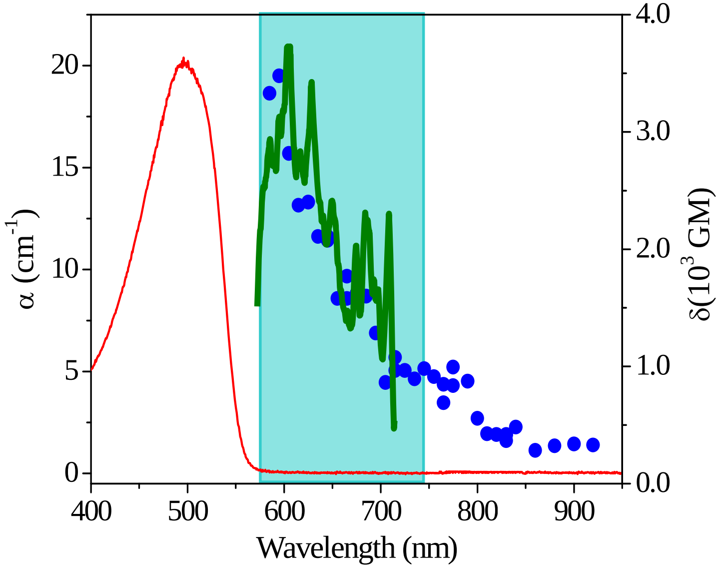




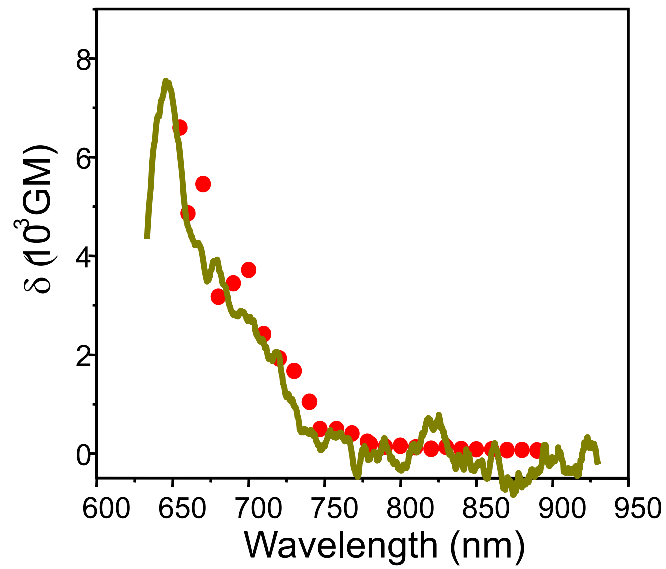
White light continuum Z-scan

Non resonant effects

MeH-PPV



Perylenes derivatives



each measurement takes only a few minutes

fs-laser microfabrication

Novel concept:

build a microstructure using fs-laser and nonlinear optical processes

two-photon polymerization

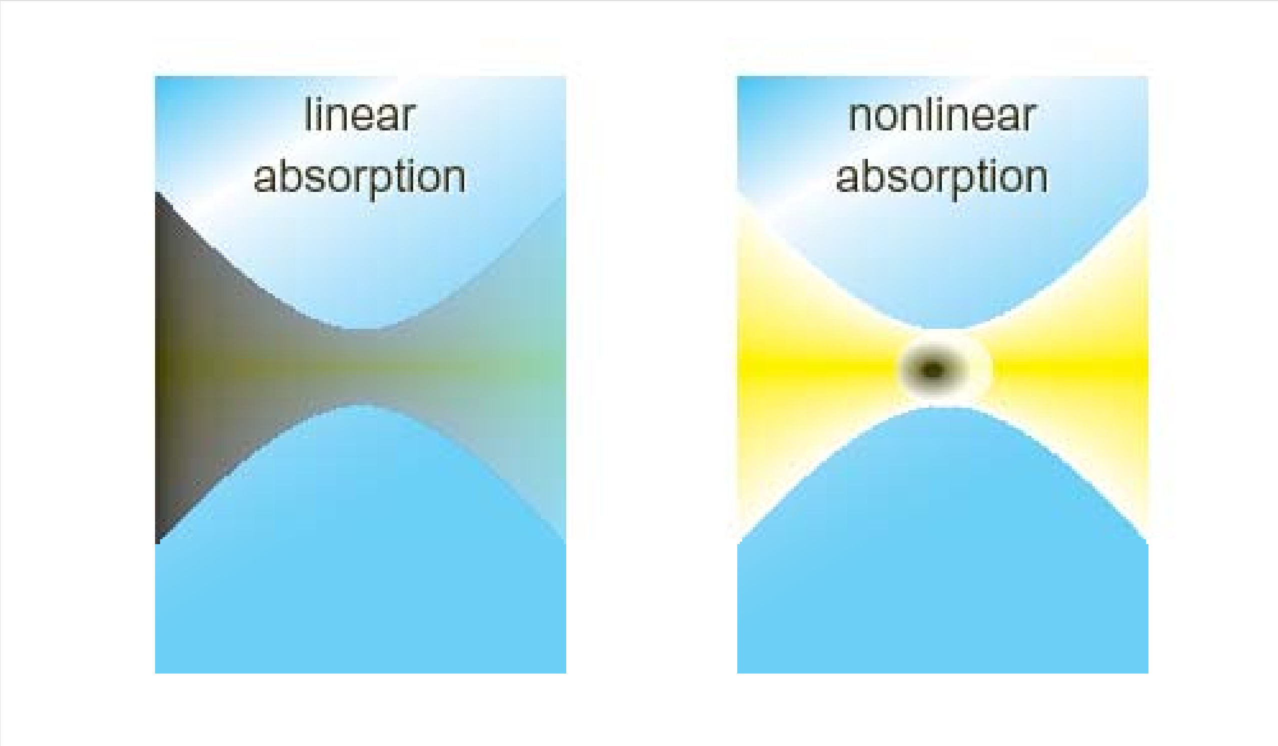
applications

- micromechanics
- waveguides
- microfluidics
- biology
- optical devices

Two-photon absorption

Nonlinear interaction provides spatial confinement of the excitation

fs-microfabrication



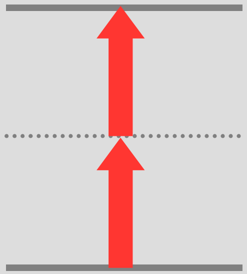
$$\alpha = \alpha_0 \qquad\qquad \alpha = \alpha_0 + \beta I$$

Two-photon polymerization

Monomer + Photoinitiator → Polymer

↑ light

Photoinitiator is excited by ***two-photon absorption***

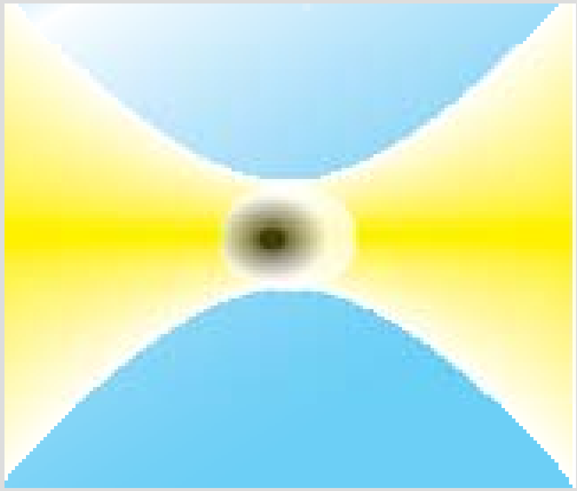


$$R_{2PA} \propto I^2$$

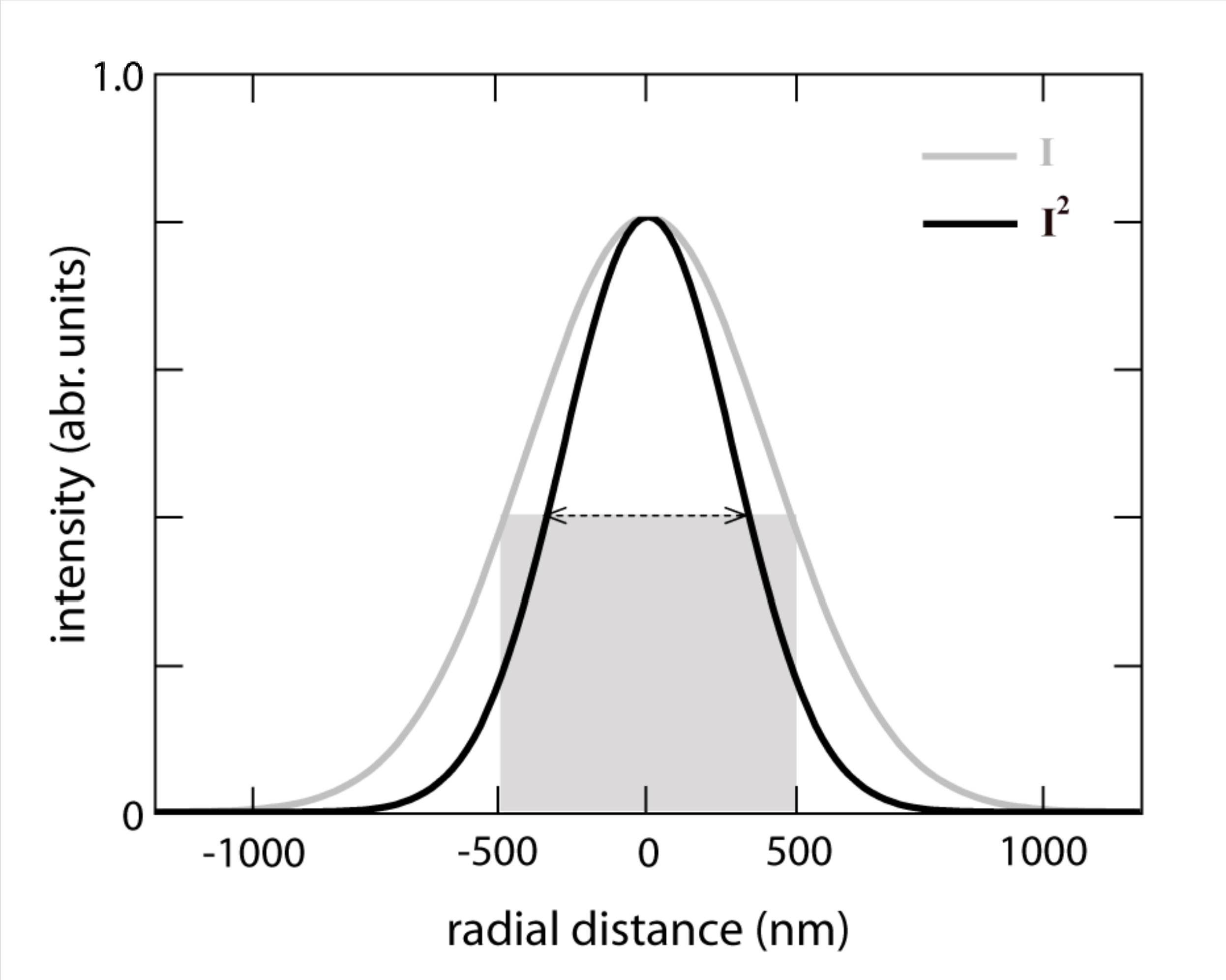
The polymerization is confined to the focal volume.

↓

High spatial resolution

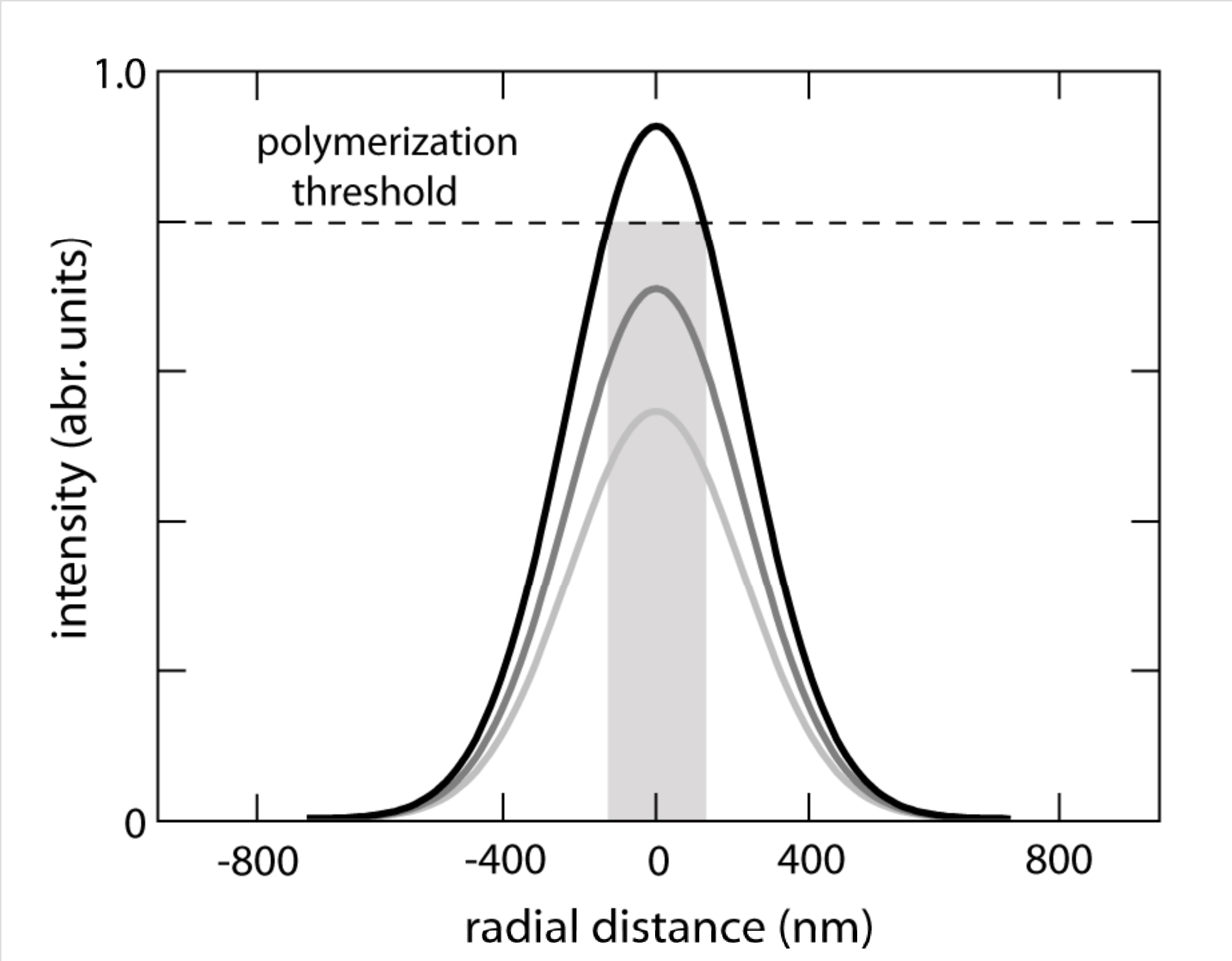


Two-photon polymerization



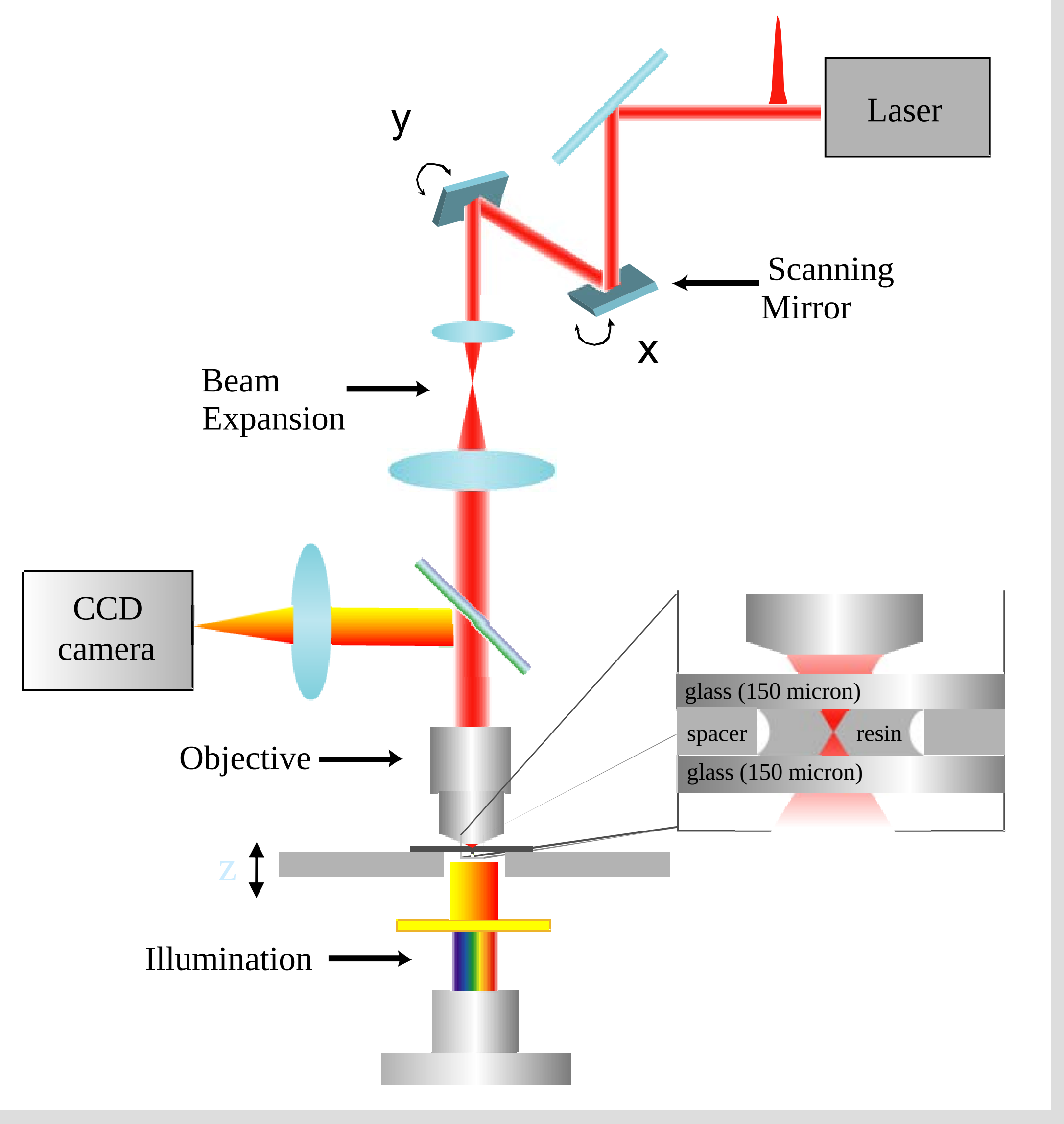
bellow the diffraction limit

Two-photon polymerization



even higher spatial resolution

Two-photon polymerization setup



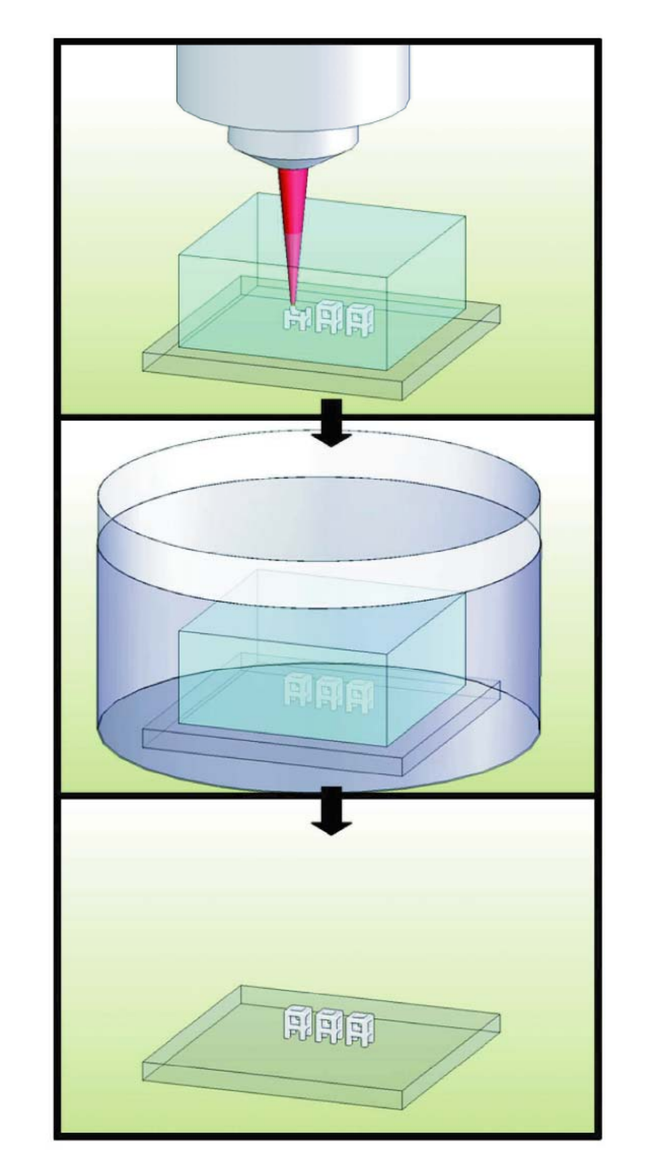
Ti:sapphire laser oscillator

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

Objective

40 x
0.65 NA

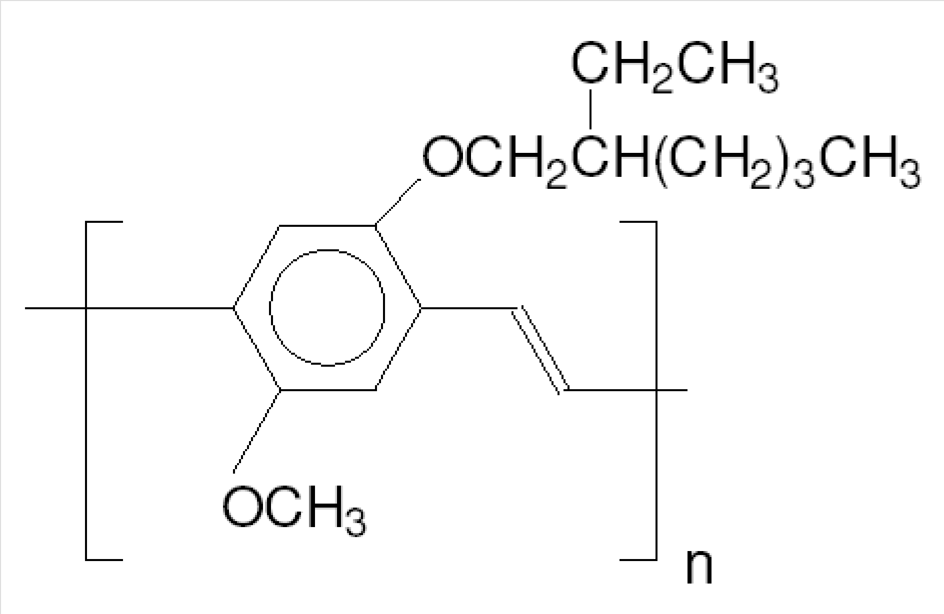
Two-photon polymerization



After the fabrication, the sample is immersed in ethanol to wash away any unsolidified resin and then dried

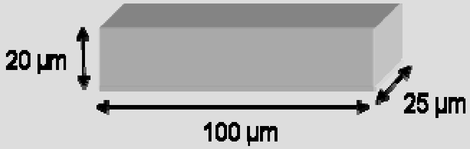
Microstructures containing MEH-PPV

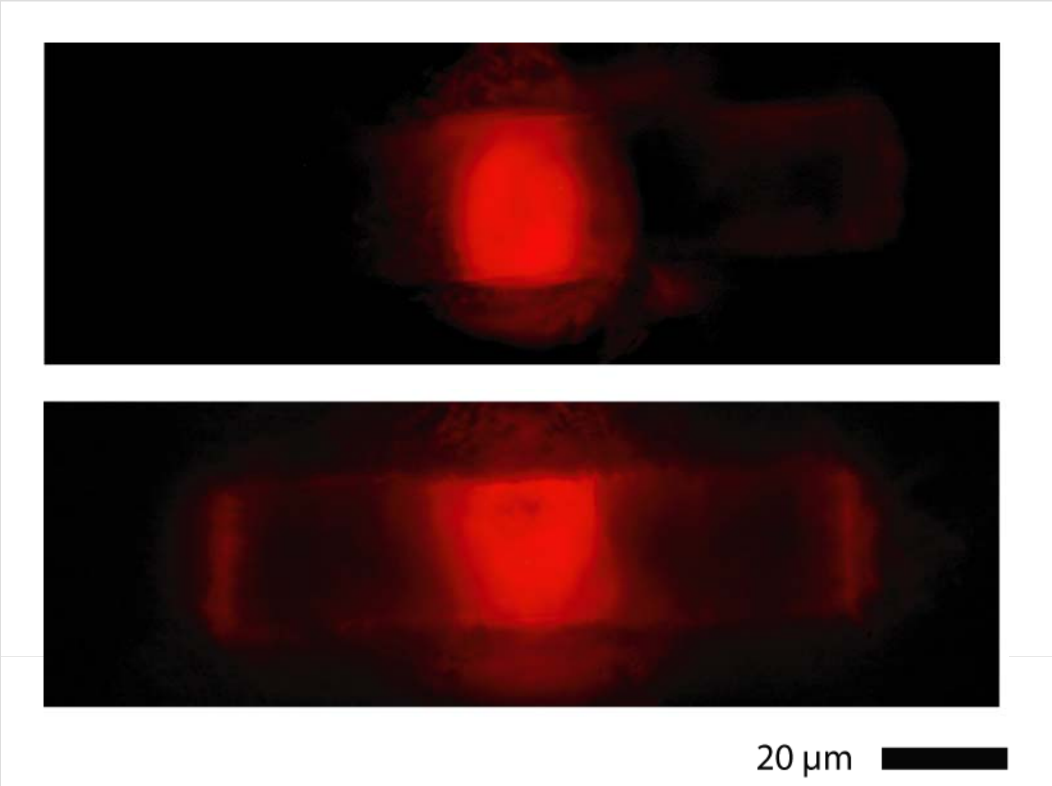
MEH-PPV

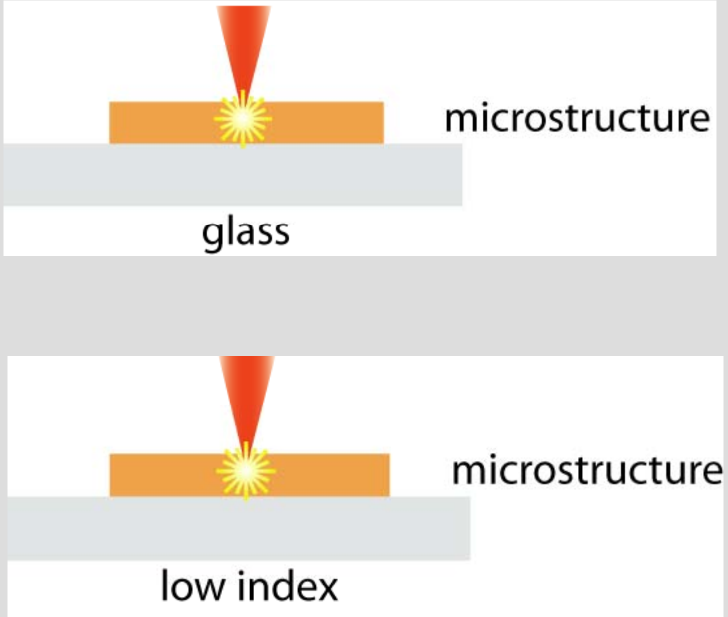


Fluorescence
Electro Luminescent
Conductive

Microstructures containing MEH-PPV





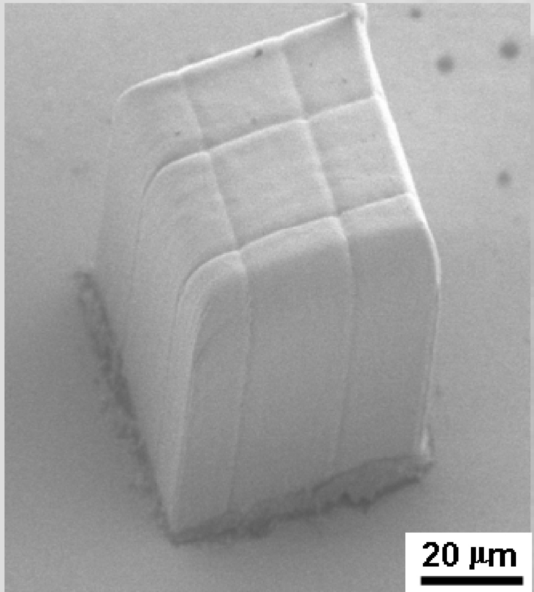


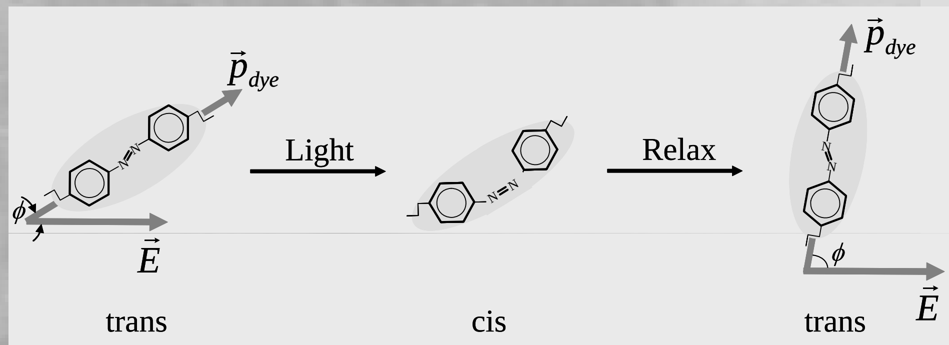
waveguiding of the microstructure fabricated on porous silica substrate (*n*= 1.185)

Applications: micro-laser; fluorescent microstructures; conductive microstructures

Other studies

- microstructures for optical storage – birefringence





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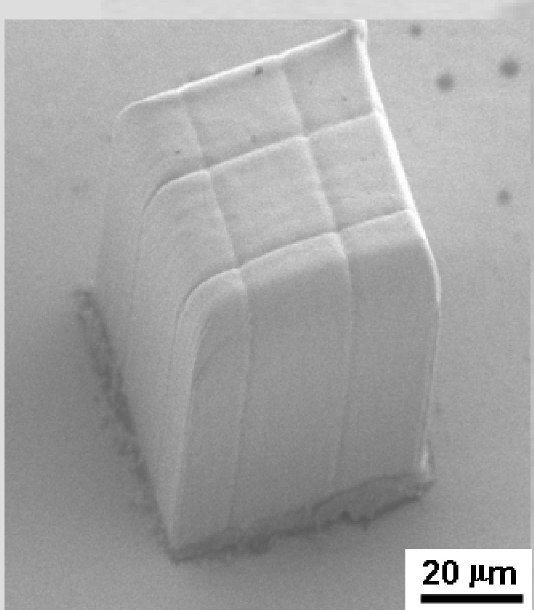
Other studies

- microstructures for optical storage – birefringence



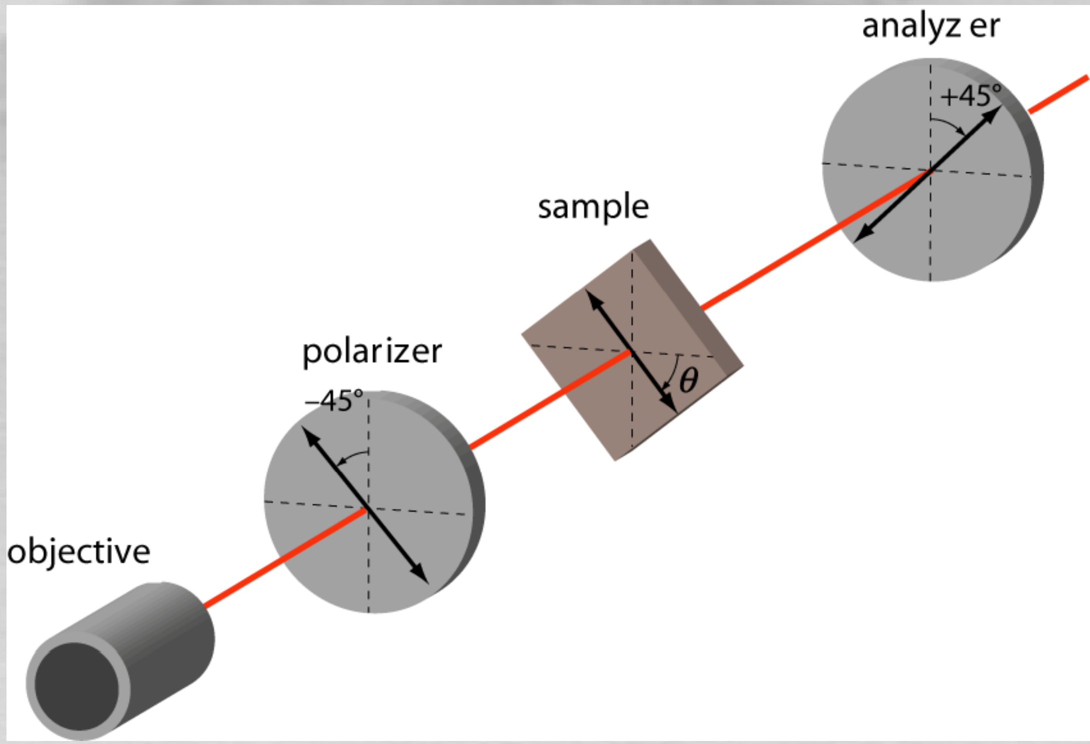
Ar^+ ion laser irradiation

- 514.5 nm
- one minute
- intensity of 600 mW/cm^2

Other studies

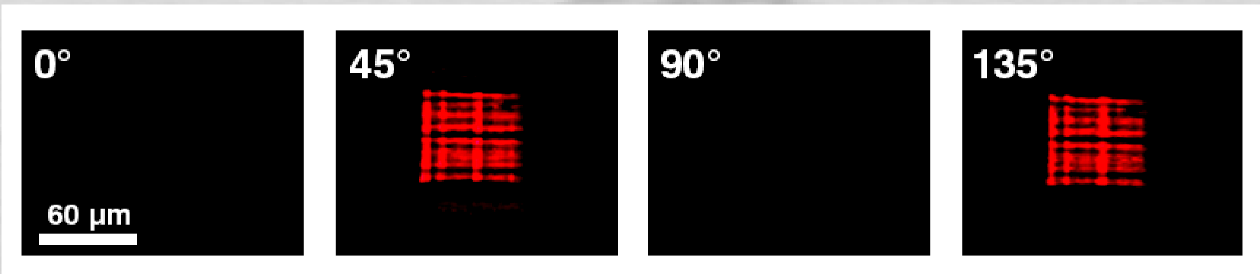
- microstructures for optical storage – birefringence

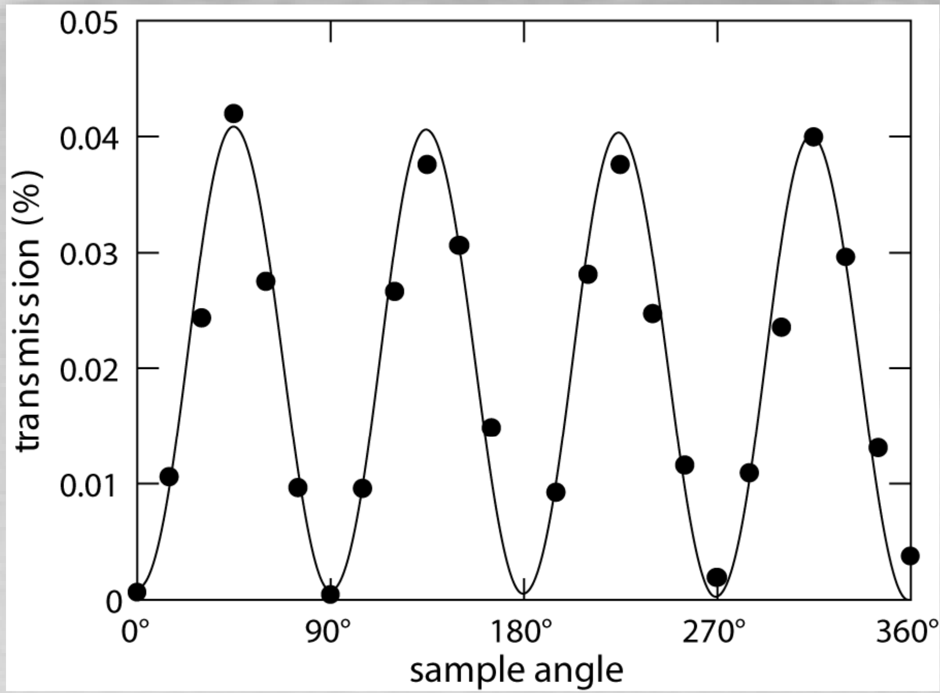
The sample was placed under an optical microscope between crossed polarizers and its angle was varied with respect to the polarizer angle



Other studies

- microstructures for optical storage – birefringence





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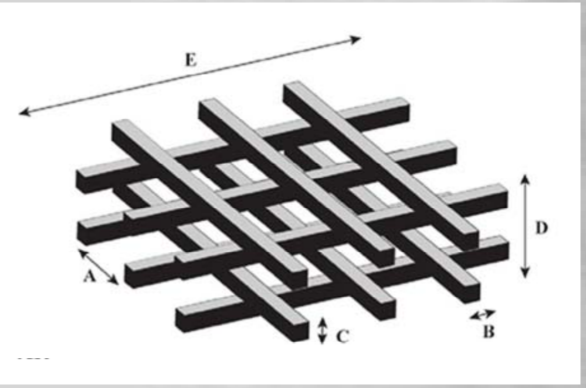
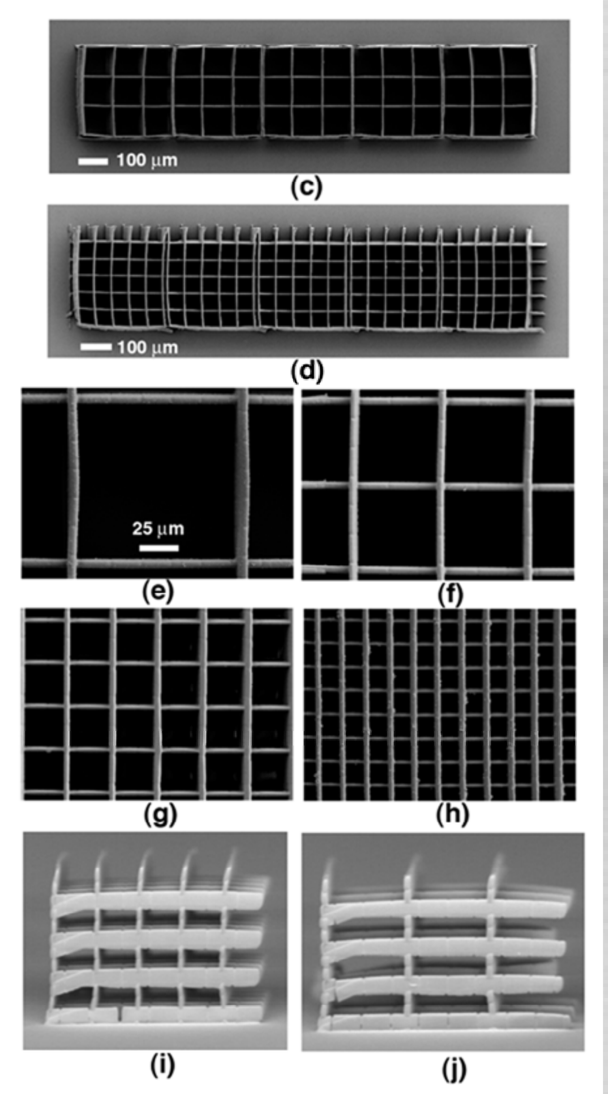
Other studies

- 3D cell migration studies in micro-scaffolds





SEM of the scaffolds

110 µm pore size

52 µm pore size

Top view

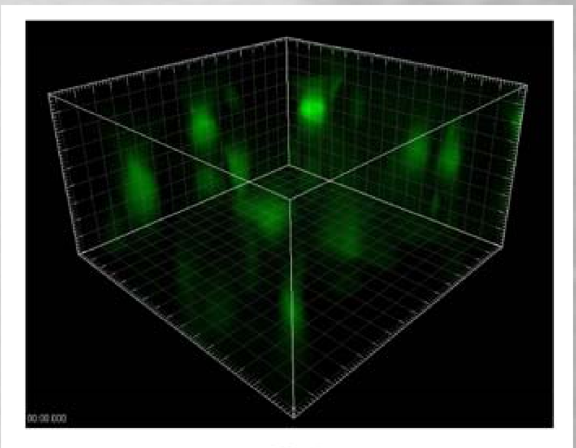
110, 52, 25, 12 µm pore size

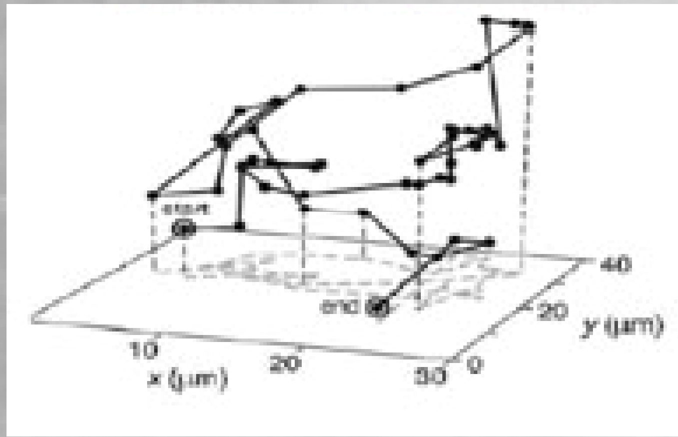
Side view

25, 52 µm pore size

Other studies

- 3D cell migration studies in micro-scaffolds





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Thank you !

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