Class 1

Introduction to Nonlinear Optics

Prof. Cleber R. Mendonca

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presentations

Outline

Linear optics

Introduction to nonlinear optics

Second order nonlinearities

Third order nonlinearities

Two-photon absorption

Conclusions

Linear optics vs Nonlinear optics

Optics is a branch of physics that describes the behavior and properties of light and the interaction of light with matter. Explains optical phenomena.

Nonlinear Optics

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

Linear optics

Maxwell equations

$$\vec{\nabla}.\vec{D} = \rho$$

$$\vec{\nabla}.\vec{B} = 0$$

$$\vec{\nabla}\times\vec{E} = -\partial\vec{B}/\partial t$$

$$\vec{\nabla}\times\vec{H} = \vec{J} + \frac{\partial\vec{D}}{\partial t}$$

ρ*:* charge density
J: current density

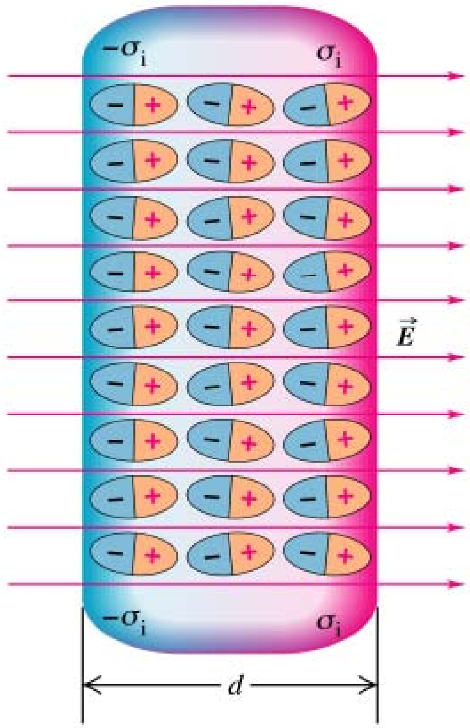
$$\vec{D} = \varepsilon_0\vec{E} + \vec{P}$$
$$\vec{H} = \vec{B}/\mu_0 - \vec{M}$$

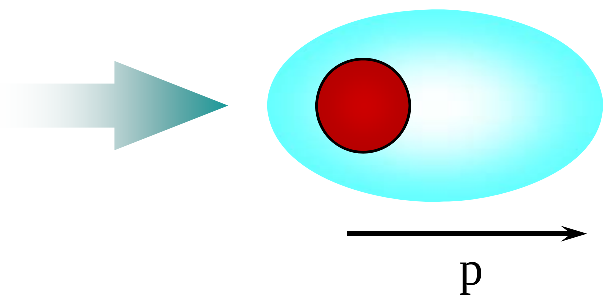
P: electric polarization
M: magnetization

Linear optics

P e **M**: response of the media to the applied field

Electric Polarization





Linear optics

Maxwell equations can be combined, leading to a equation describing the electromagnetism

Constitutive relationships

$$\vec{P} = \chi\vec{E}$$

$$\vec{M} = \chi_m \vec{H}$$

$$\vec{J} = \sigma\vec{E}$$

response of the media to the applied field

Linear optics

wave equation ($\rho = 0; \vec{J} = 0$)

$$\nabla^2 \vec{E} - \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2}$$

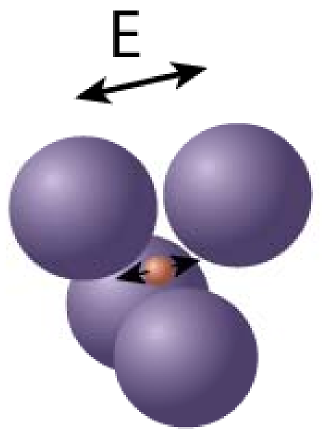
left

right

Light propagation in vacuum

Matter-light interaction

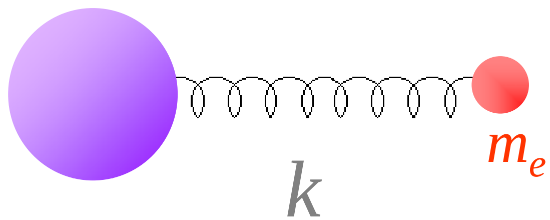
Linear optics



harmonic oscillator

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

electron on a spring



oscillation frequency

$$\omega_0 = \sqrt{\frac{k}{m_e}}$$

Linear optics

electron on a spring

$$F_{binding} = -m_e \omega_o^2 x$$

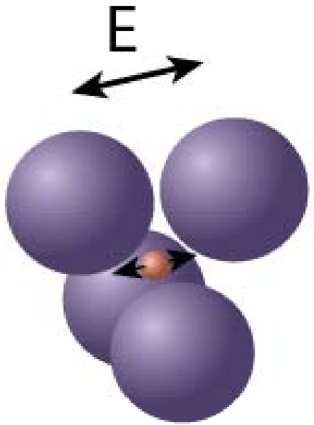
$$F_{damping} = -m_e \gamma \frac{dx}{dt}$$

$$F_{driving} = -eE = -eE_o e^{-i\omega t}$$

equation of motion

$$m \frac{d^2x}{dt^2} = \sum F$$

Linear optics



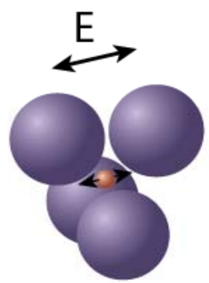
harmonic oscillator

$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{dt} + m\omega_o^2 x = -eE$$

Steady state: electron oscillates at driving frequency

$$x(t) = x_o e^{-i\omega t} \qquad x_o = -\frac{e}{m}\frac{1}{(\omega_o^2 - \omega^2) - i\gamma\omega}E_o$$

Linear optics



Oscillating dipole

$$p(t) = -e\,x(t) = \frac{e^2}{m}\frac{1}{(\omega_o^2 - \omega^2) - i\gamma\omega}E_o e^{-i\omega t}$$

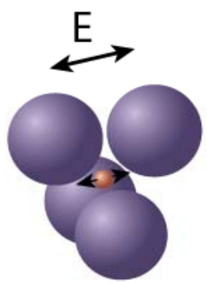
Polarization oscillator

$$P(t) = \frac{Ne^2/m}{\left(\omega_0^2 - \omega_0^2\right) - i\omega\gamma}E$$

linear response

$$P = \chi E$$

Linear optics



by comparison

$$\tilde{\chi} = \frac{Ne^2/m}{\left(\omega_0^2 - \omega_0^2\right) - i\omega\gamma}$$

which is a complex number

then

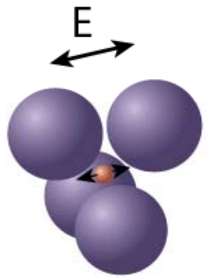
$$\tilde{n} = \sqrt{\left(1+\tilde{\chi}\right)} \approx 1 + \frac{1}{2}\tilde{\chi} + \ldots.. = n + i\,\kappa$$

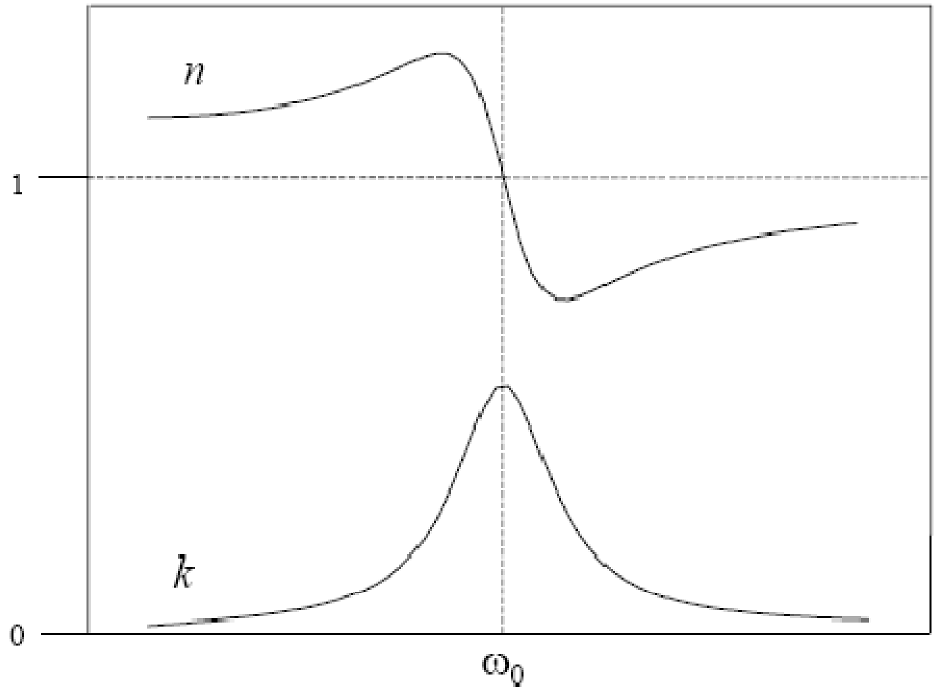
where n and κ are the real and imaginary parts of the complex index of refraction

n → refraction

κ → absorption

Linear optics





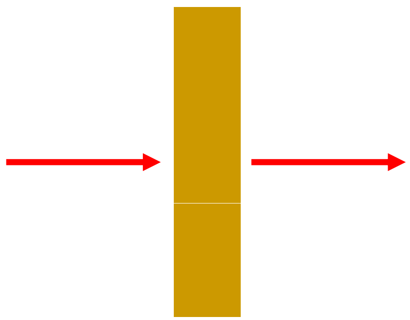
$$n = 1 + \left(\frac{Ne^2}{2m\varepsilon_0}\right)\frac{(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+(\omega b)^2}$$

$$\alpha(\omega) = \left(\frac{Ne^2}{mce_0}\right)\frac{\omega^2 b}{(\omega_0^2-\omega^2)^2+(\omega b)^2}$$

Linear optical process

absorption

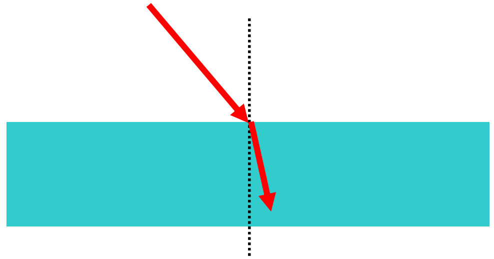
α_0 does not depend on light intensity



absorption of 10 %

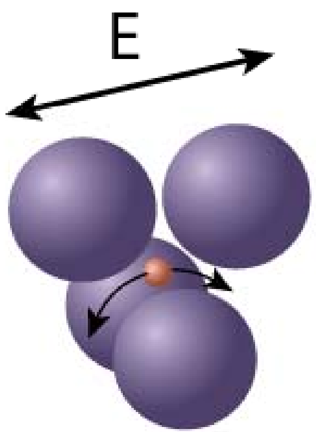
refraction

n_0 does not depend on light intensity



index of refraction 1.3

Nonlinear optics

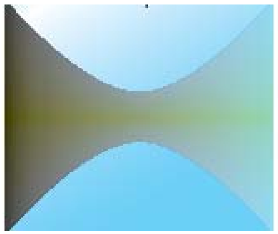


high light intensity

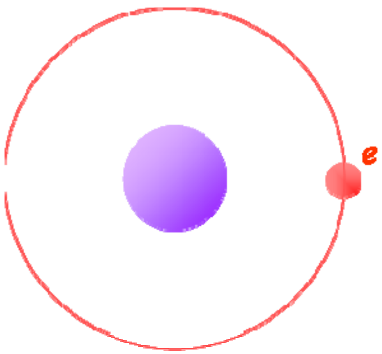
$E_{rad.} \sim E_{inter.}$

How high should be the light intensity ?

Nonlinear optics



Inter-atomic electric field



$e = 1.6 \times 10^{-19}$ C
$r \sim 4$ Å

$E \sim 1 \times 10^{10}$ V/m

cw laser

P = 20 W
$w_o = 20\ \mu m$

$$I = \frac{2P}{\pi w_0^2}$$

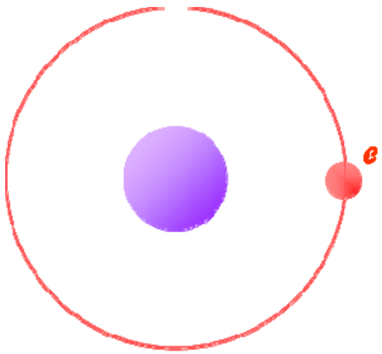
$I = 3 \times 10^{10}\ W/m^2$

$$I = \frac{1}{2} c n \varepsilon_0 E_0^2$$

$E_o = 4 \times 10^6$ V/m

Nonlinear optics

Inter-atomic electric field



E ~ 1 × 10^{10} V/m

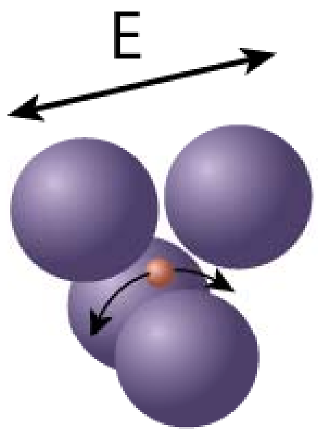
pulsed laser

I = 10 GW/cm^2 =
10 × 10^{13} W/m^2

$$I = \frac{1}{2} c n \varepsilon_0 E_0^2$$

E_o= 1 × 10^8 V/m

Nonlinear optics



high light intensity

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

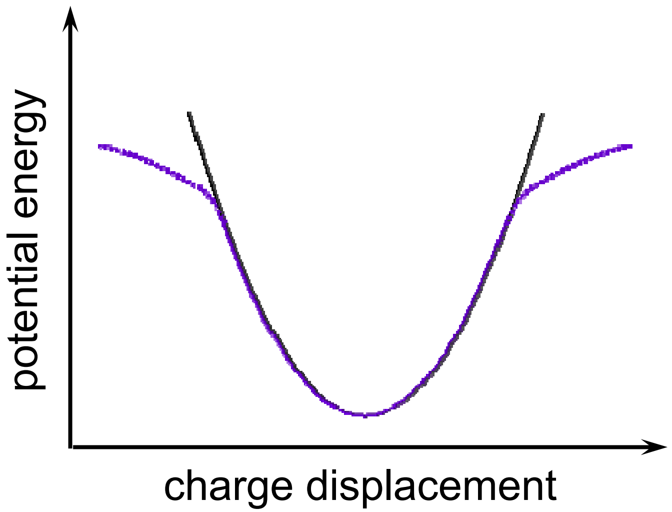
anharmonic oscillator

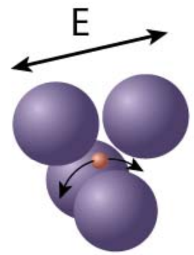
$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{dt} + m\omega_o^2 x + \max^2 = -eE$$

anharmonic term

Nonlinear optics

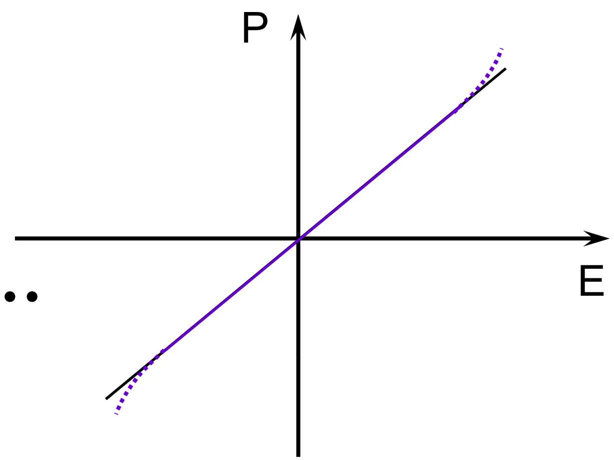
anharmonic oscillator



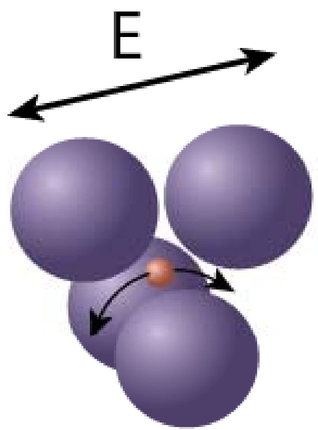


nonlinear polarization response

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



Nonlinear optics



anharmonic oscillator

high light intensity

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

nonlinear polarization response

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

Nonlinear optics

wave equation ($\rho = 0; \vec{J} = 0$)

$$\nabla^2 \vec{E} - \mu_0 \varepsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \mu_0 \frac{\partial^2 \vec{P}}{\partial t^2}$$

left

right

Light propagation in vacuum

Matter-light interaction

$$\vec{P}(\vec{r}, t) = \vec{P}^{(1)}(\vec{r}, t) + \vec{P}^{NL}(\vec{r}, t)$$

Nonlinear optics

nonlinear expansion of the polarization

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

linear processes

SHG

THG
Kerr effect

Nonlinear optics

nonlinear expansion of the polarization

$$P = \chi^{(1)} \cdot E + \chi^{(2)} EE + \chi^{(3)} EEE +$$

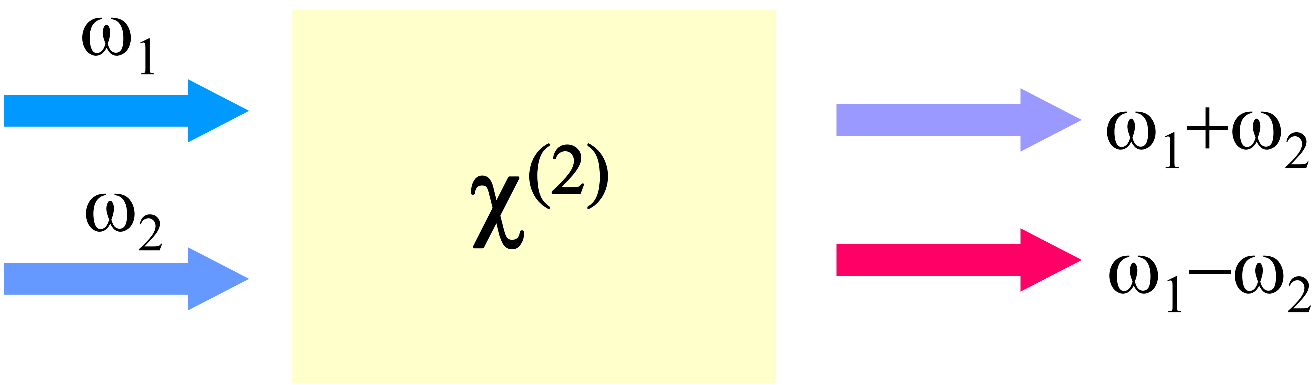
$$E_{(z,t)} = E_0 \cos(\omega t - kz)$$

$$P = \chi^{(1)} E_0 \cos(\omega t - kz) + \chi^{(2)} E_0^2 \cos^2(\omega t - kz) + \chi^{(3)} E_0^3 \cos^3(\omega t - kz) \ldots$$

$$P = \chi^{(1)} E_0 \cos(\omega t - kz) + \frac{1}{2} \chi^{(2)} E_0^2 \left[1 + \cos(2\omega t - 2kz)\right]$$
$$+ \chi^{(3)} E_0^3 \left[\frac{3}{4} \cos(\omega t - kz) + \frac{1}{4} \cos(3\omega t - 3kz)\right] \ldots$$

Nonlinear Optics

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



– If $\omega_1 = \omega_2$

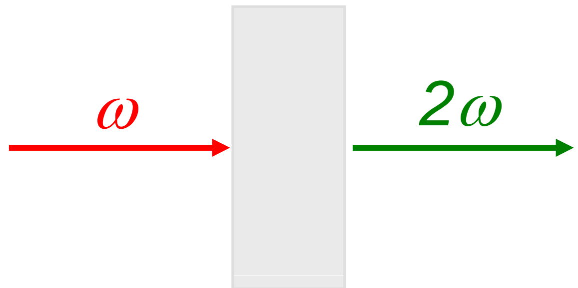
– second harmonic generation: 2ω

– optical retificatio: 0

Nonlinear Optics

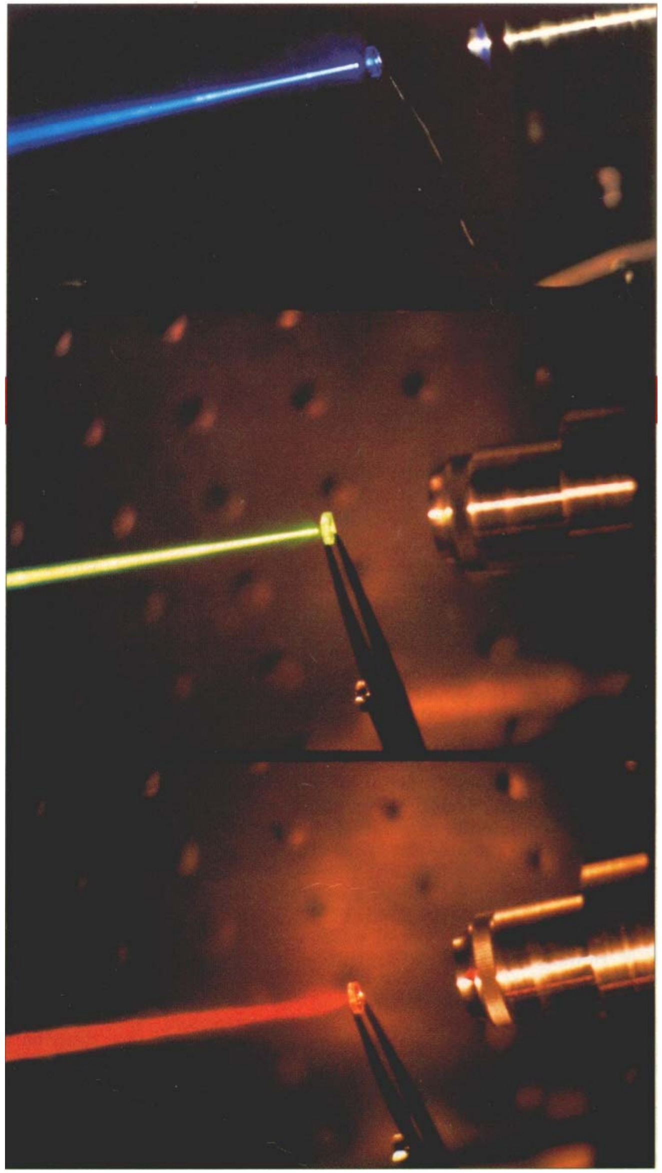
Second order processes $\chi^{(2)}$

Second Harmonic Generation



λ = 1064nm

λ = 532nm



Second Harmonic Generation

$\chi^{(2)}$

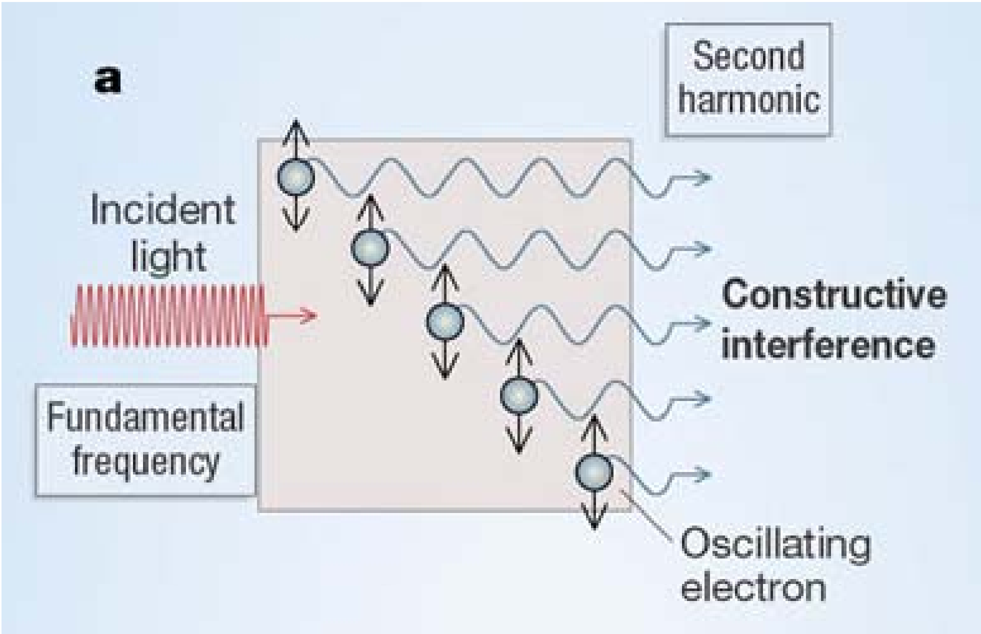
1- higher energy light

2- transparent material

Second Harmonic Generation

$$\chi^{(2)}$$

Phase Matching



$$v(\omega) = v(2\omega)$$

Nonlinear Optics

in medium with inversion symmetry

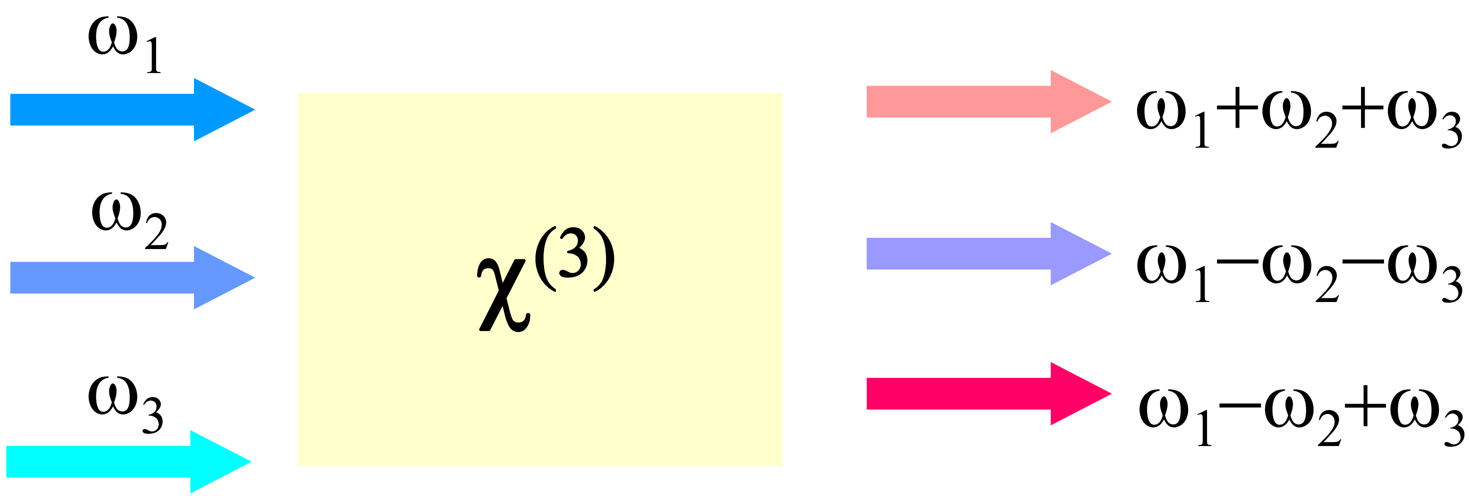
$$\vec{P}^{(2)} = \overset{\rightarrow}{\vec{\chi}}^{(2)} : \vec{E}\,\vec{E} \quad \Rightarrow \quad -\vec{P}^{(2)} = \overset{\rightarrow}{\vec{\chi}}^{(2)} : (-\vec{E})(-\vec{E})$$

and consequently

$$\chi^{(2)} = -\chi^{(2)} = 0$$

Nonlinear Optics

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

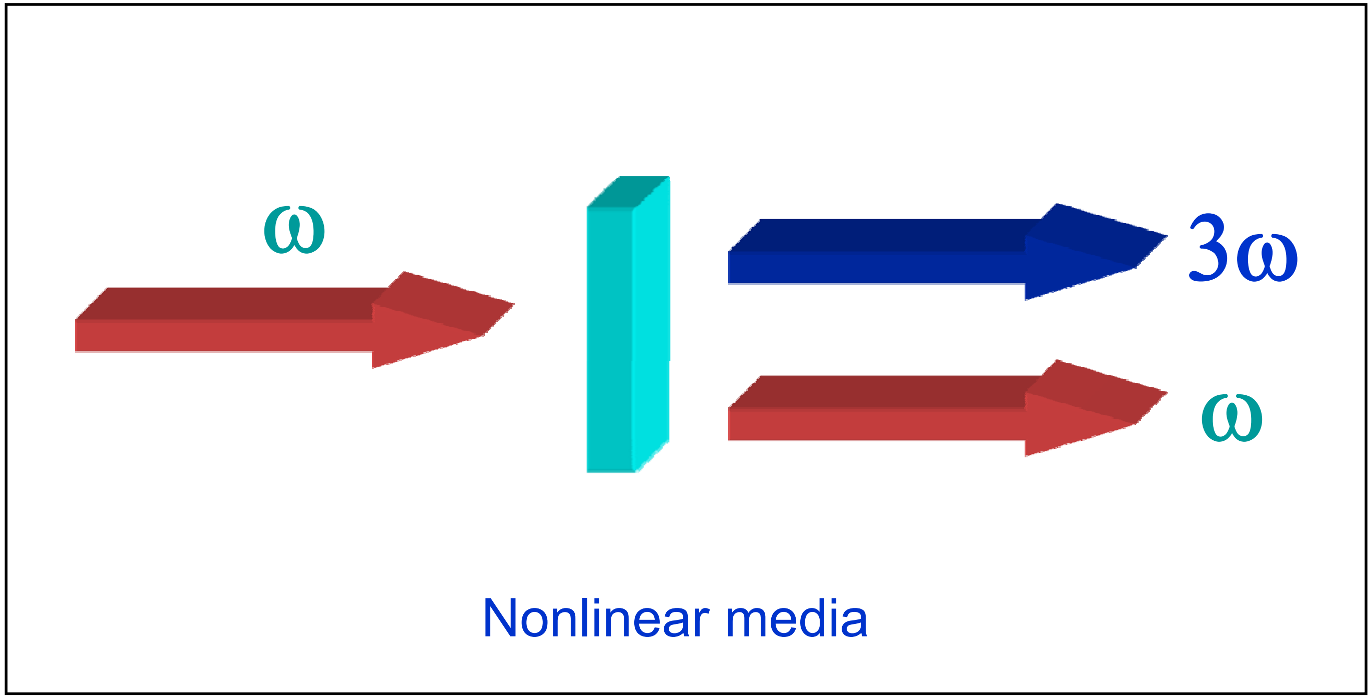


– If $\omega_1 = \omega_2 = \omega_3$

 – Third harmonic generation: 3ω

 – Self phase modulation: ω

Third Harmonic Generation $\chi^{(3)}$



Nonlinear Optics

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

Nonlinear polarization

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

Third order polarization

$$P^{(3)}(t) = \chi^{(3)}E(t)E^*(t)E(t) = \chi^{(3)}I(t)E(t)$$

Nonlinear Optics

consequently

$$P = P^{(1)} + P^{(3)} = (\chi^{(1)} + \chi^{(3)} I)E \equiv \chi_{eff} E$$

and

$$n = \sqrt{\epsilon} = \sqrt{1 + \chi_{eff}} \approx \sqrt{1 + \chi^{(1)}} + \frac{1}{2}\frac{\chi^{(3)} I}{\sqrt{1 + \chi^{(1)}}} = n_o + n_2 I$$

Kerr media

$$n = n_0 + n_2 I$$

Nonlinear Optics

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

$$n_2 \approx \chi^{(3)}$$

Kerr media:

$$n = n_0 + n_2 I$$

Index of refraction depends on the light intensity

Self phase modulation

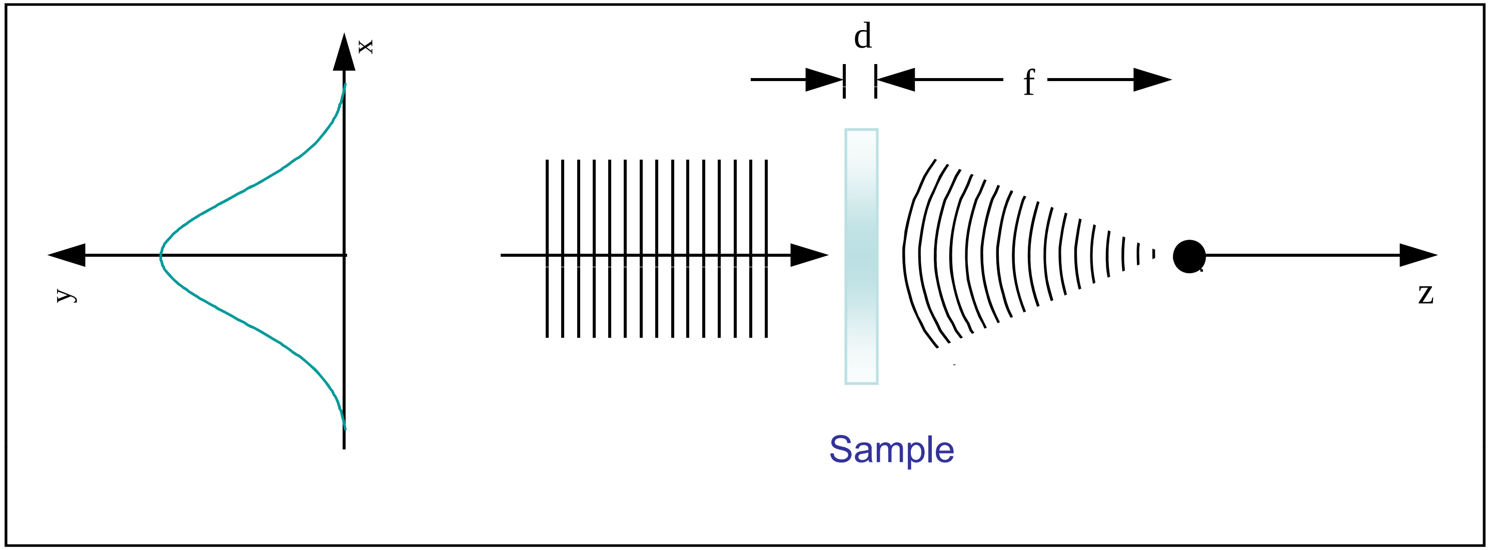
Kerr media:

$$n = n_0 + n_2 I$$

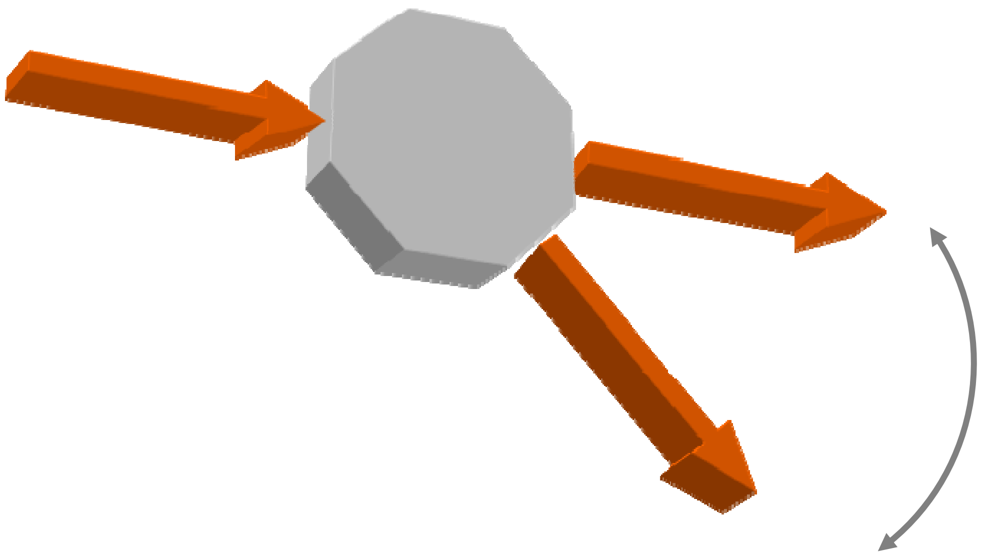
centre symmetric: $\chi^{(2)} = 0$

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

$n_2 > 0$ Material behaves as a convergent lens



Optical switching



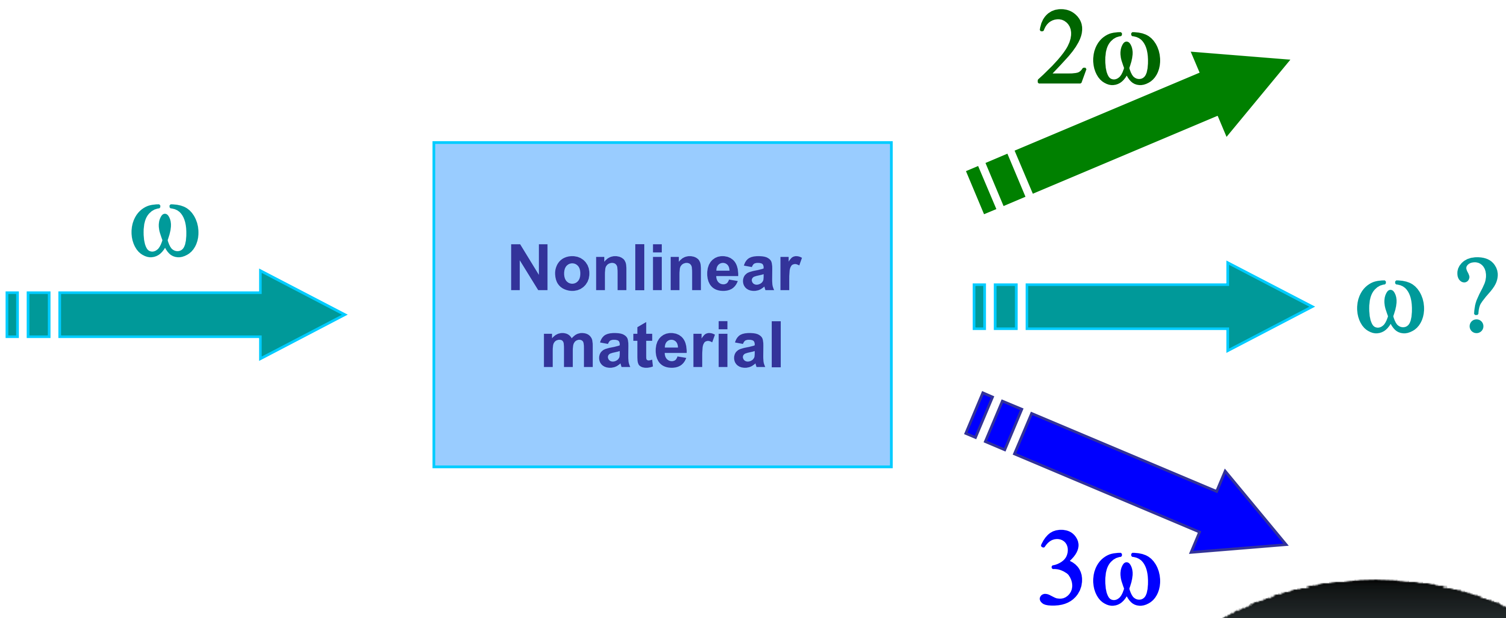
response time: 10^{-15} s

response time	1×10^{-9}	1×10^{-15}

1GHz → 1 THz

1 million times faster

Nonlinear optics



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

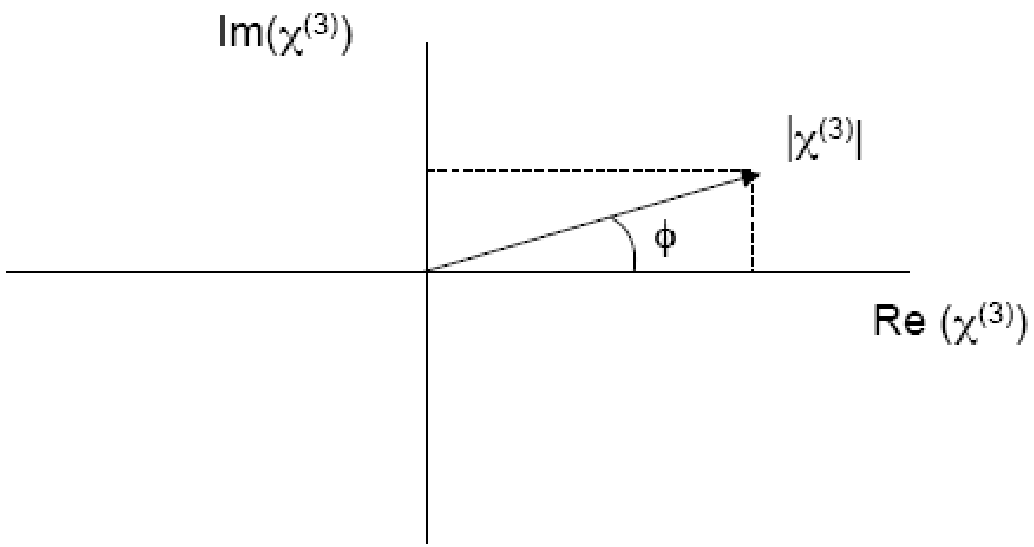
Nonlinear Optics

$\chi^{(3)}$ 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

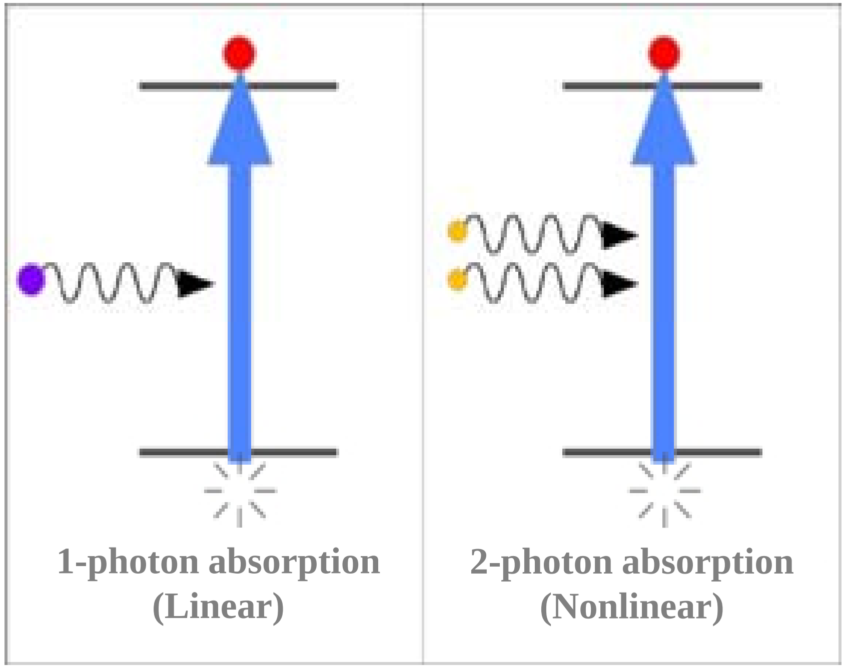
Absorptive process:

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

- nonlinear absorption
- two-photon absorption

Two-photon absorption (2PA) process

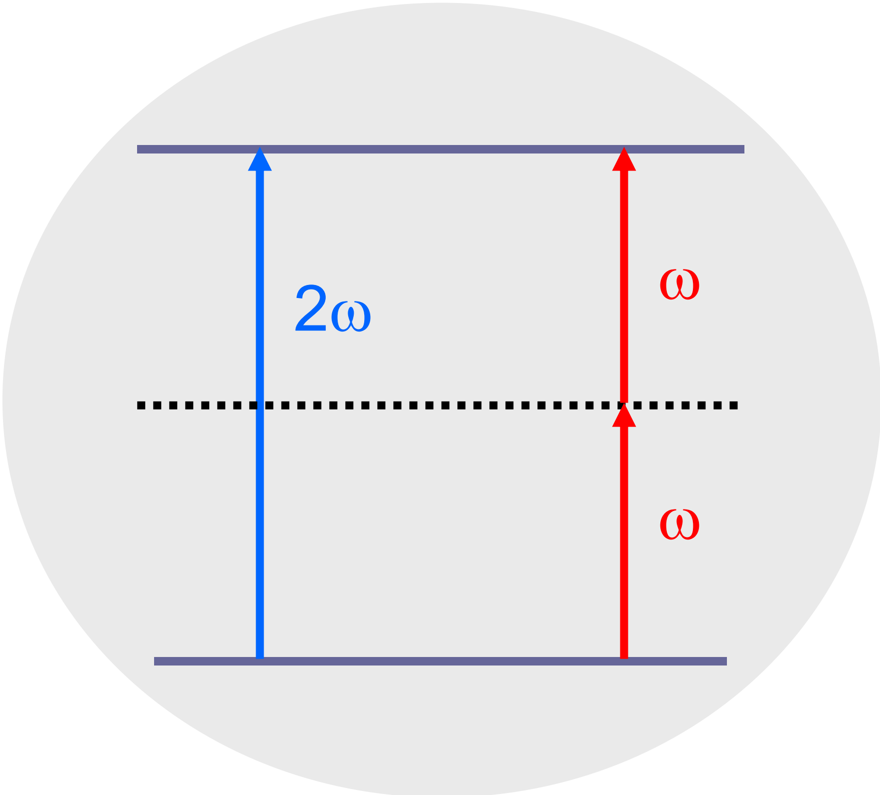
Phenomenon does not described for the Classical Physics and does not observed until the development of the Laser.



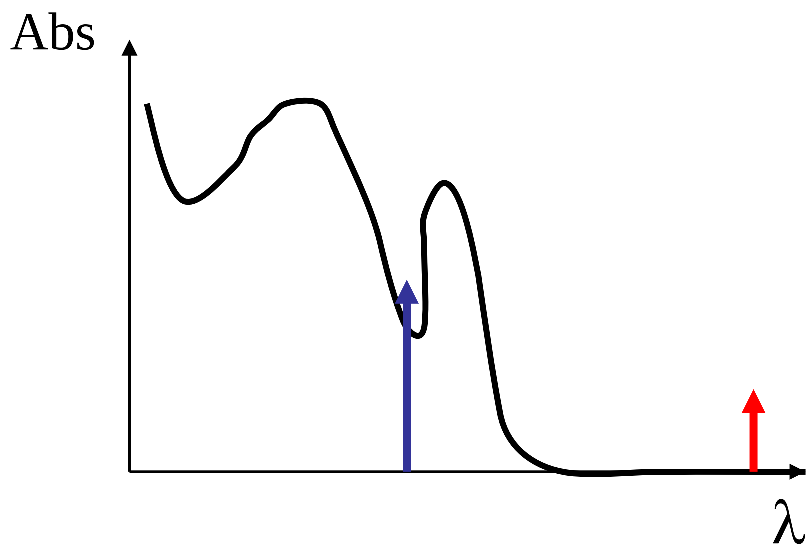
Theoretical model: Maria Göppert-Mayer, 1931

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.

two-photon absorption



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



Applications:

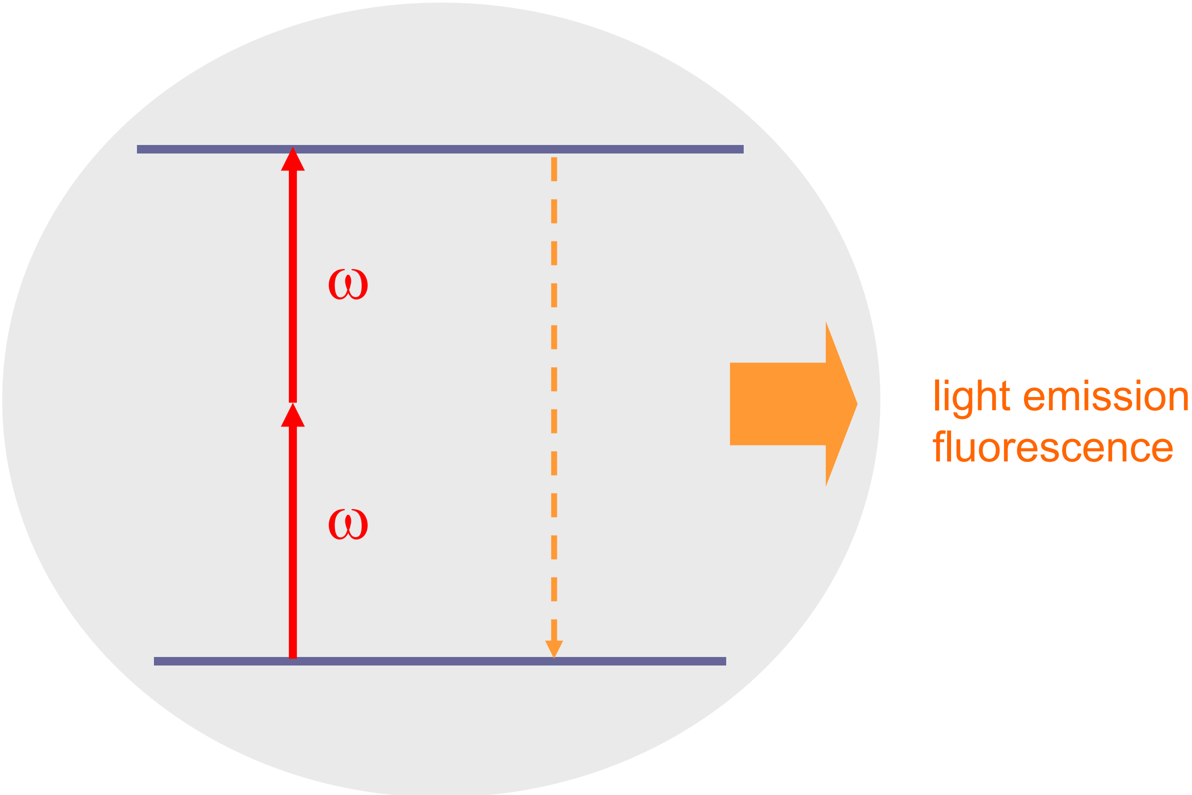
optical limiting

fluorescence microscopy

microfabrication

two-photon fluorescence

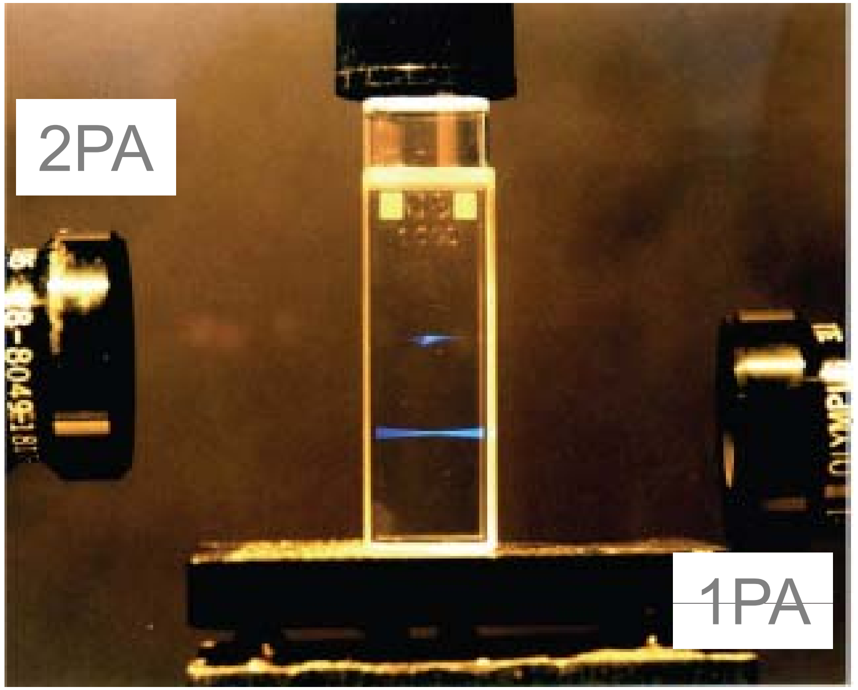
$$\alpha = \alpha_0 + \beta I$$

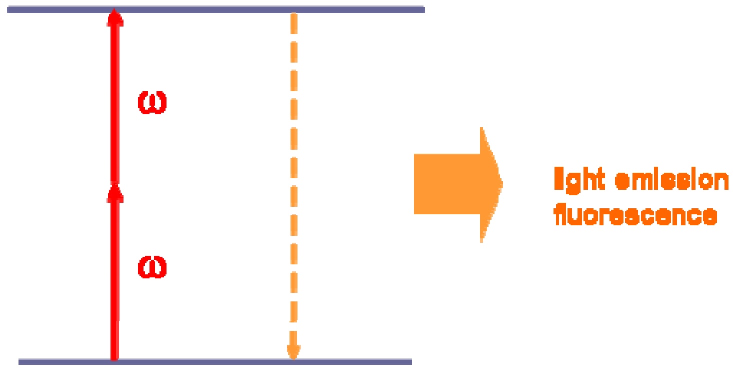


$$\text{TPA rate constant} \propto \delta I^2$$

localization of the excitation with 2PA

dilute solution of fluorescent dye





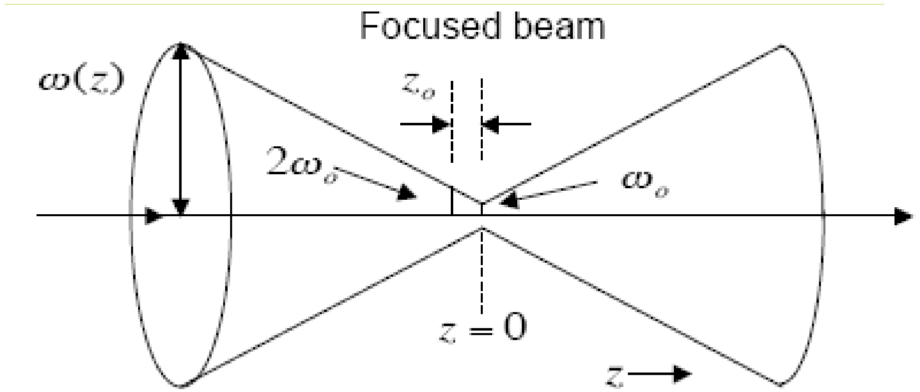
$$\mathrm{TPA} \propto \delta I^2$$

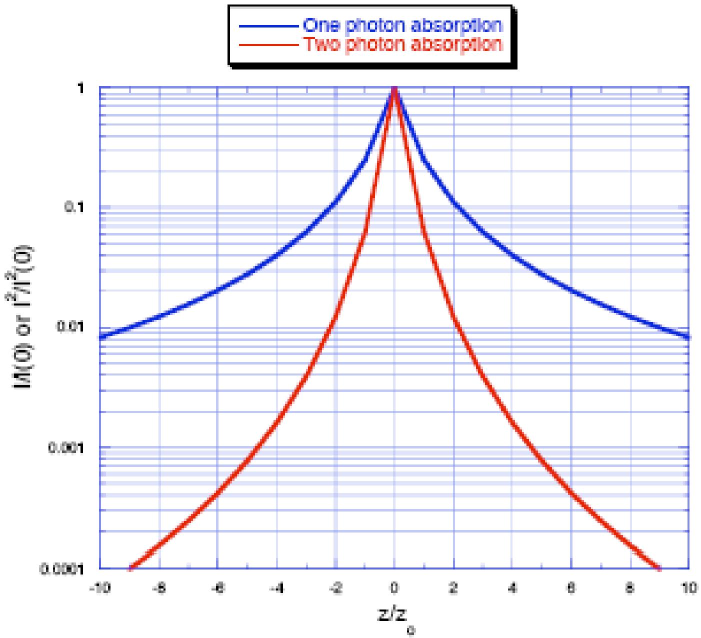
$$I \sim \frac{1}{z^2}$$

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

spatial confinement of excitation

excitation profile along z





Radius, area and intensity of focused beam

$$\omega(z) = \omega_0\left(1+\frac{z}{z_0}\right)$$

$$A(z) = \pi\omega^2 = \pi\omega_0^2\left(1+\frac{z}{z_0}\right)^2$$

$$I(z) = \frac{E}{At} \propto \frac{1}{A} = \frac{1}{\pi\omega_0^2\left(1+\frac{z}{z_0}\right)^2}$$

Normalized excitation rates
(ignoring beam attenuation)

one photon

$$\frac{I(z)}{I(0)} = \left(1+\frac{z}{z_0}\right)^{-2}$$

two photon

$$\frac{I(z)}{I(0)} = \left(1+\frac{z}{z_0}\right)^{-4}$$

Class 2

Studying optical nonlinearities

Prof. Cleber R. Mendonca

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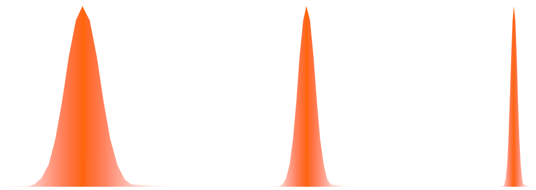
Investigating nonlinear optical materials

Very intense light: femtosecond pulses

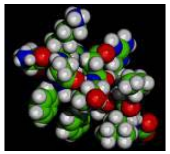
Ti:Sapphire lasers



100 fs   50 fs   20 fs

1 fs = 10^{-15} s

1 fs ⟶ 1s



Laser intensities ~ 100 GW/cm^2

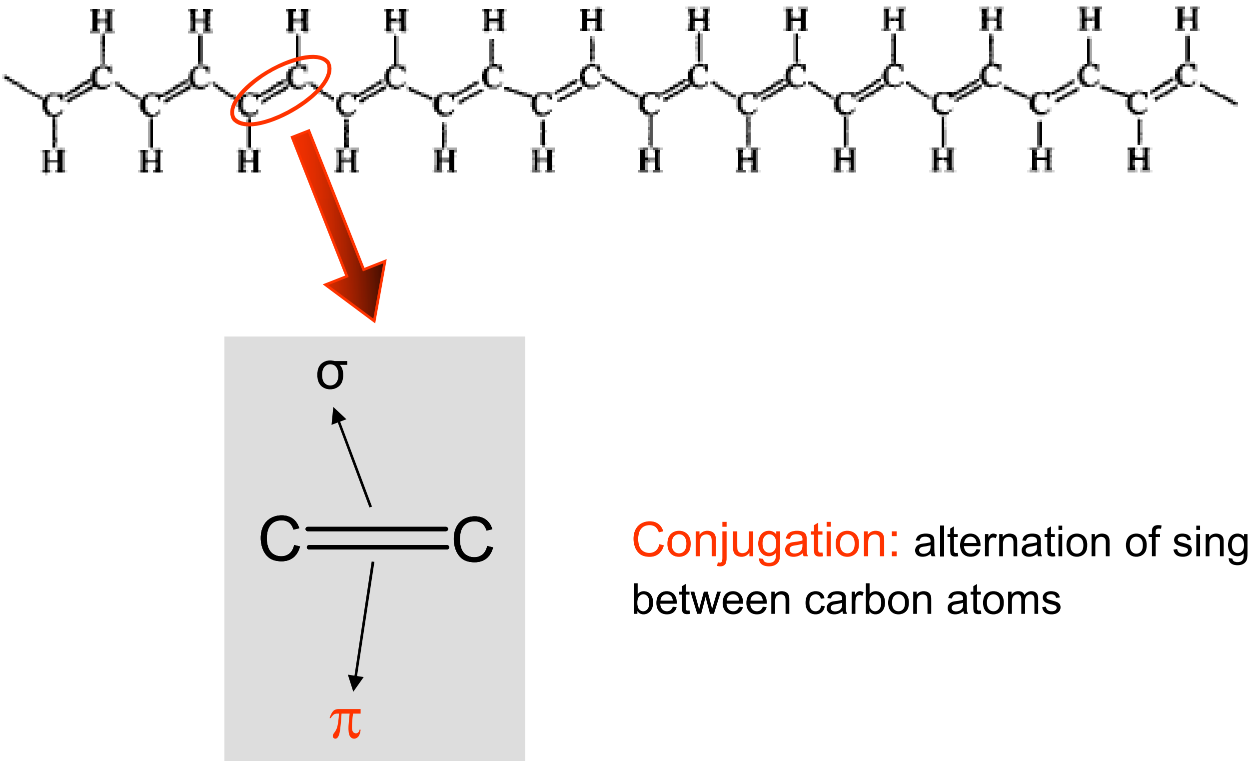
1 x 10^{11}W/cm^2

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

Organic materials

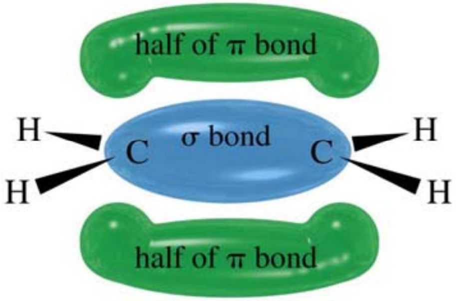
• Flexibility to tune the nonlinear optical response by manipulating the molecular structure

• π-conjugated structures



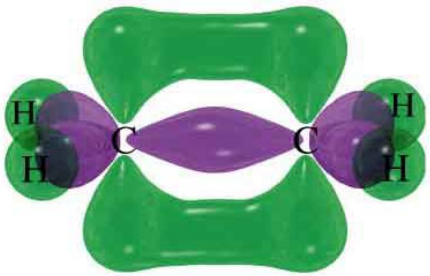
Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation



σ bond: forms a strong chemical bond; localized

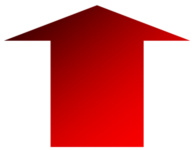
π bond: weaker bond; out of the C atoms axis



"Free electrons" that are easier to move under an applied electric filed

π bond in conjugated system: delocalized electrons

high optical nonlinearities

 $\chi^{(3)}$

Research

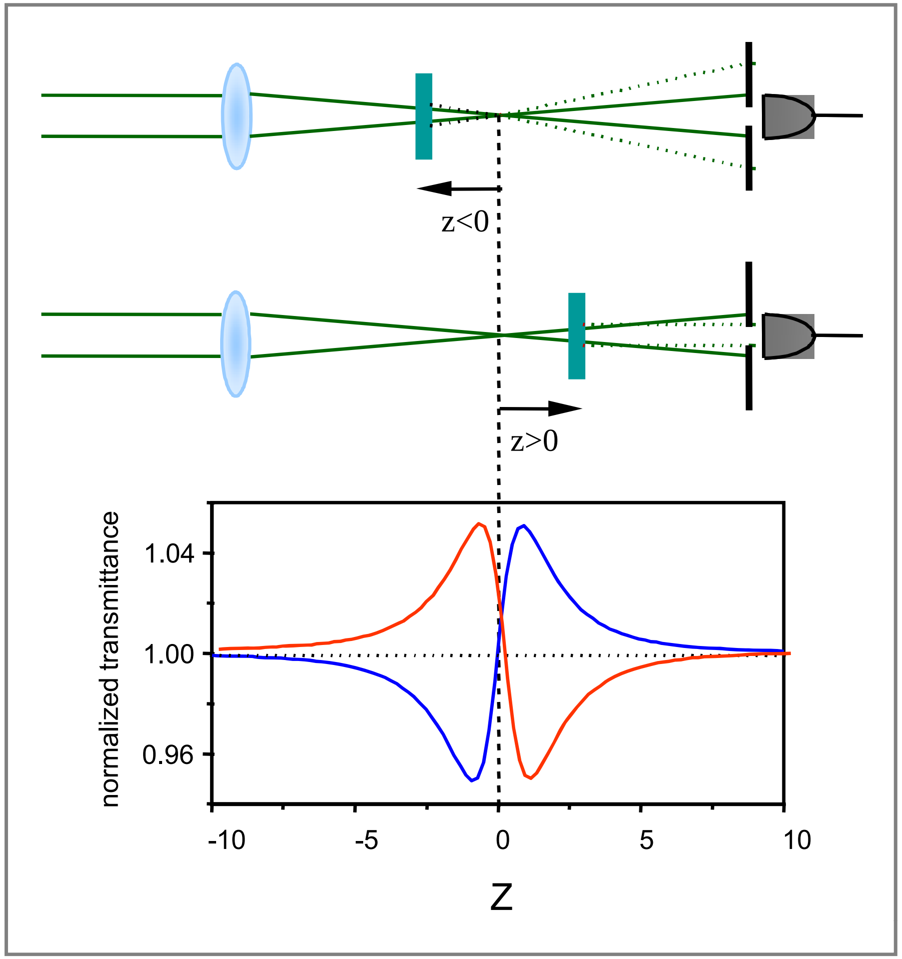
• Understanding the physical principles behind two-photon absorption

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

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

Z-scan

closed aperture Z-scan

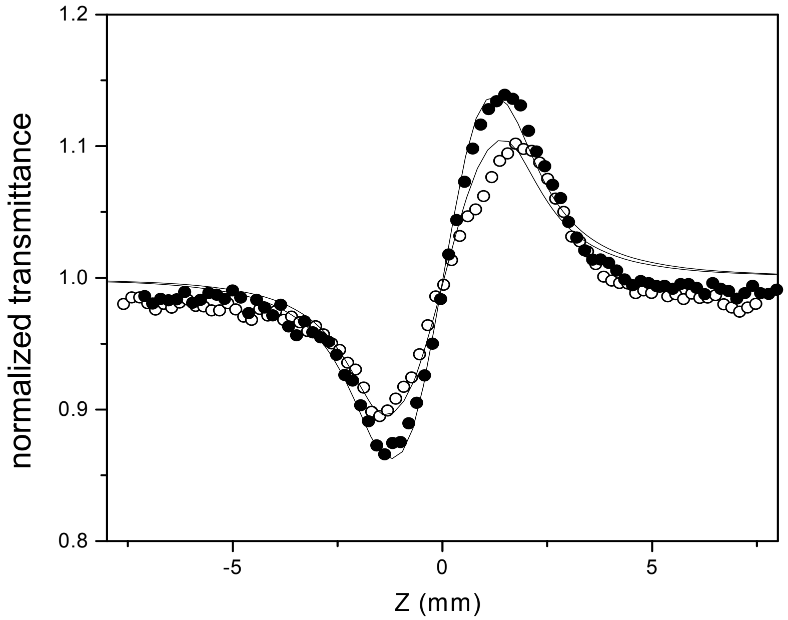


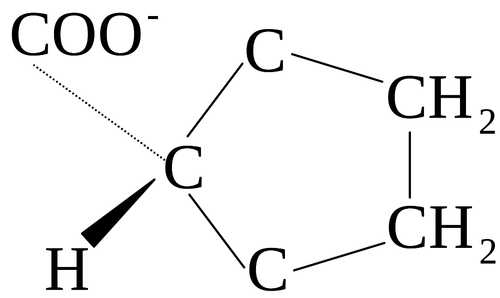
$$n = n_0 + n_2 I$$

$$\Delta T \propto n_2 I$$

Nonlinear refraction

Aminoacids





L-Proline

$$\Delta T_{pv} = 0.406\Delta\Phi_0 = 0.406\left(\frac{2\pi}{\lambda}n_2 I_0 L\right)$$

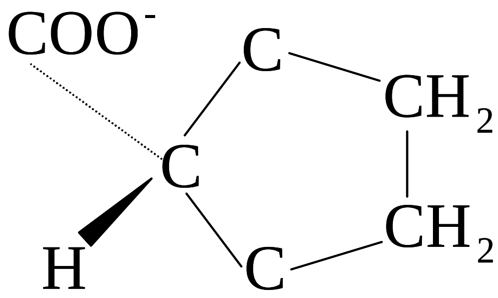
150 fs 100 GW/cm^2

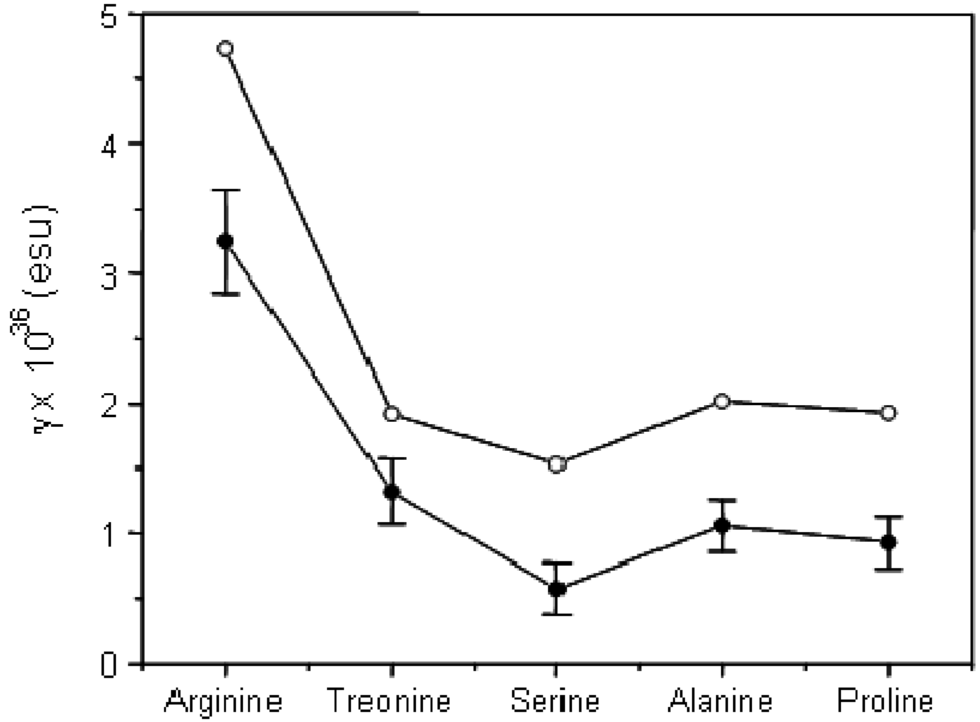
775 nm

$$n_2 \propto \chi^{(3)}$$

Nonlinear refraction

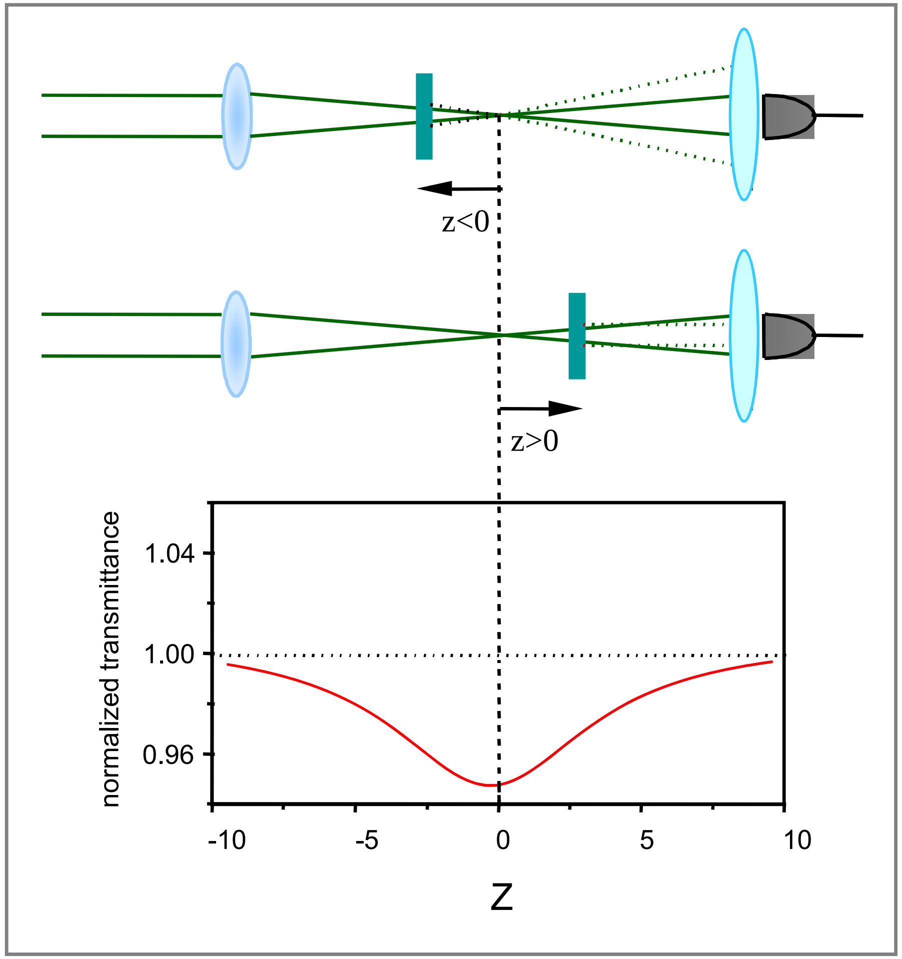
L-Proline





Z-scan (nonlinear absorption)

open aperture Z-scan



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

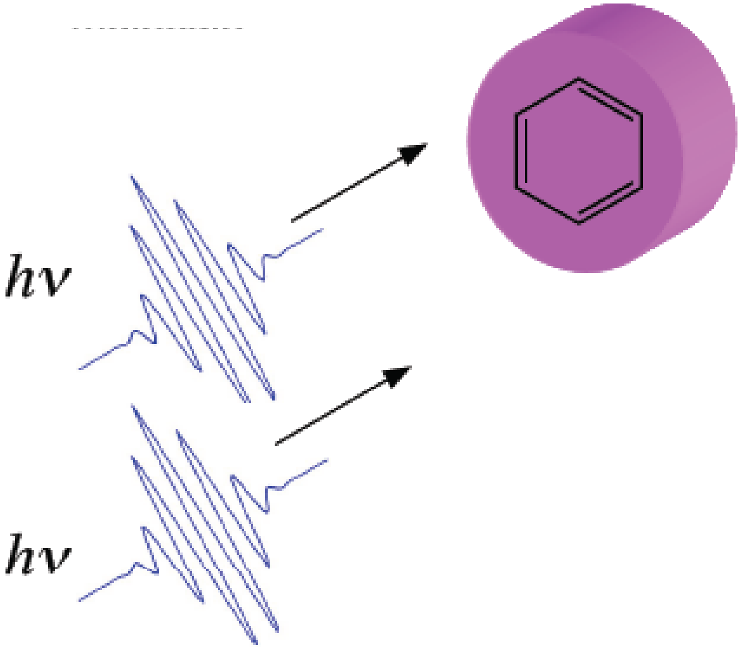
$$\Delta T \propto \beta I$$

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

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

two-photon absorption cross-section

A pair of photon incident on a molecule



For two-photon absorption to occur, a pair of photons must be incident within a cross sectional area and within the lifetime of the virtual sate, $\tau \sim 10^{-15}$ s

Relation between molecular TPA cross section and TPA absorption coefficient

$$\delta = \frac{h\nu\beta}{N}$$

Representative values for TPA transitions:

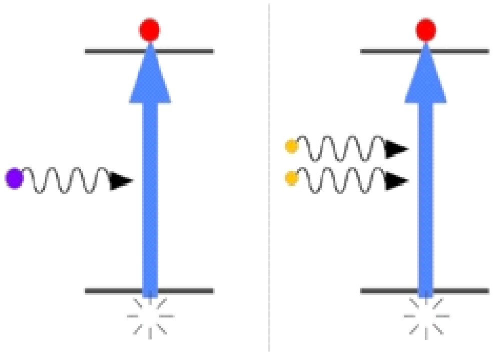
δ = 10 to 1000 x 10^{-50} cm^4 s $photon^{-1}$

β ~ 10 to 100 cm GW^{-1} for a neat material

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

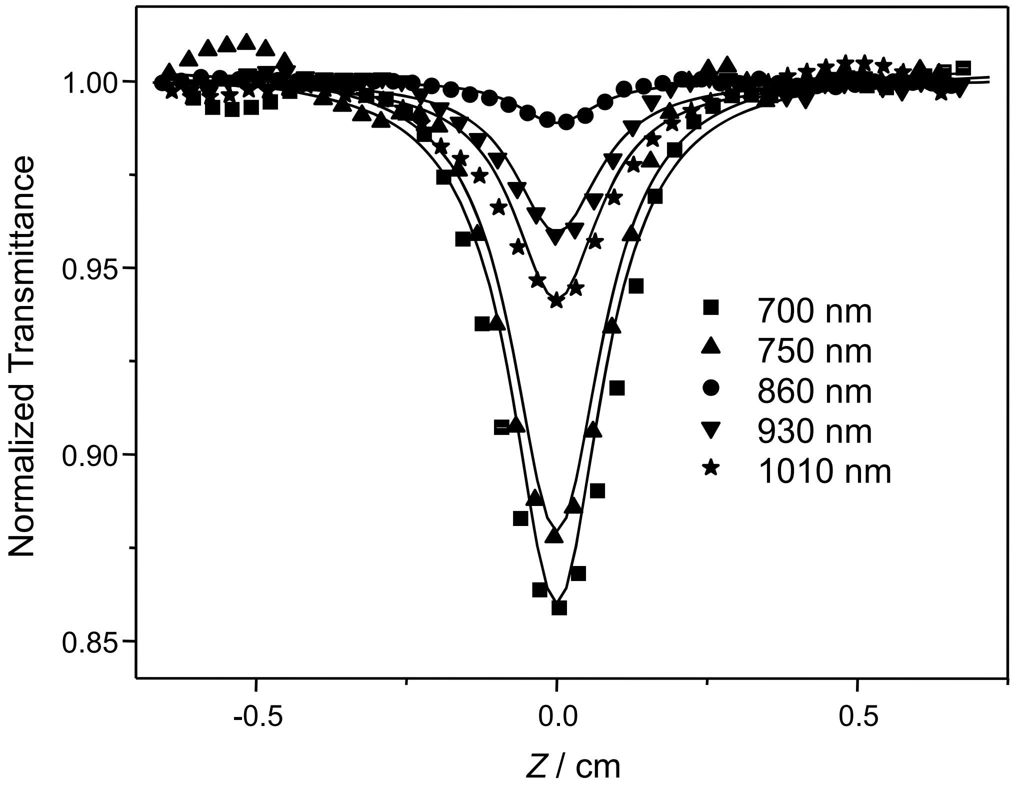
Optical parametric amplifier

460 - 2600 nm

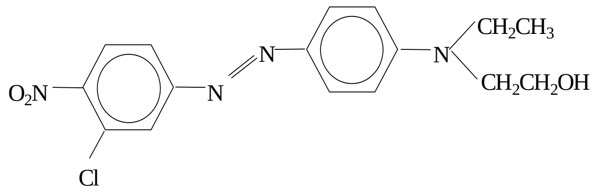
$\approx$ *120 fs*

20-60 μJ

Two-photon absorption



DR13

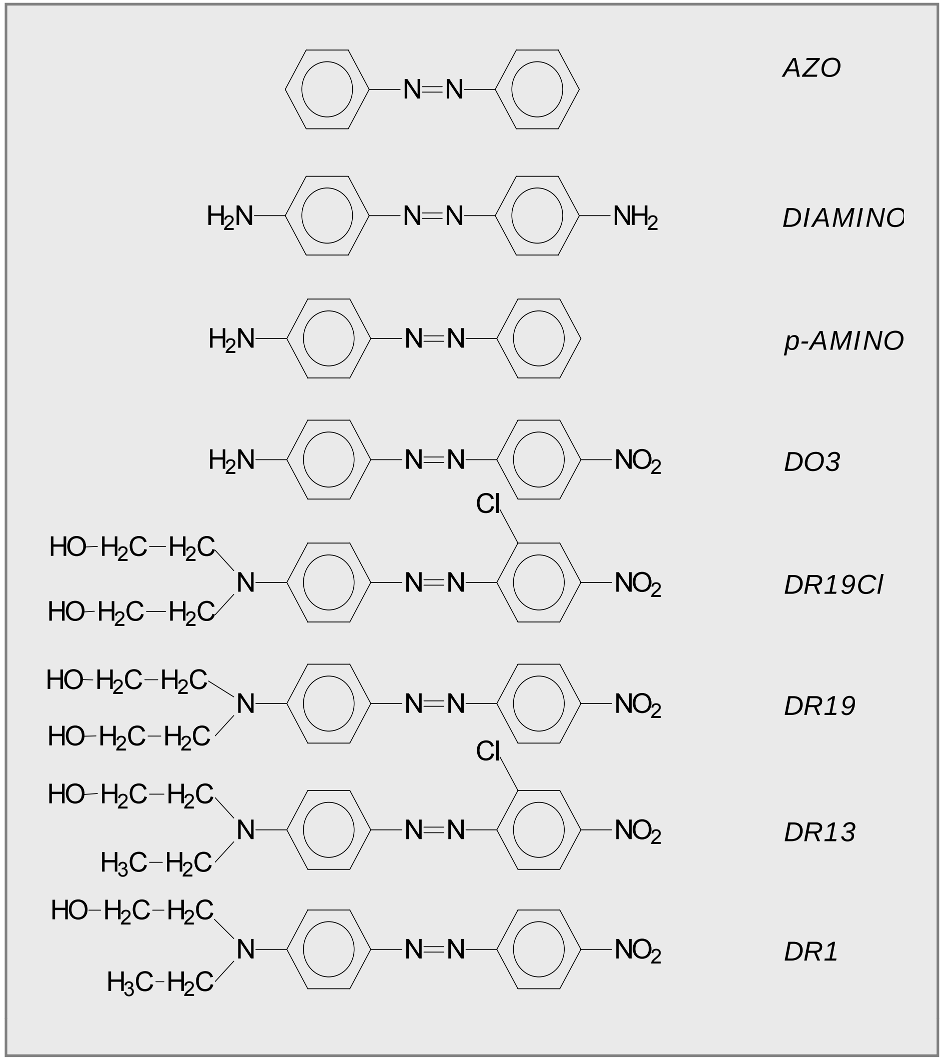


$$T(z) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}}$$

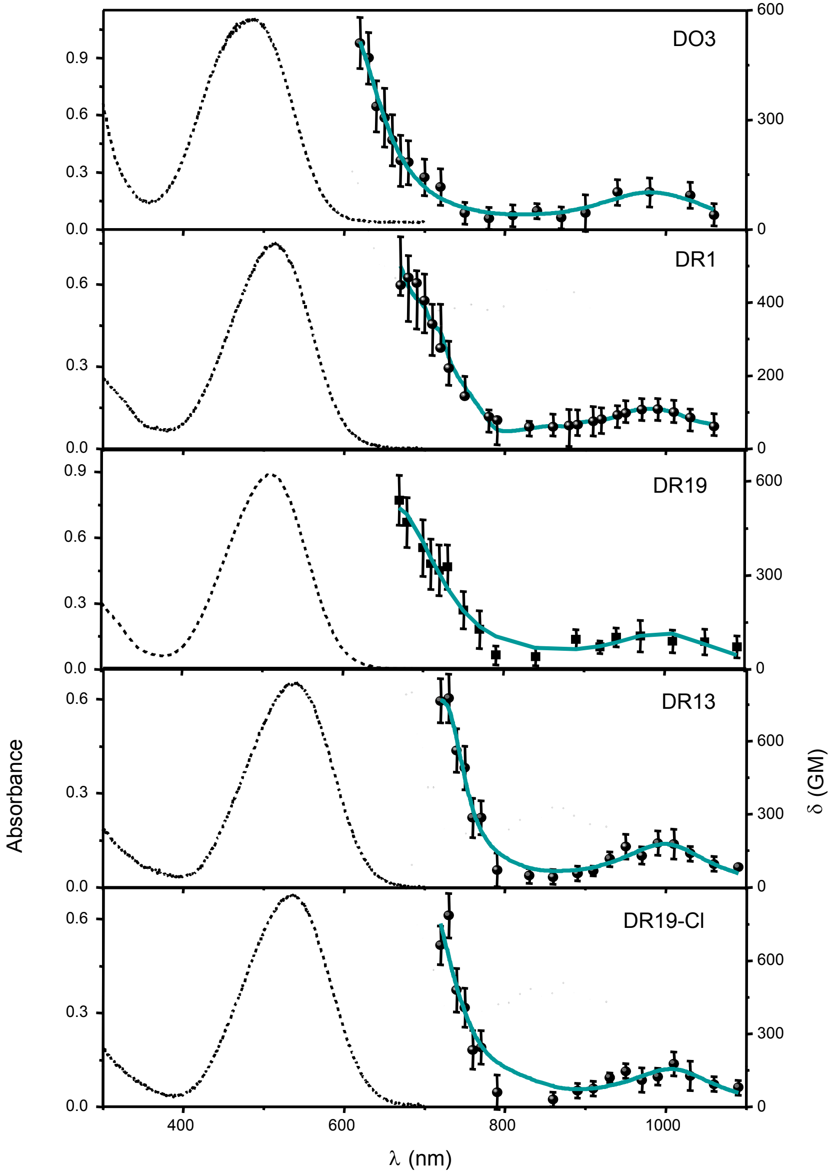
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

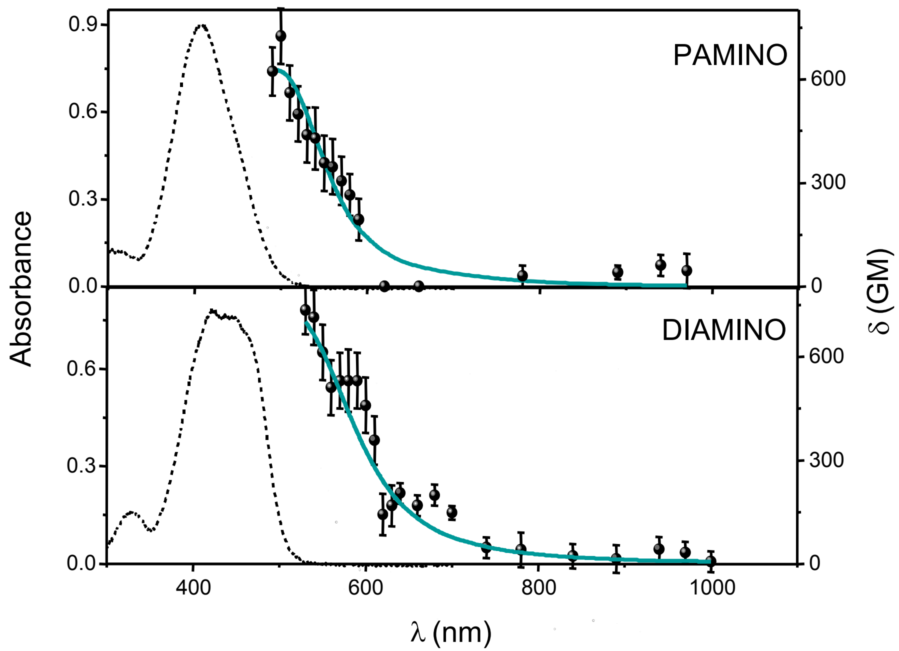
Azoaromatic samples



Psuedostilbenos

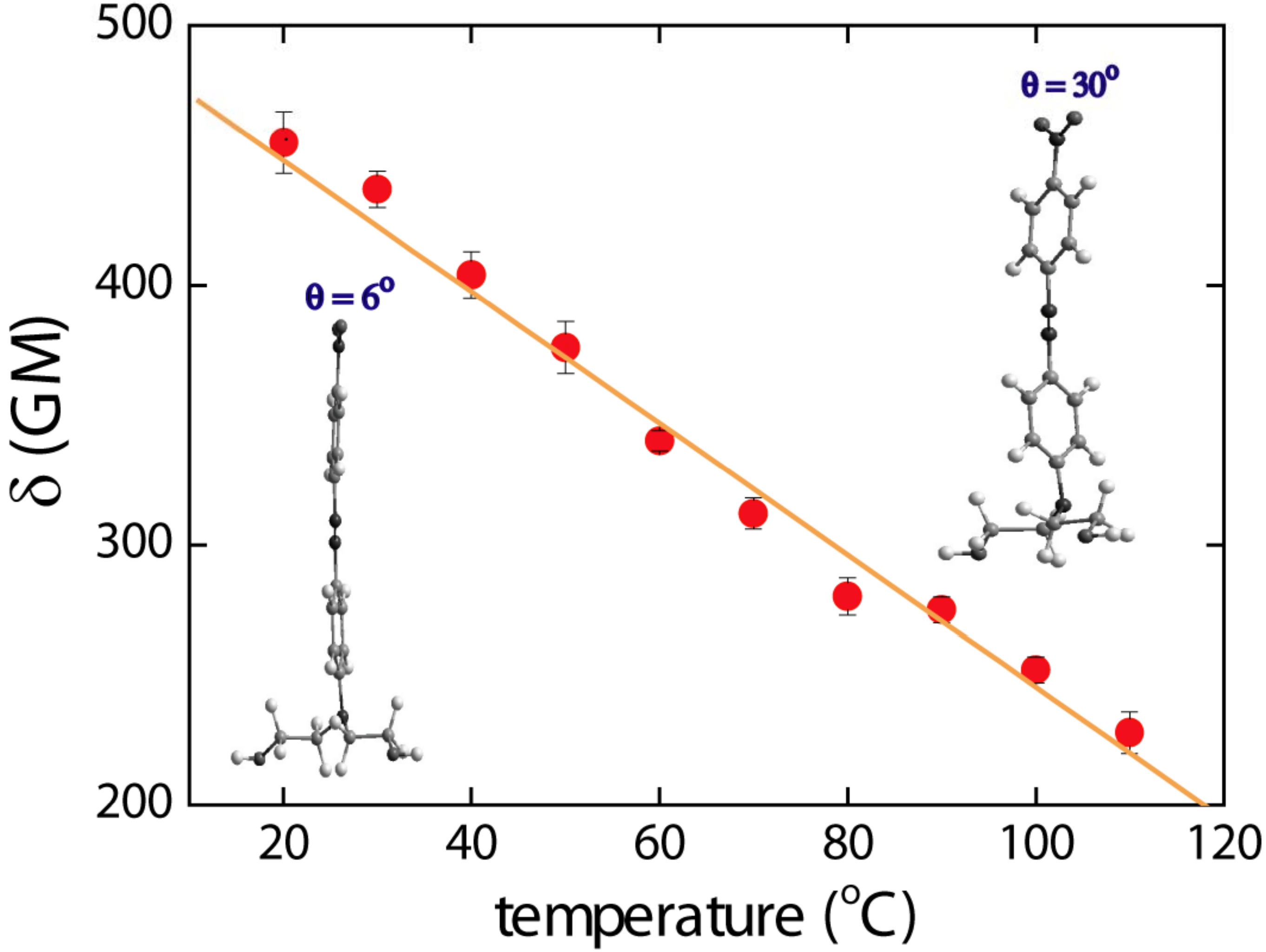


Aminoazobenzenos



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

Planarity of the π-bridge

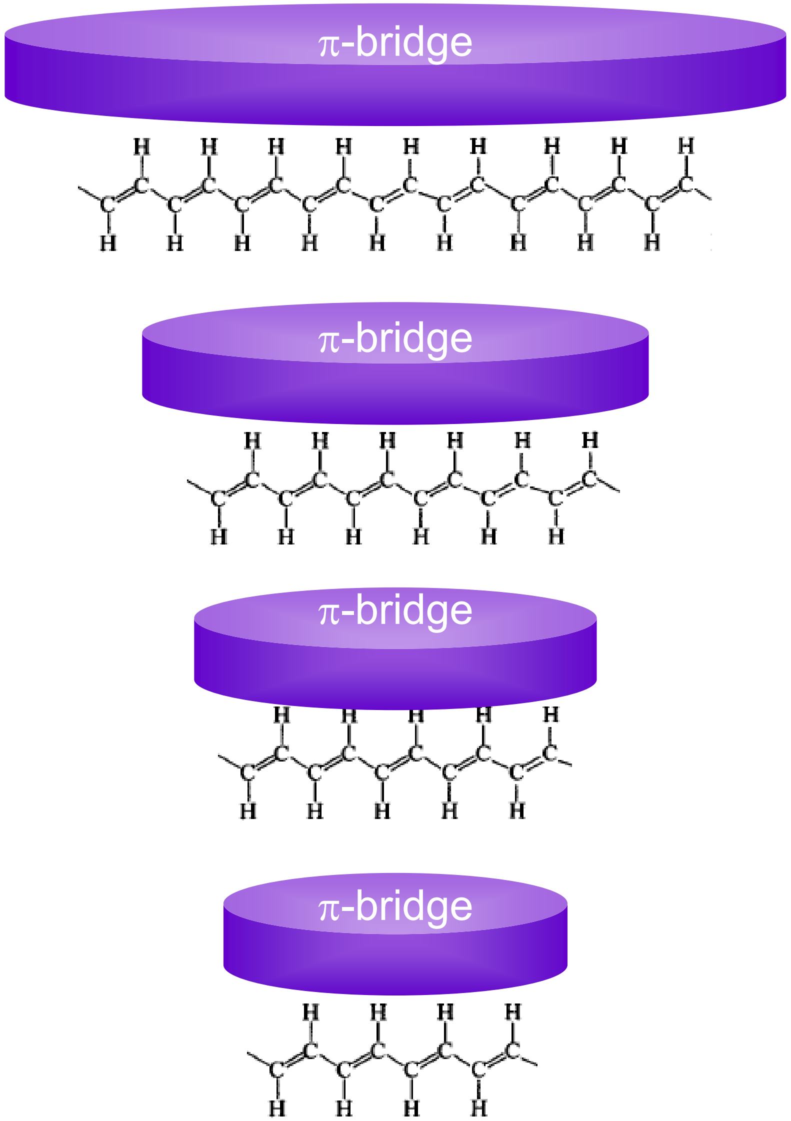


Thermally induced torsion in the molecular structure

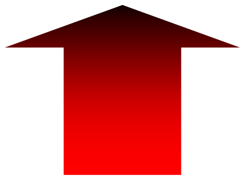
Molecular design strategy

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

Increasing the conjugation

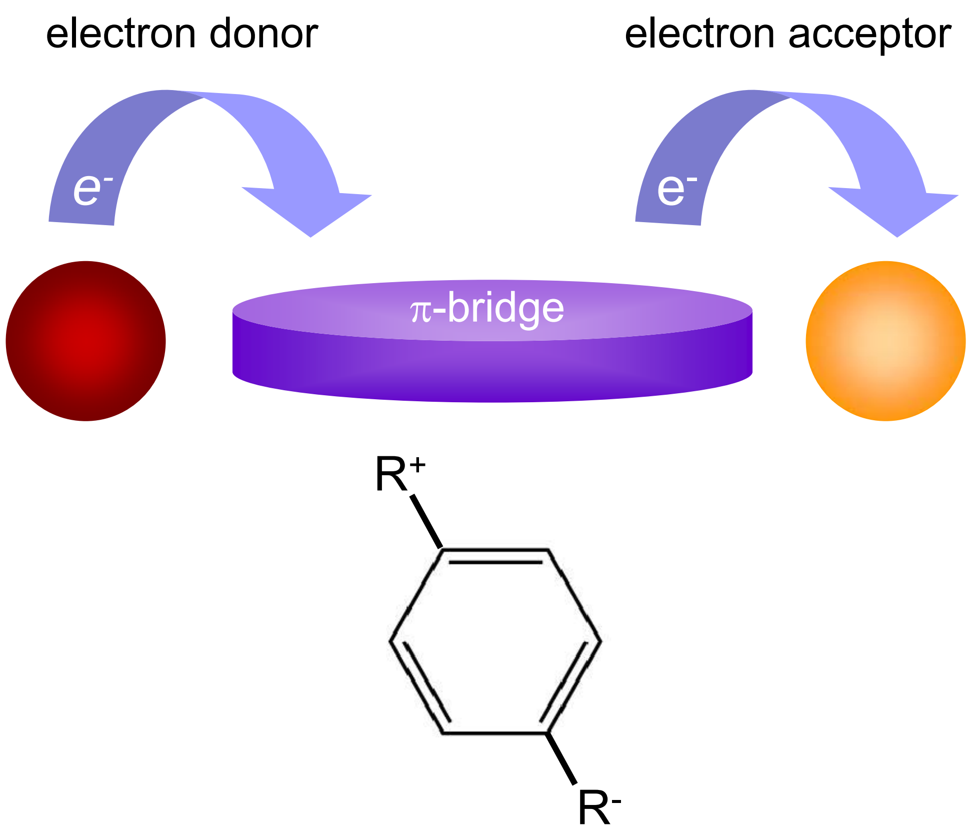


Increase in the optical nonlinearity



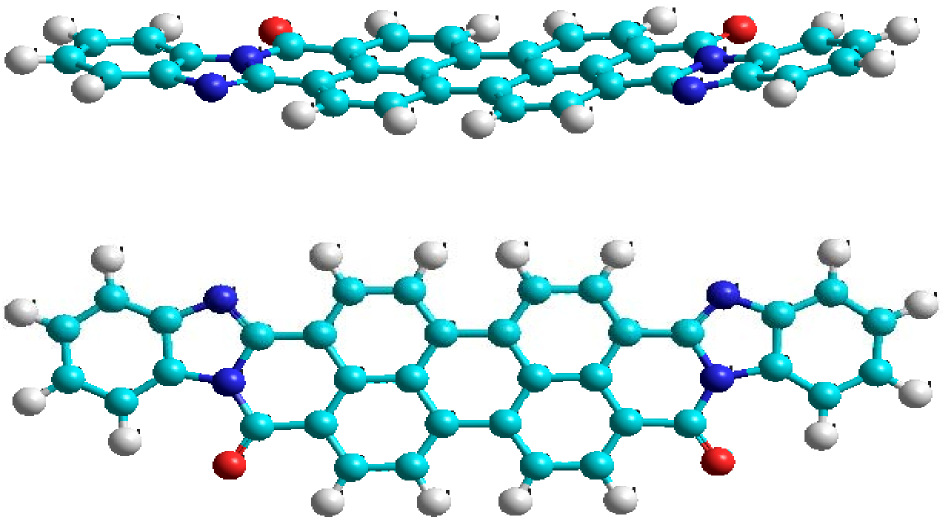
Increasing the π-conjugation

Donor and acceptor groups



Incorporating electron donor and acceptor groups in a predictable way leads to an enhancement of the optical nonlinearity

Planarity of the π-bridge



Perylene compounds are very planar molecules, which explains its high optical nonlinearities

Class 3

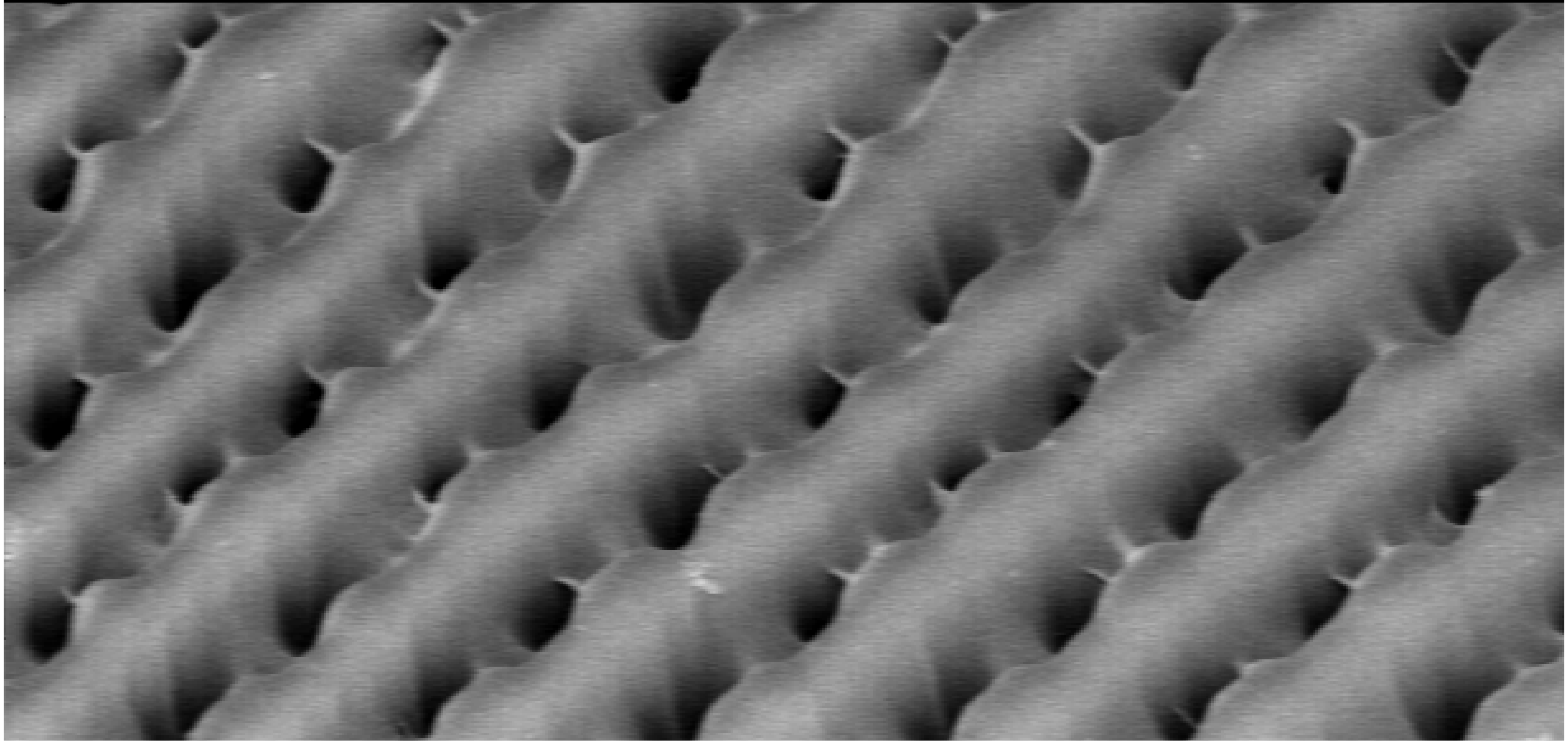
Applications of nonlinear optics

Prof. Cleber R. Mendonca

Fotônica

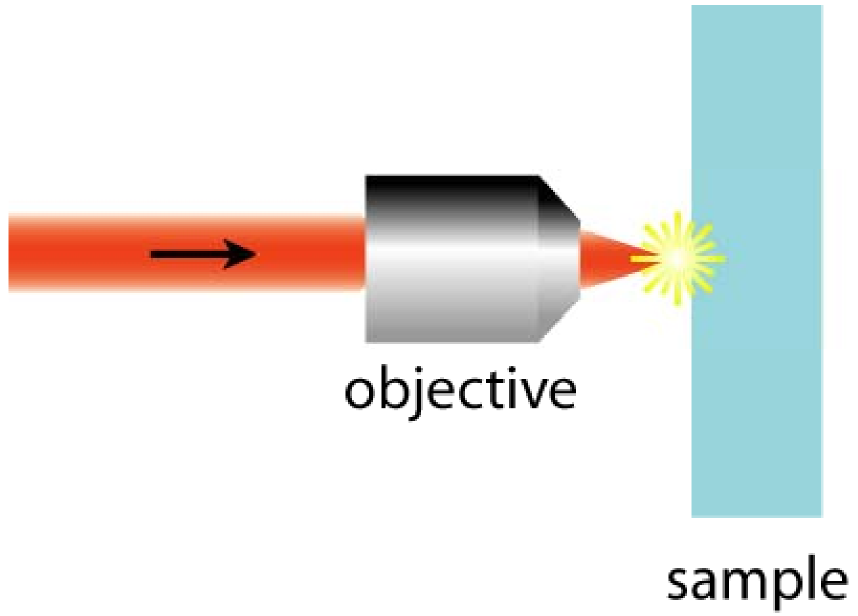
http://www.fotonica.ifsc.usp.br

Sculpturing with light: micro/nanofabrication using ultrashort pulses

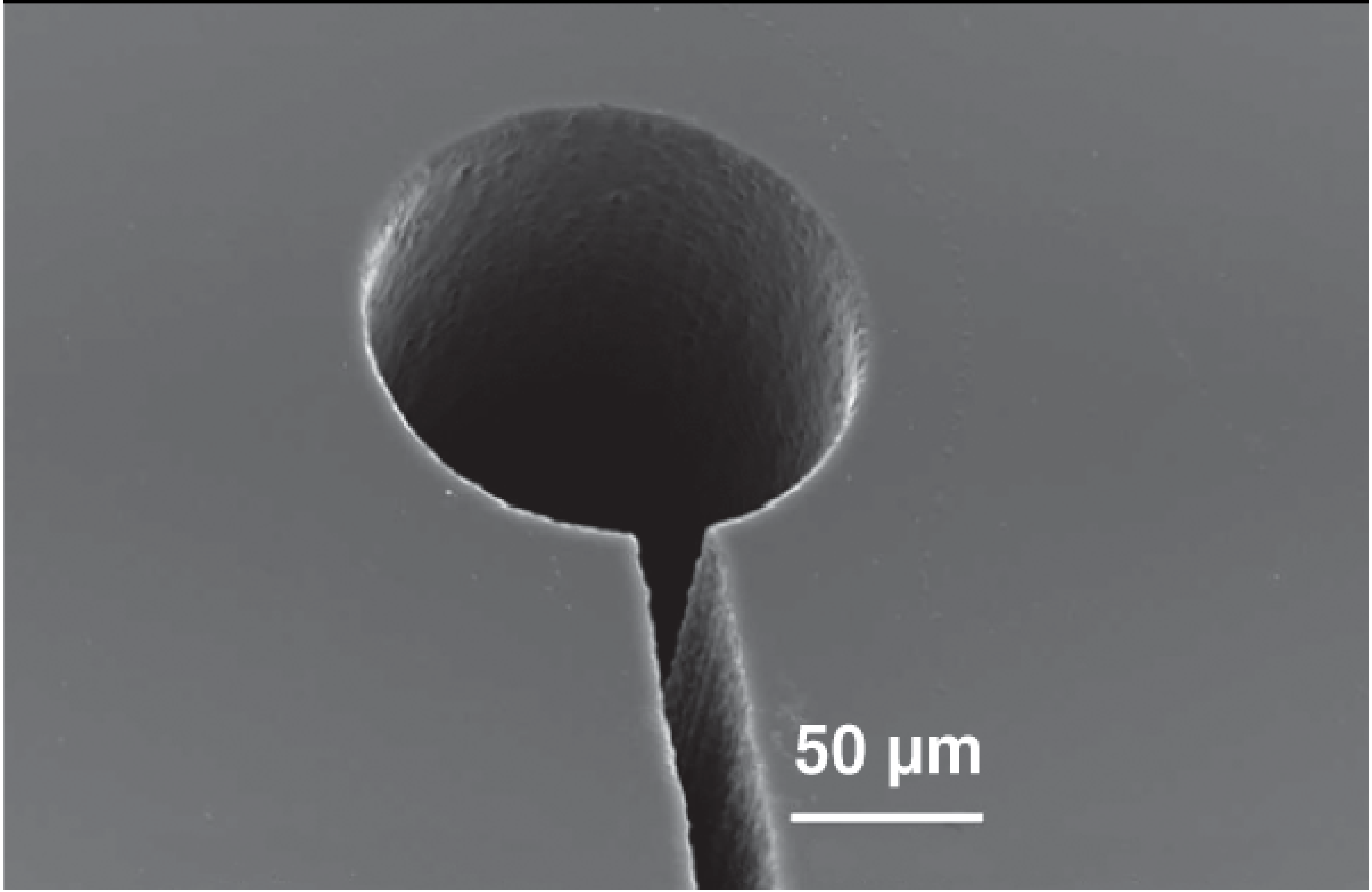


laser microfabrication

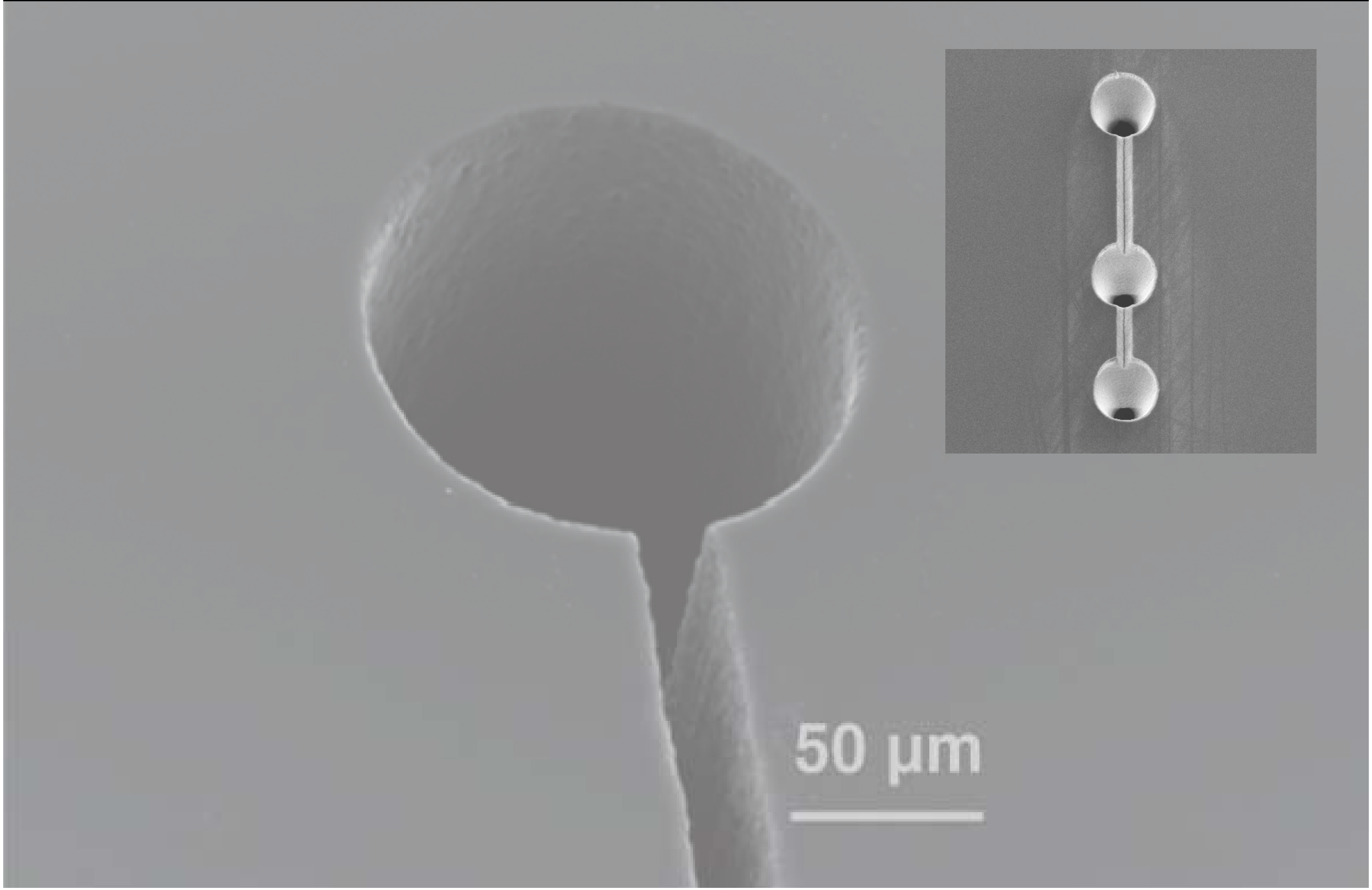
focus laser beam on material’s surface



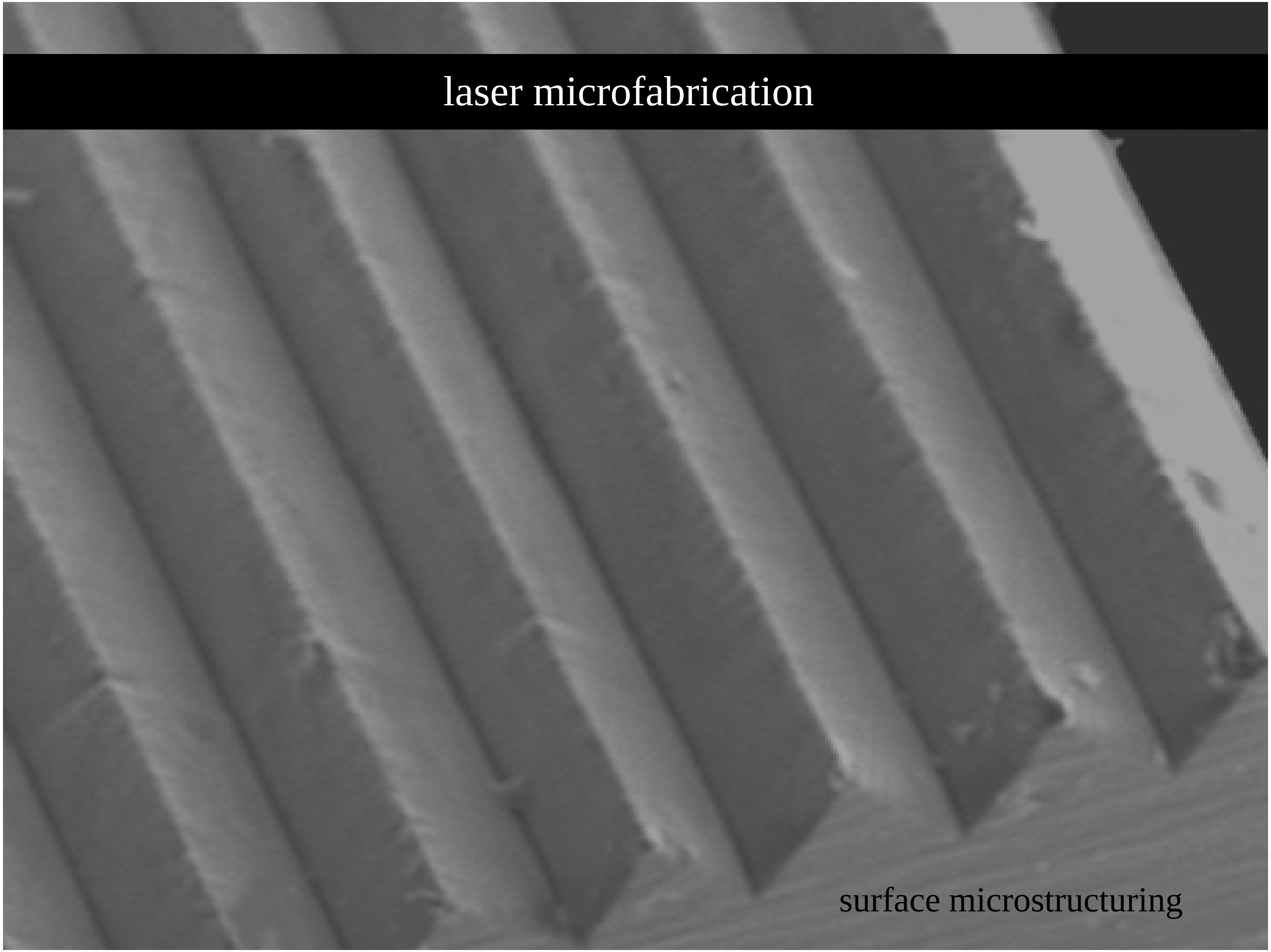
laser microfabrication



laser microfabrication



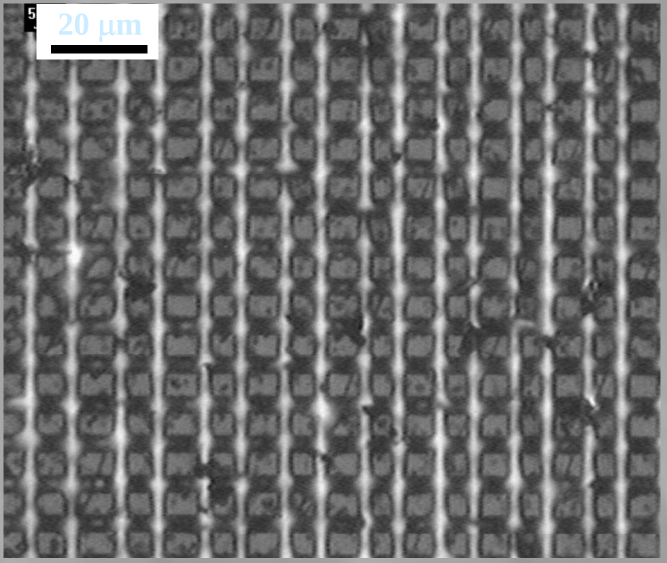
laser microfabrication

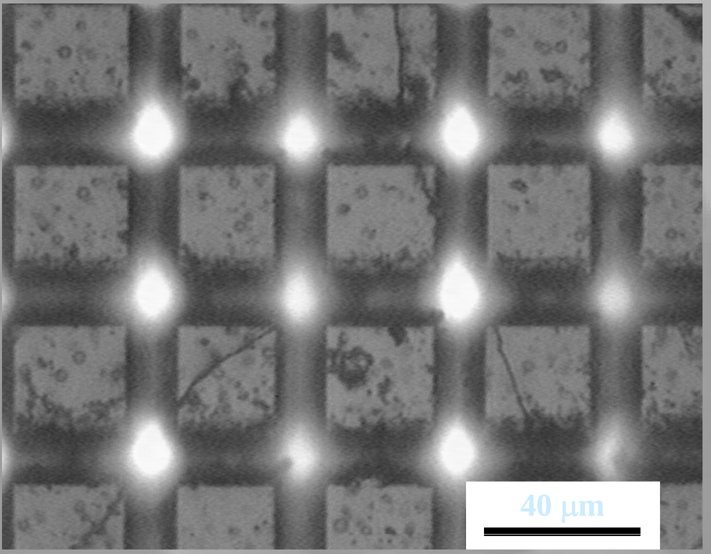


surface microstructuring

laser microfabrication

examples of fabricated surfaces





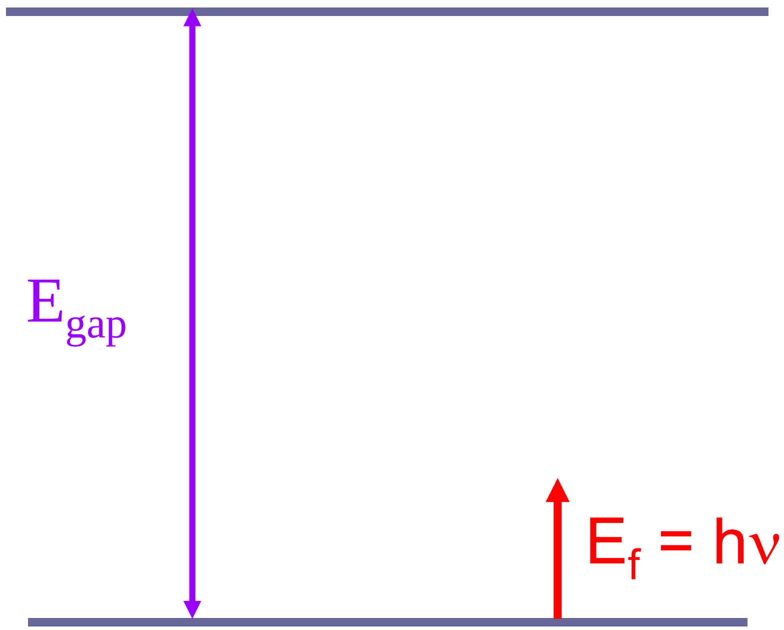
fs-laser microfabrication

photon energy < bandgap

nonlinear interaction

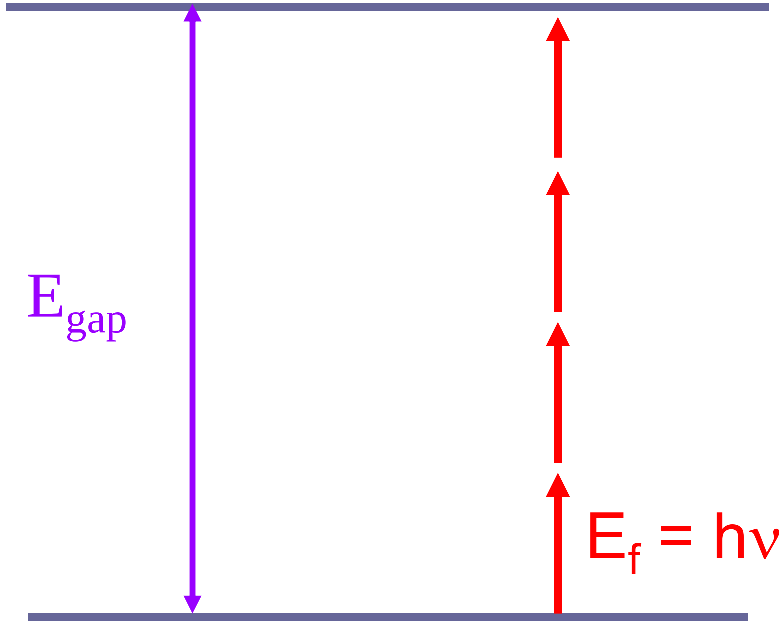
fs-laser microfabrication

nonlinear interaction



fs-laser microfabrication

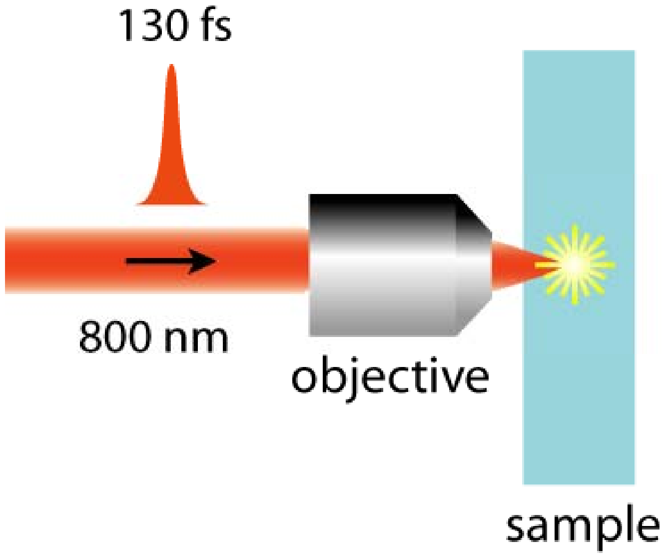
nonlinear interaction



multiphoton absorption

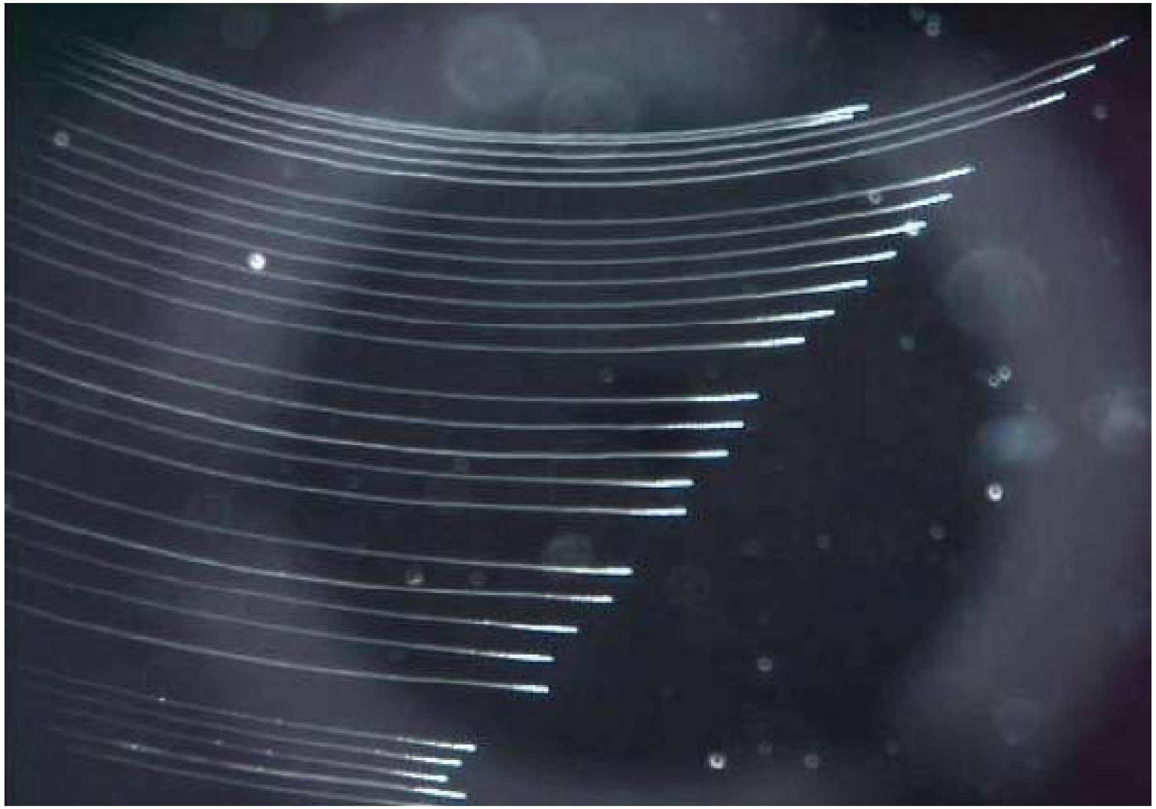
fs-laser microfabrication

focus laser beam inside material



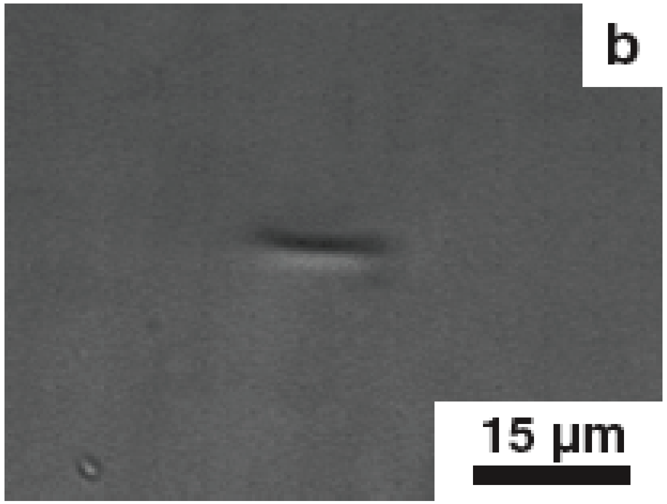
fs-laser microfabrication

curved waveguides inside glass



fs-laser microfabrication

3D waveguides in PMMA



cross-section view

Applied Surface Science, 254, 1135–1139 (2007)

Optics Express, 16, 200-205 (2008)

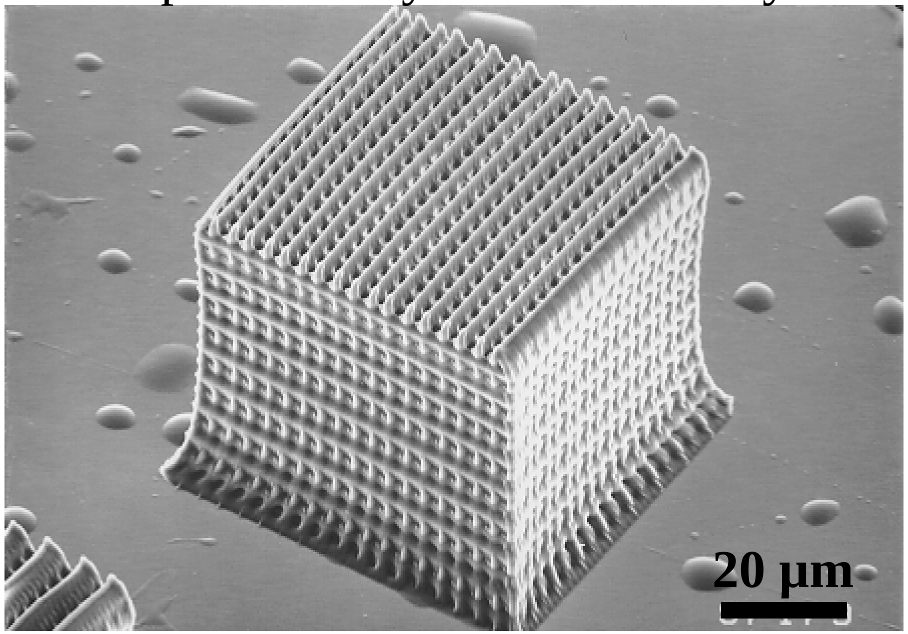
fs-laser microfabrication

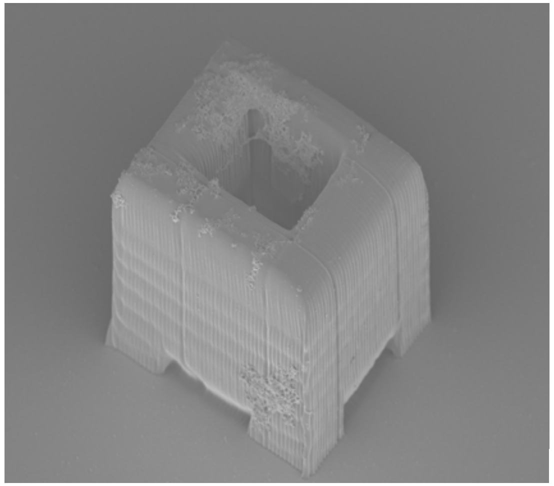
Novel concept:

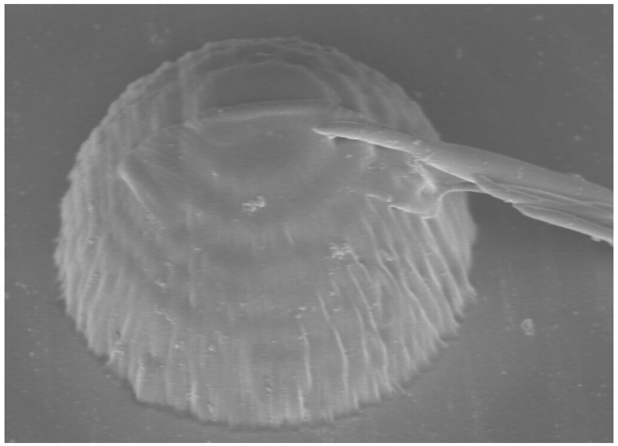
build a microstructure using fs-laser and nonlinear optical processes

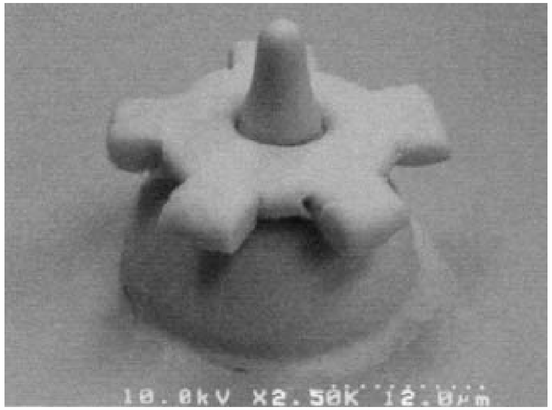
two-photon polymerization

photonic crystal – J. W. Perry









two-photon polymerization

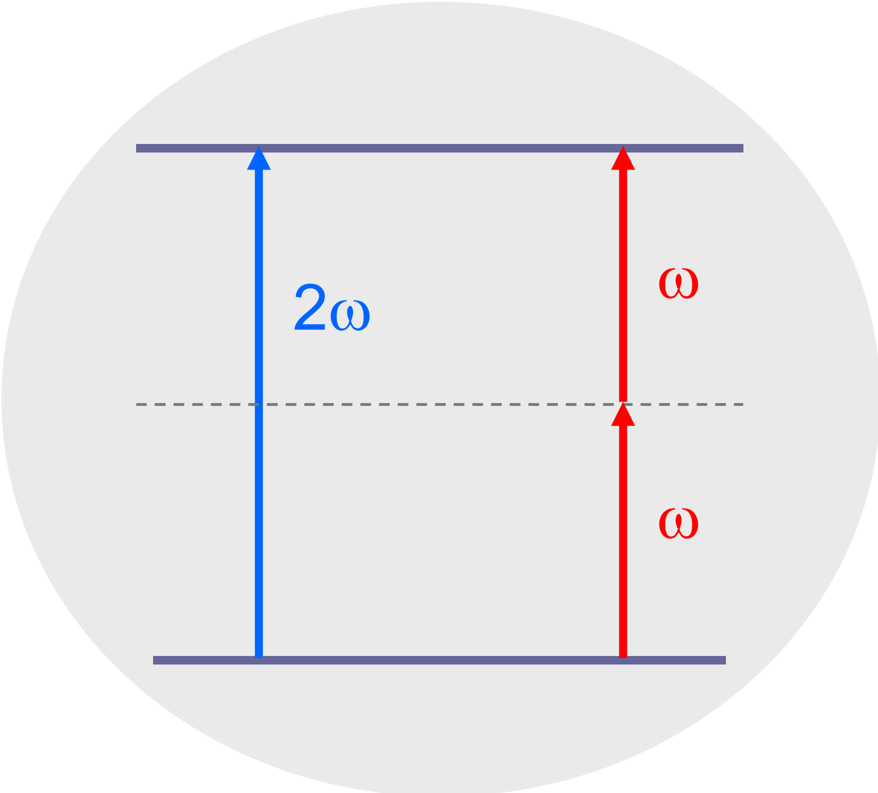
applications

- micromechanics
- waveguides
- microfluidics
- biology
- optical devices

Outline

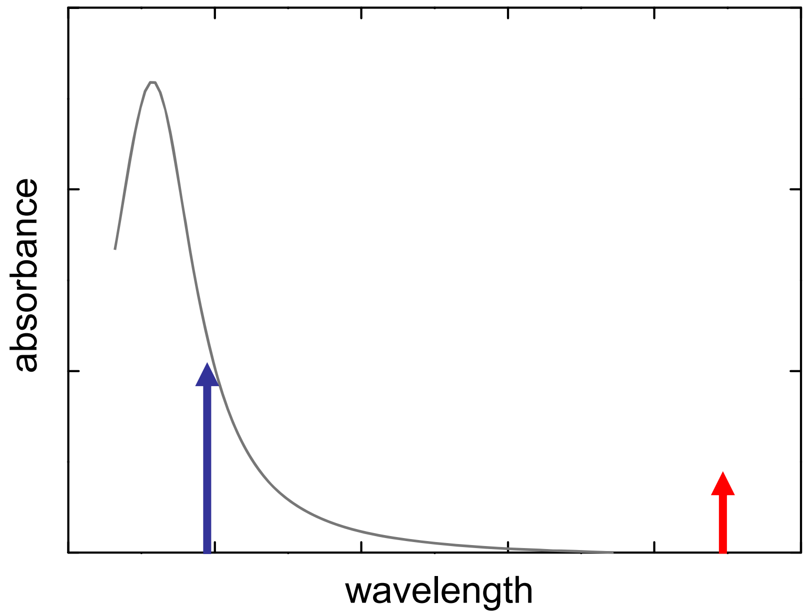
- two-photon polymerization microfabrication
- microstructures containing MEH-PPV
- waveguiding the MEH-PPV emission
- other studies
- summary

Two-photon absorption



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

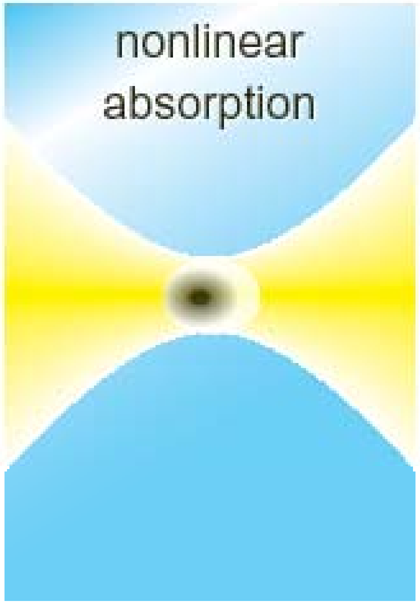
Third order processes $\chi^{(3)}$



Two-photon absorption

Nonlinear interaction provides spatial confinement of the excitation

fs-microfabrication



$$\alpha = \alpha_0$$

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

Two-photon absorption

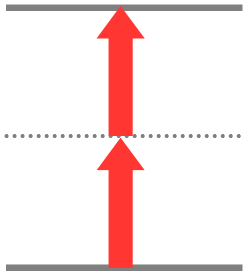
spatial confinement of excitation

Two-photon polymerization

Monomer + Photoinitiator → *Polymer*

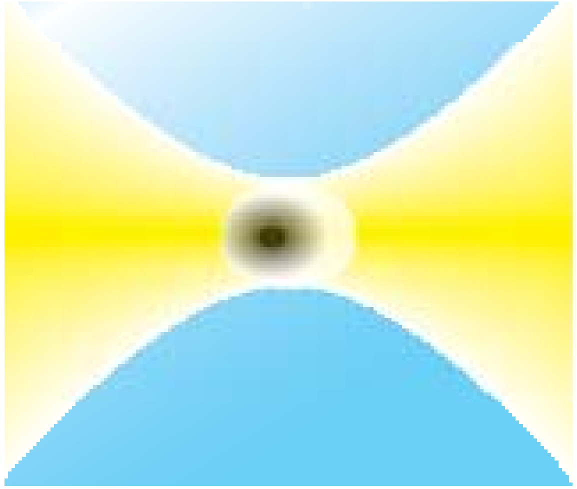
light

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



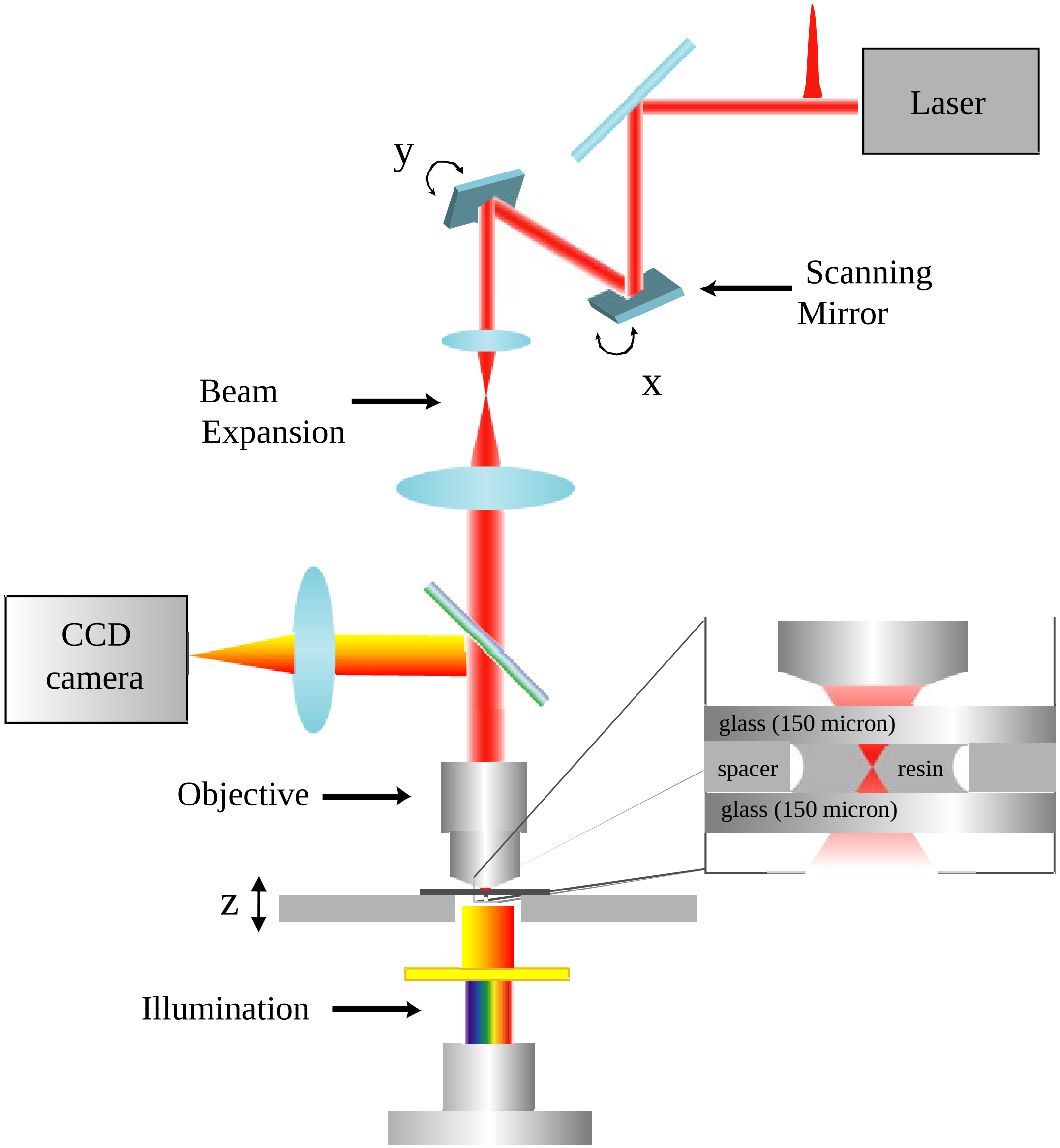
$$R_{2PA} \propto I^2$$

The polymerization is confined to the focal volume.



High spatial resolution

Two-photon polymerization setup



Ti:sapphire laser oscillator

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

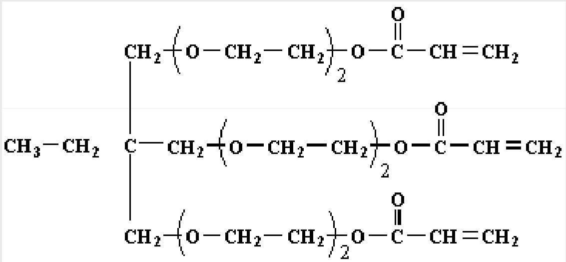
Objective

40 x
0.65 NA

Resin preparation

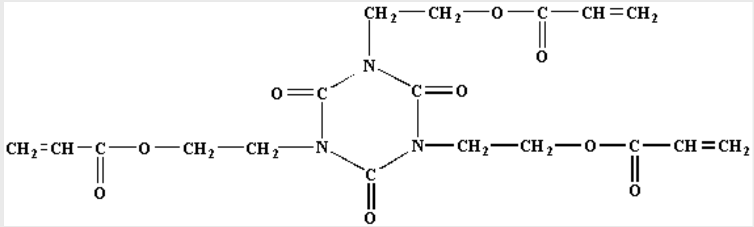
Monomers

Monomer A



reduces the shrinkage upon polymerization

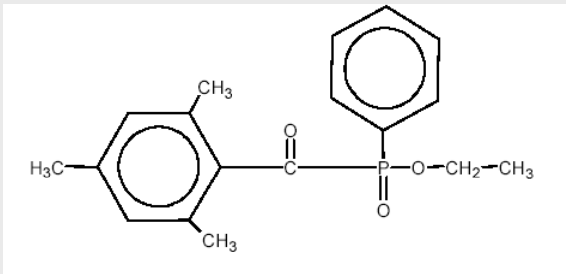
Monomer B



gives hardness to the polymeric structure

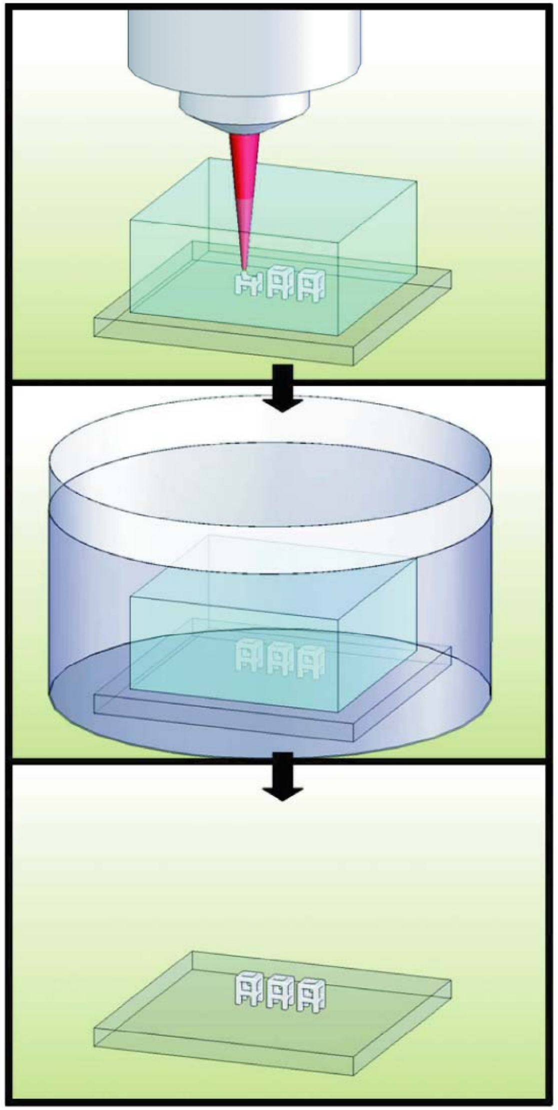
Photoinitiator

Lucirin TPO-L



Appl. Phys. A, 90, 633–636 (2008)

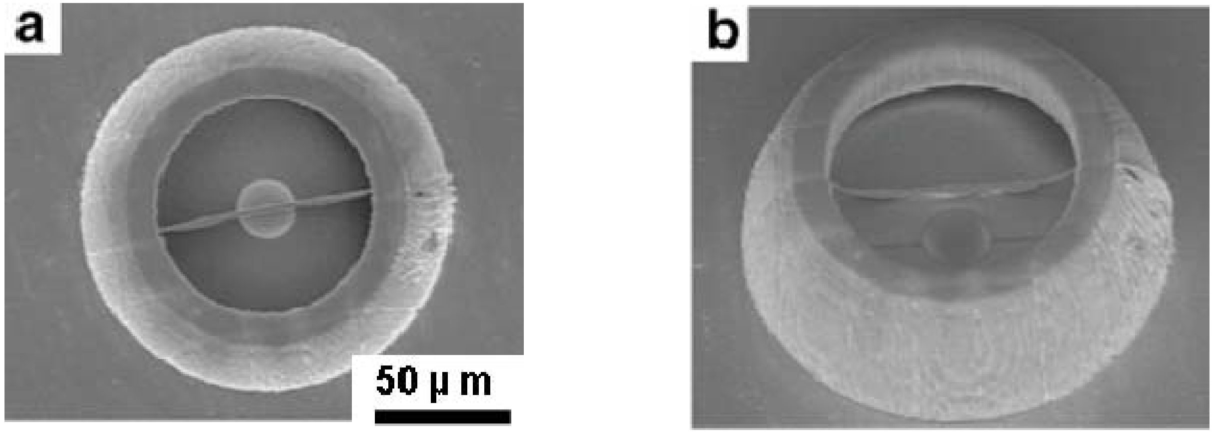
Two-photon polymerization

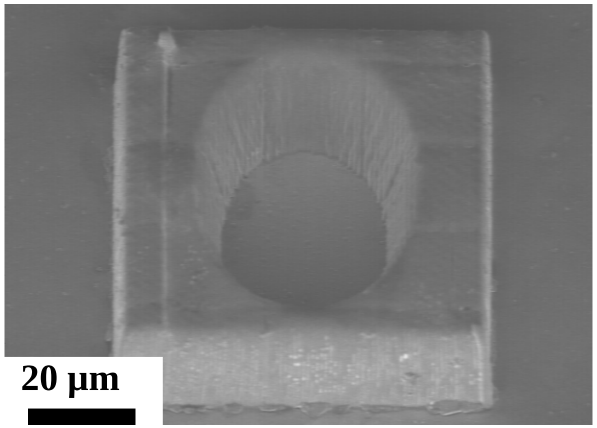


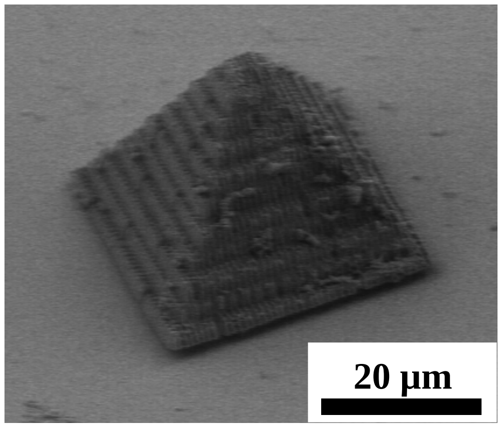
After the fabrication, the sample is immersed in ethanol to wash away any unsolidified resin and then dried

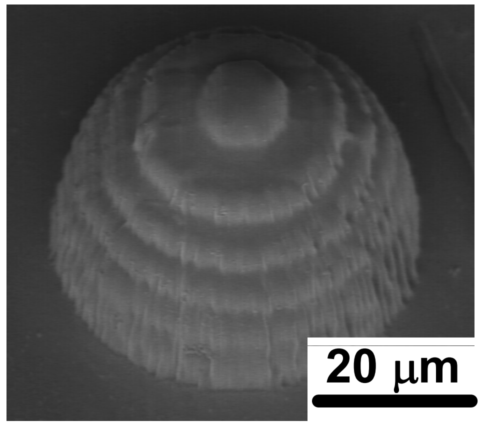
Two-photon polymerization

Microstructures fabricated by two-photon polymerization

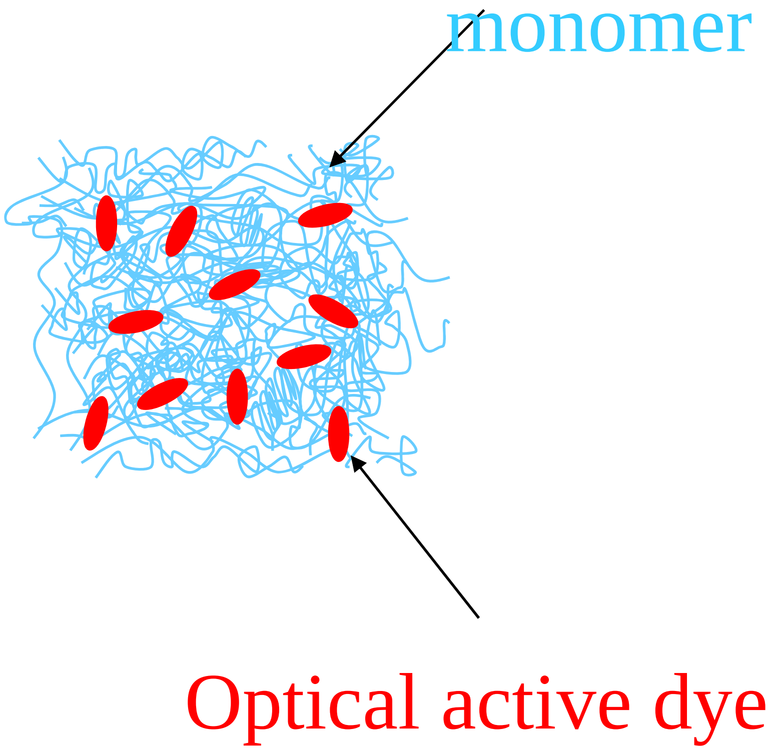


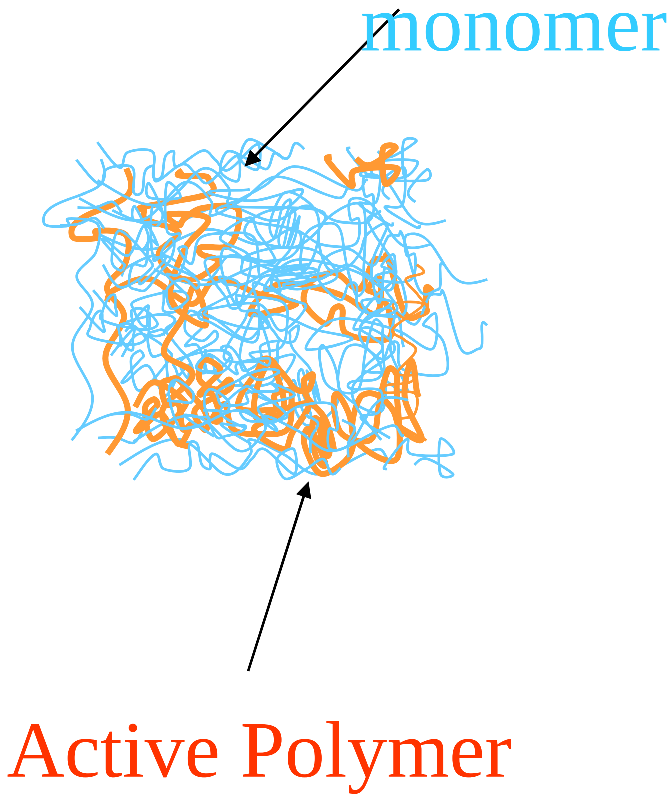






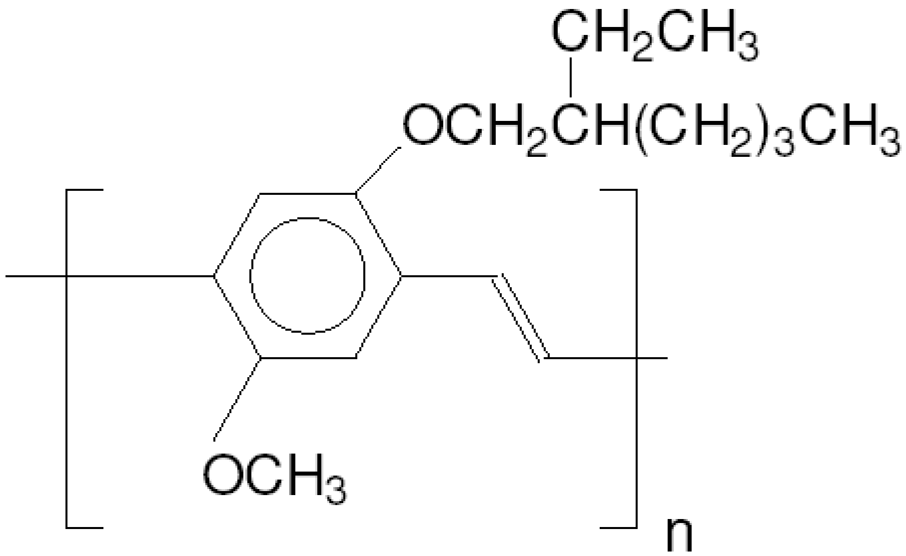
Microstructures containing active compounds





Microstructures containing MEH-PPV

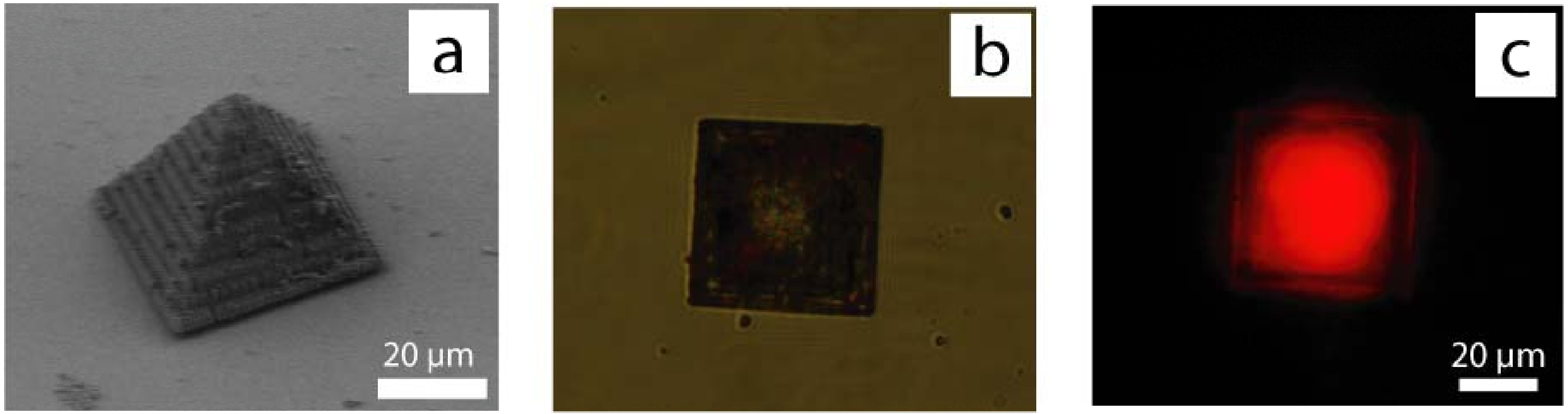
MEH-PPV



Fluorescence
Electro
Luminescent
Conductive

Microstructures containing MEH-PPV

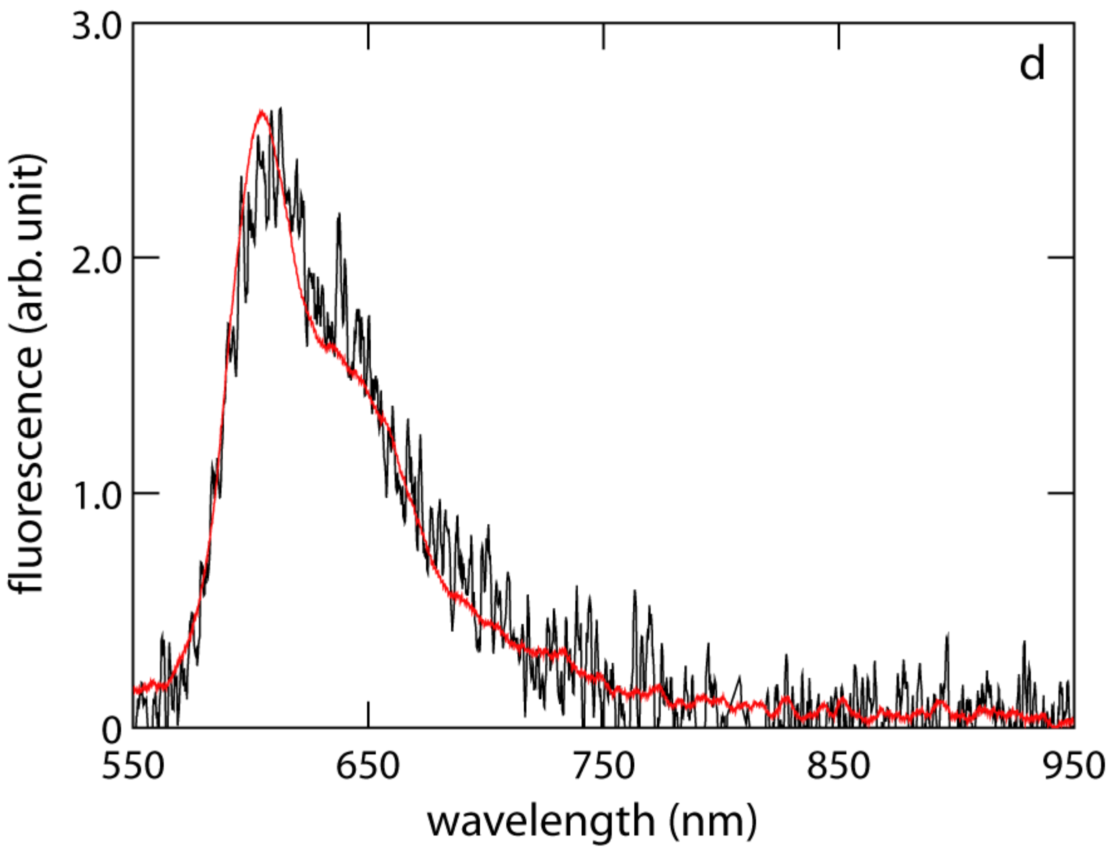
MEH-PPV: up to 1% by weight
laser power 40 mW



a - Scanning electron microscopy

b,c - Fluorescence microscopy of the microstructure with the excitation OFF (b) and ON (c)

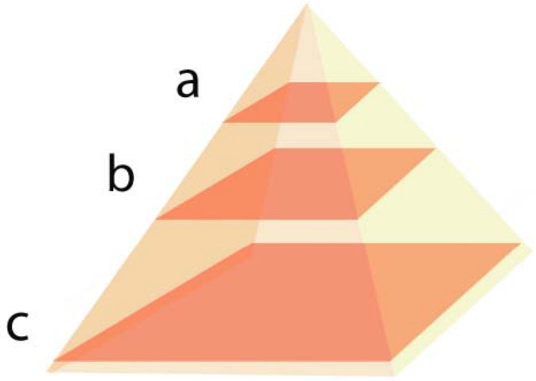
Microstructures containing MEH-PPV

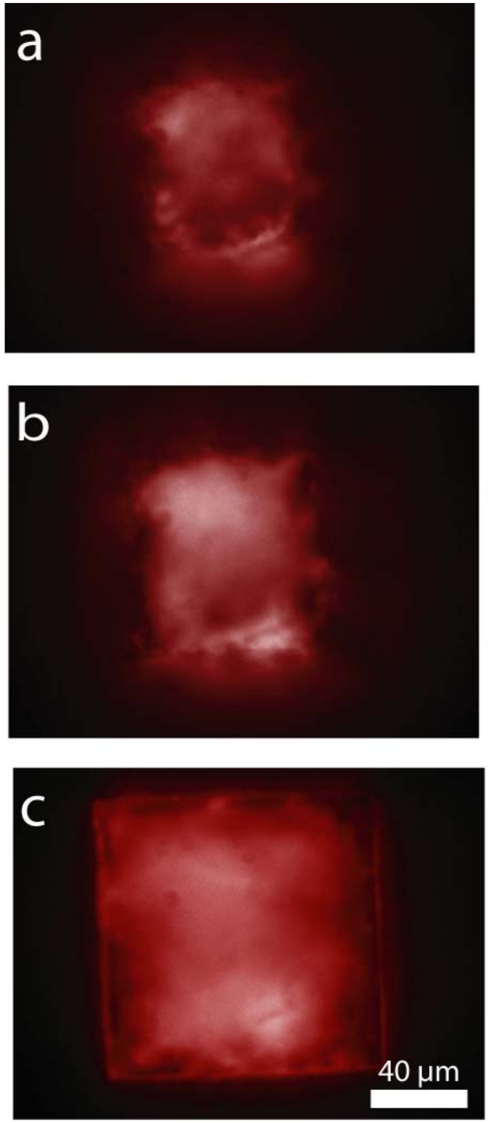


d **-** Emission of the microstructure (black line) and of a film with the same composition (red line)

Microstructures containing MEH-PPV

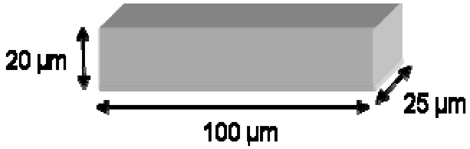
Fluorescent confocal microscopy images in planes separated by 16 μm in the pyramidal microstructure.

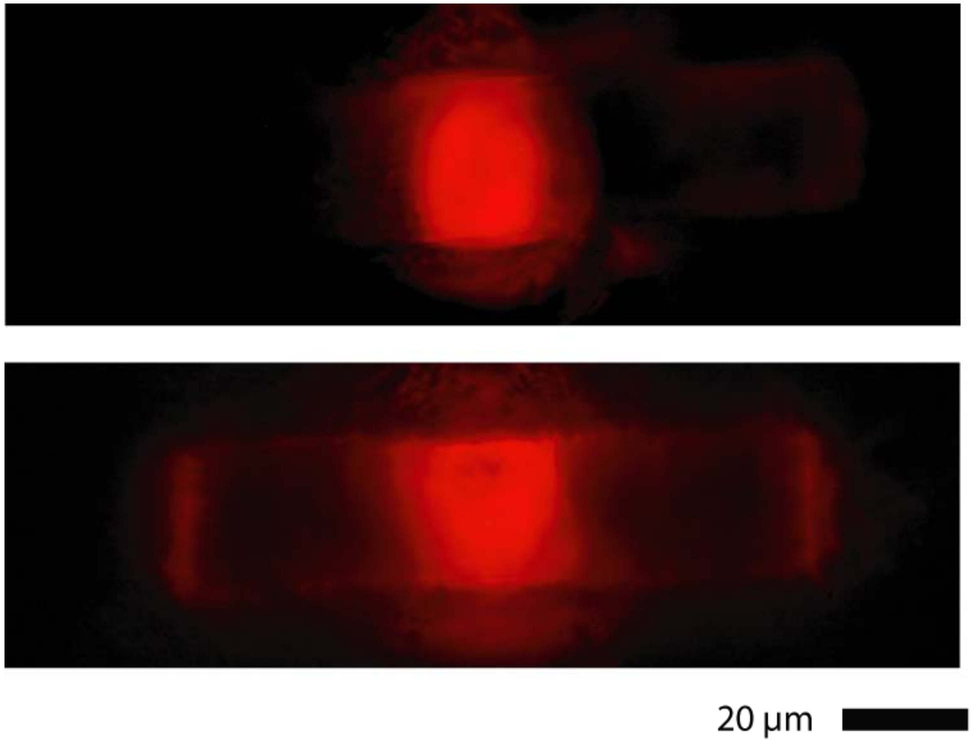


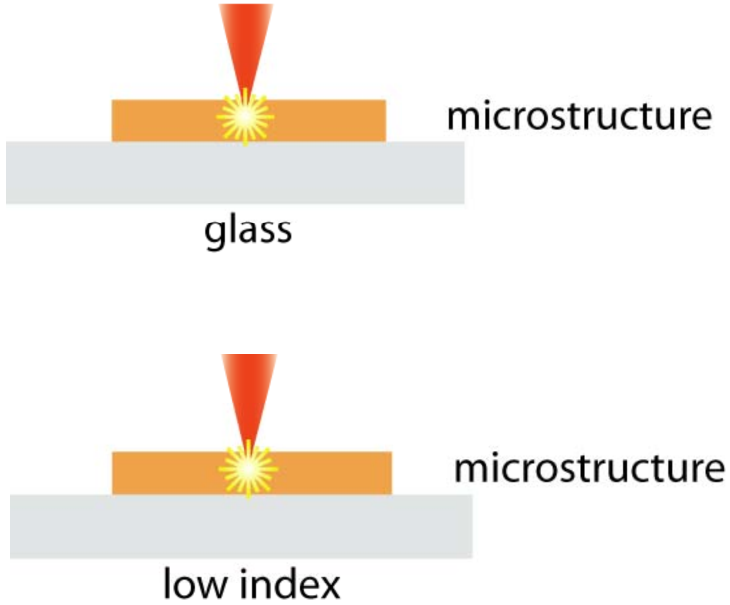


Appl. Phys. Lett 95, 113309 (2009)

Microstructures containing MEH-PPV





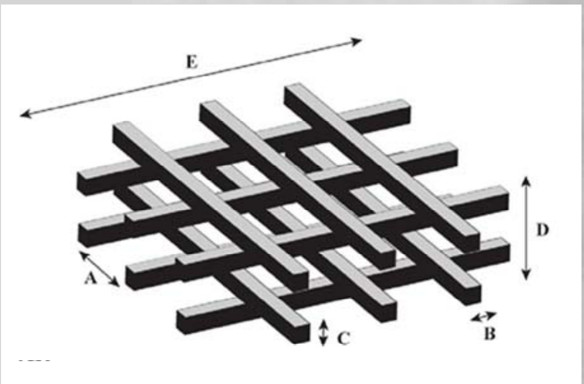


waveguiding of the microstructure fabricated on porous silica substrate (n= 1.185)

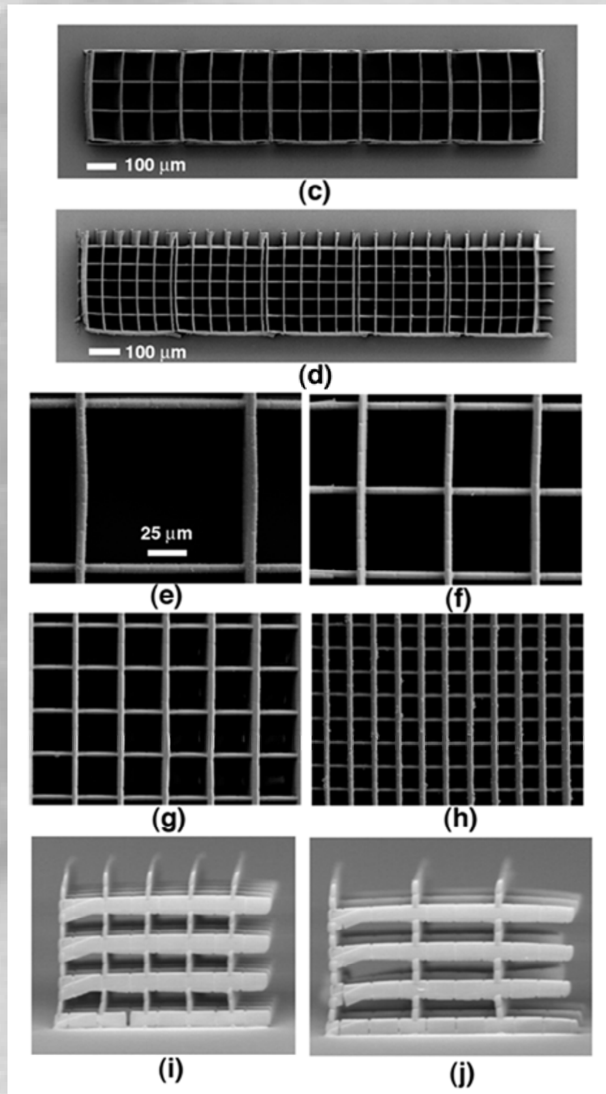
Applications: micro-laser; fluorescent microstructures; conductive microstructures

Other studies

- 3D cell migration studies in micro-scaffolds



SEM of the scaffolds



110 µm pore size

52 µm pore size

Top view

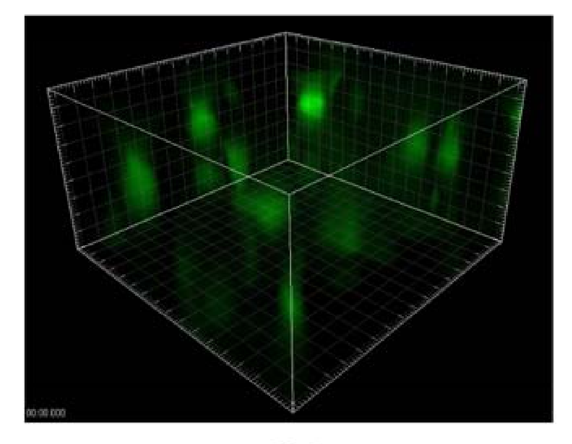
110, 52, 25, 12 µm pore size

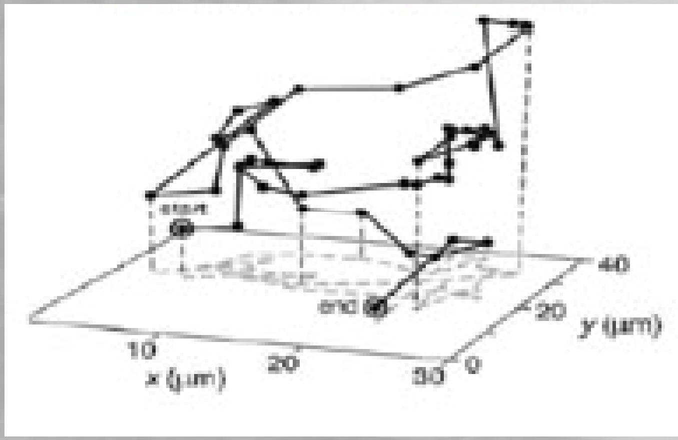
Side view

25, 52 µm pore size

Other studies

- 3D cell migration studies in micro-scaffolds





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