Multi-photon absorption spectrum in organic materials and polymers

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Outline

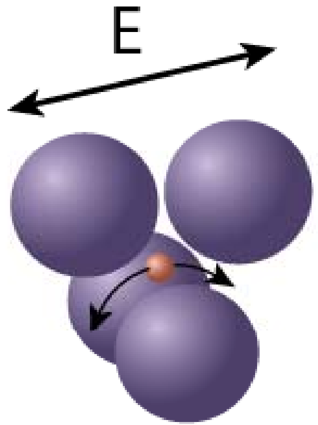
Introduction

Results of 2PA spectrum

- azoaromatic chromophores
- MEH-PPV

Two-photon polymerization microfabrication

Nonlinear optics



anharmonic oscillator

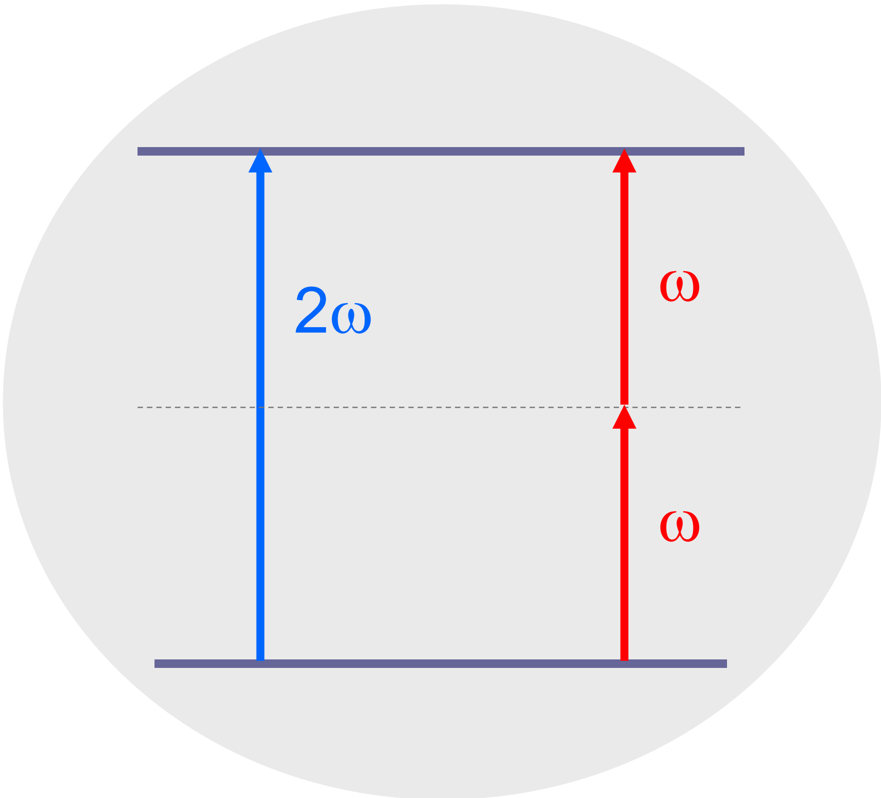
high light intensity

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

nonlinear polarization response

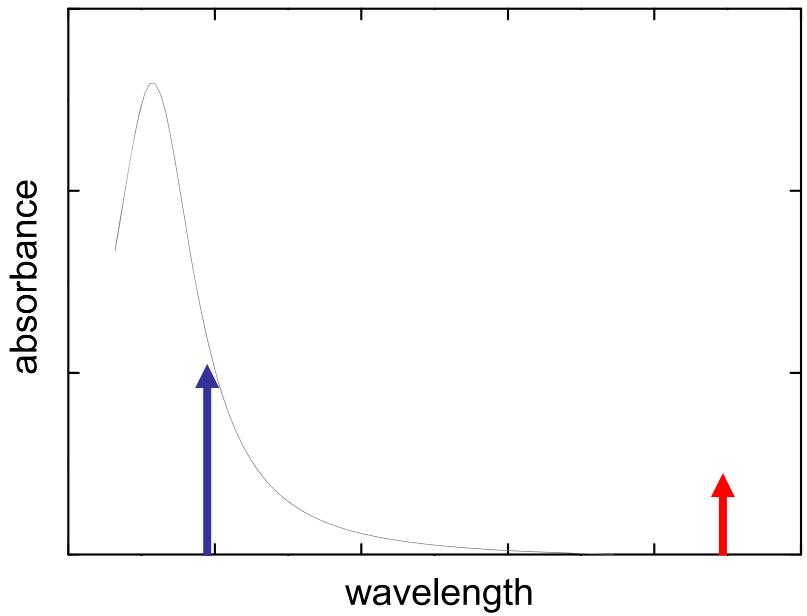
$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$$

two-photon absorption



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

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

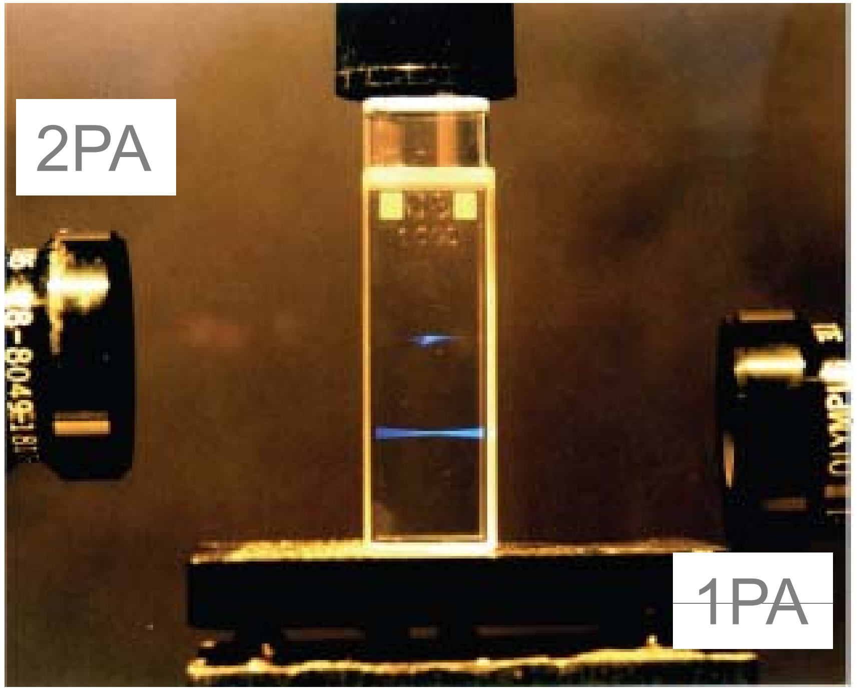


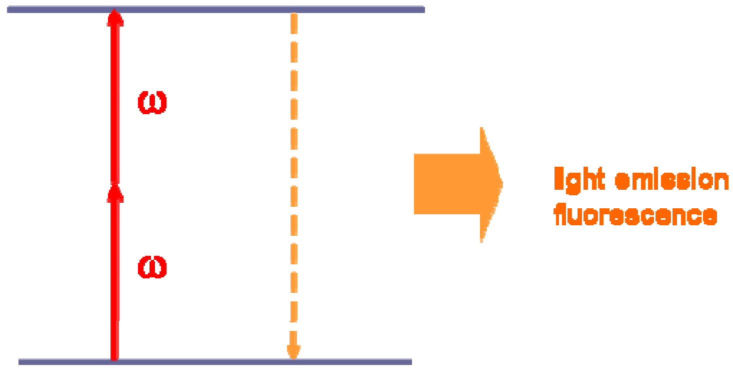
optical limiting

To protect eye and sensors from intense laser pulses

localization of the excitation with 2PA

dilute solution of fluorescent dye





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

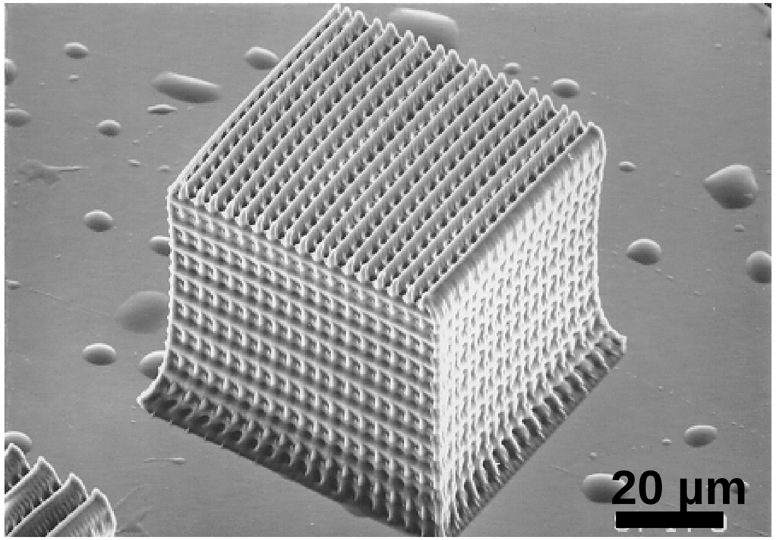
$$I \sim \frac{1}{z^2}$$

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

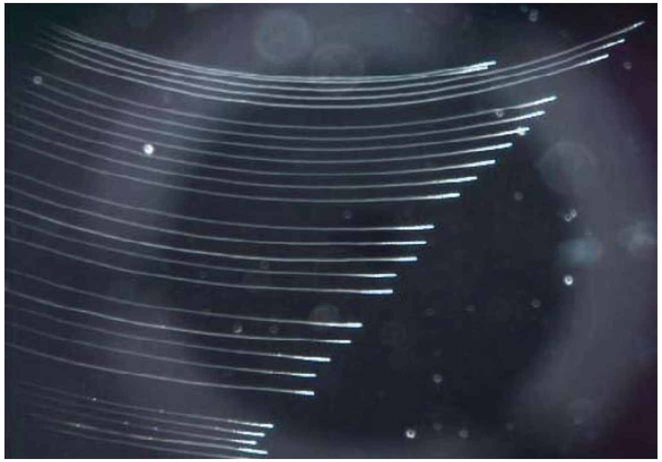
spatial confinement of excitation

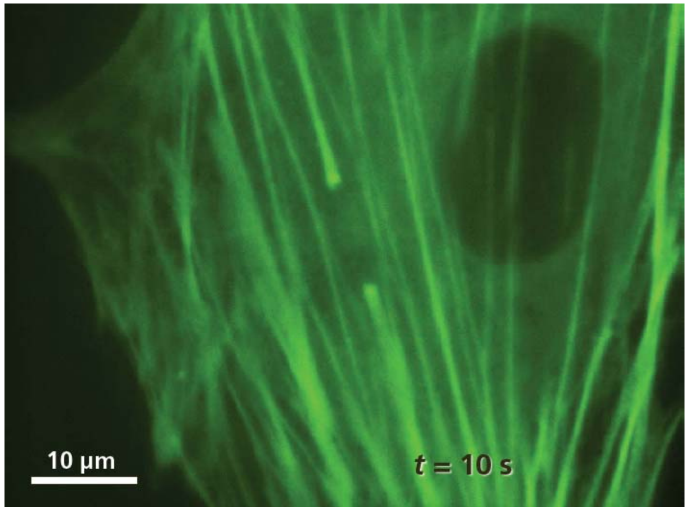
Applications: three-dimensional microfabrication

photonic crystal – J. W. Perry



curved waveguides inside glass

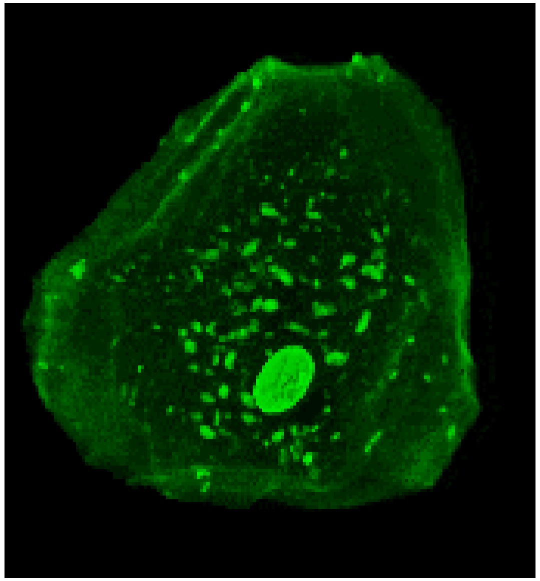




I. Maxwell, E. Mazur – Harvard University

Applications: two-photon fluorescence microscopy

3D image of a cell



Laboratory for Optics and Biosciences
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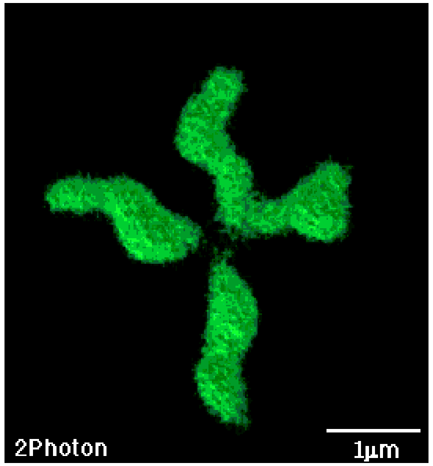


Human chromosome

Optical nonlinearities in organic materials

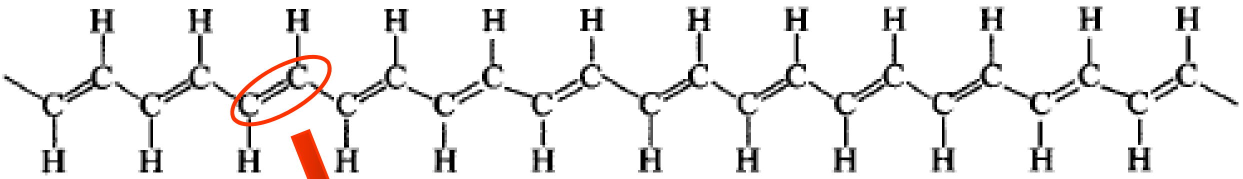
- Developing molecules with high optical nonlinearities that can be used for application

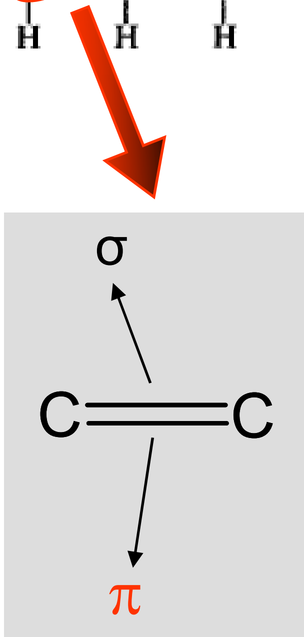
- Exploit optical properties of organics compounds without causing damage by nonlinear absorption

Organic materials

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

- π-conjugated structures

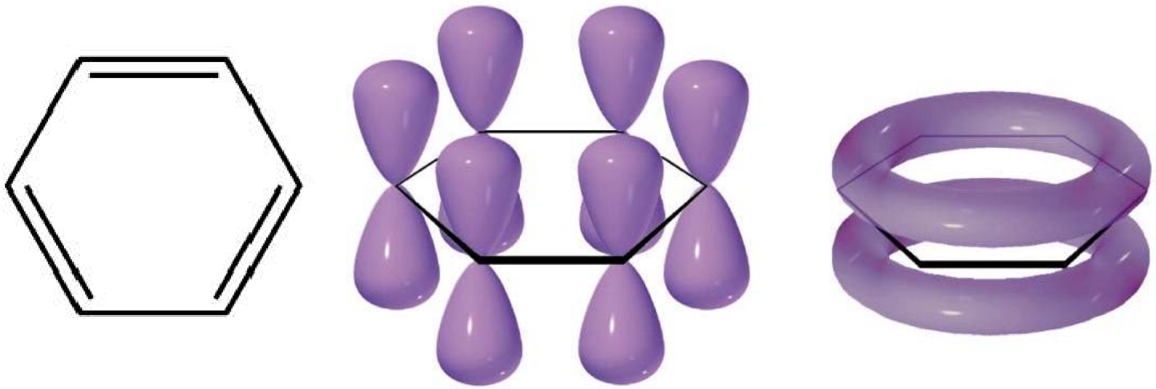




Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation

benzene p-orbitals π delocalization (π-electron cloud)



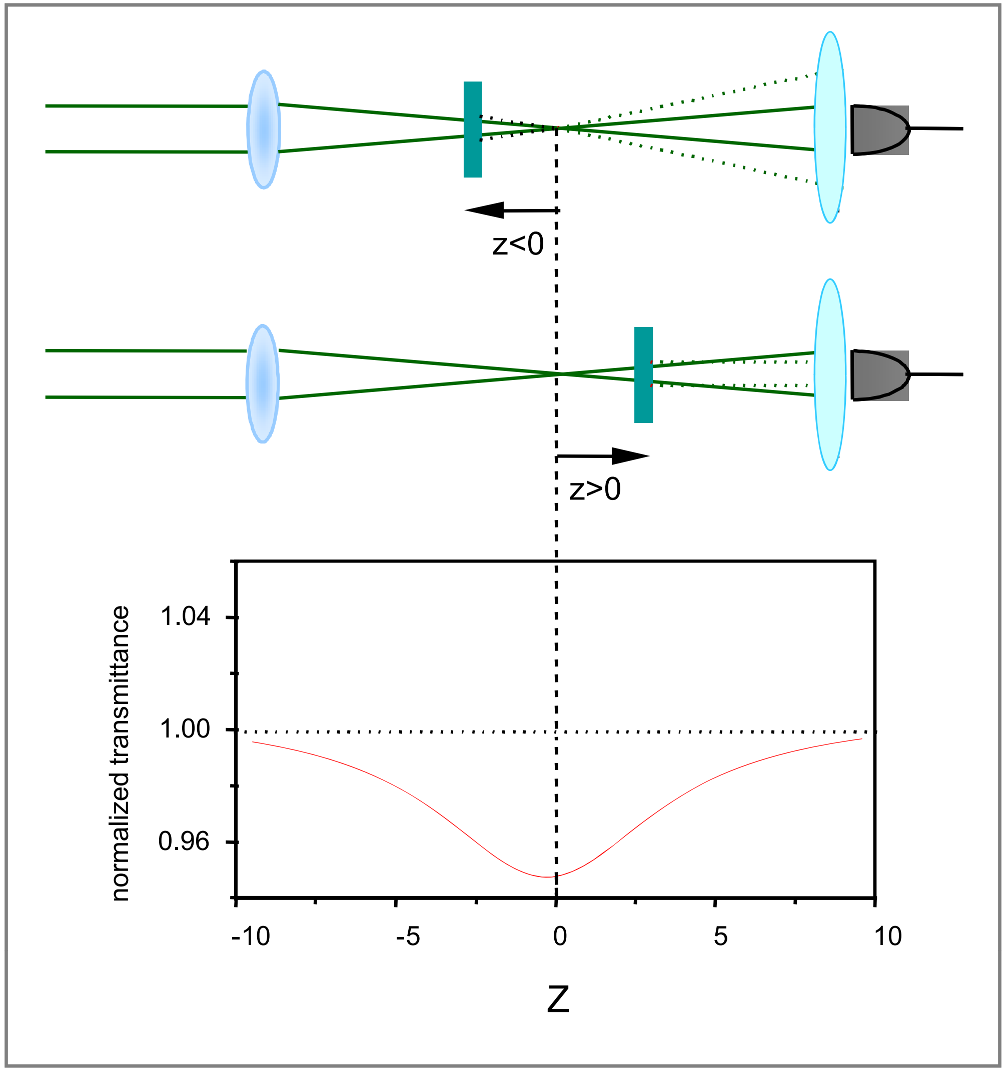
π bond in conjugated system: delocalized electrons

high optical nonlinearities

↑ $\chi^{(3)}$

Z-scan (two-photon absorption)

Summary



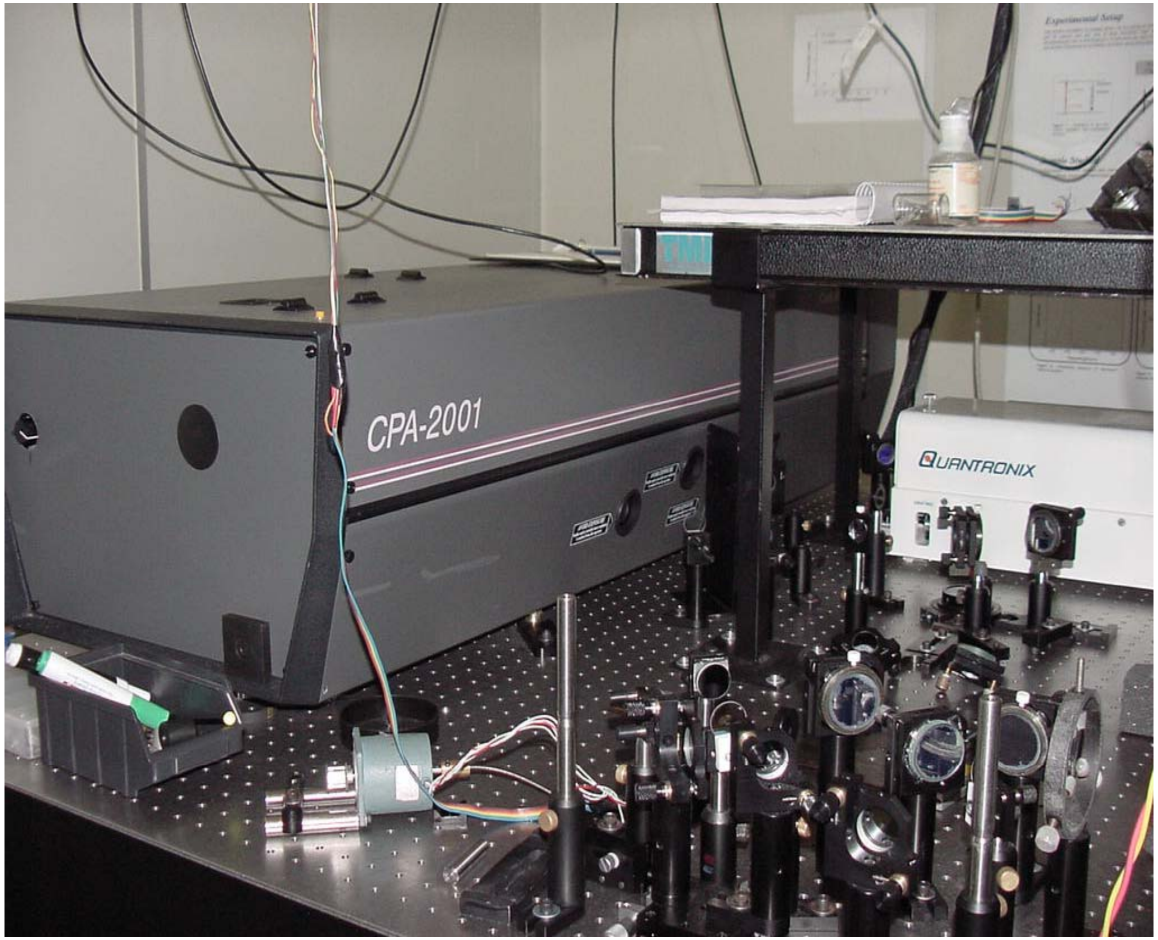
$$\alpha(I) = \alpha_0 + \beta I$$

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

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

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

Nonlinear absorption – 150 fs laser system



Ti:Sapphire amplifier

775 nm

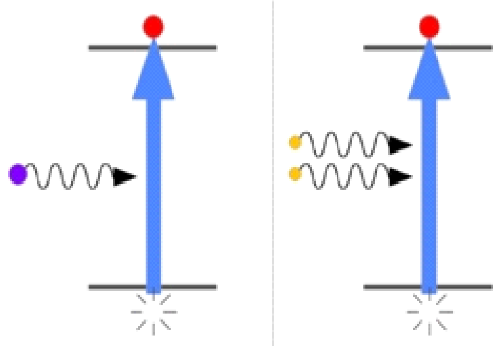
150 fs

800 μJ

Nonlinear spectrum

nonlinear absorption

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



intense laser (ultra short pulses)

discrete λ s

$\beta(\lambda)$

nonlinear spectrum ???

Nonlinear absorption spectrum

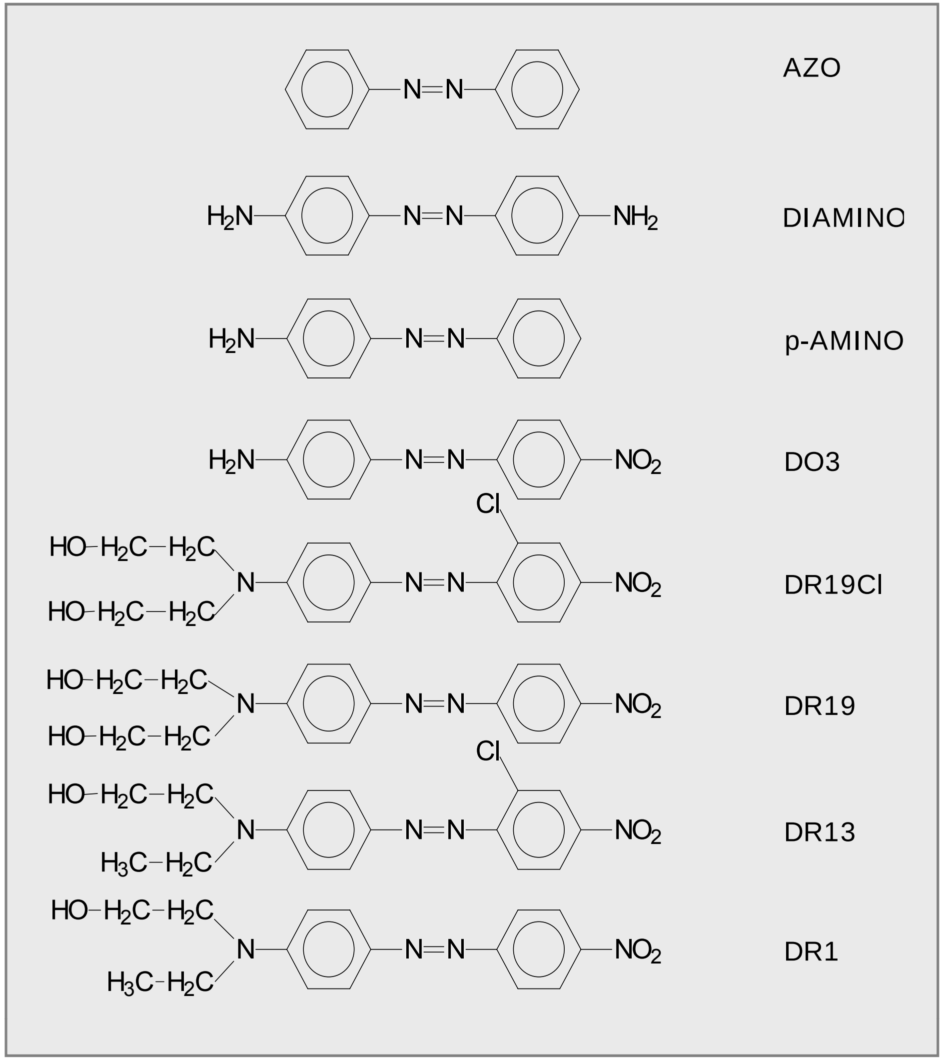
Optical parametric amplifier

460 - 2600 nm

$\approx$ *120 fs*

20-60 μJ

Azoaromatic samples

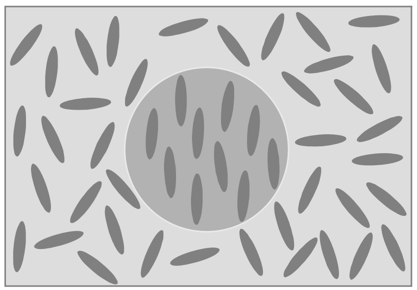


Azo-chromophores

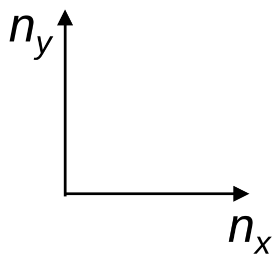
Optical Storage

Optically induced birefringence

After alignment

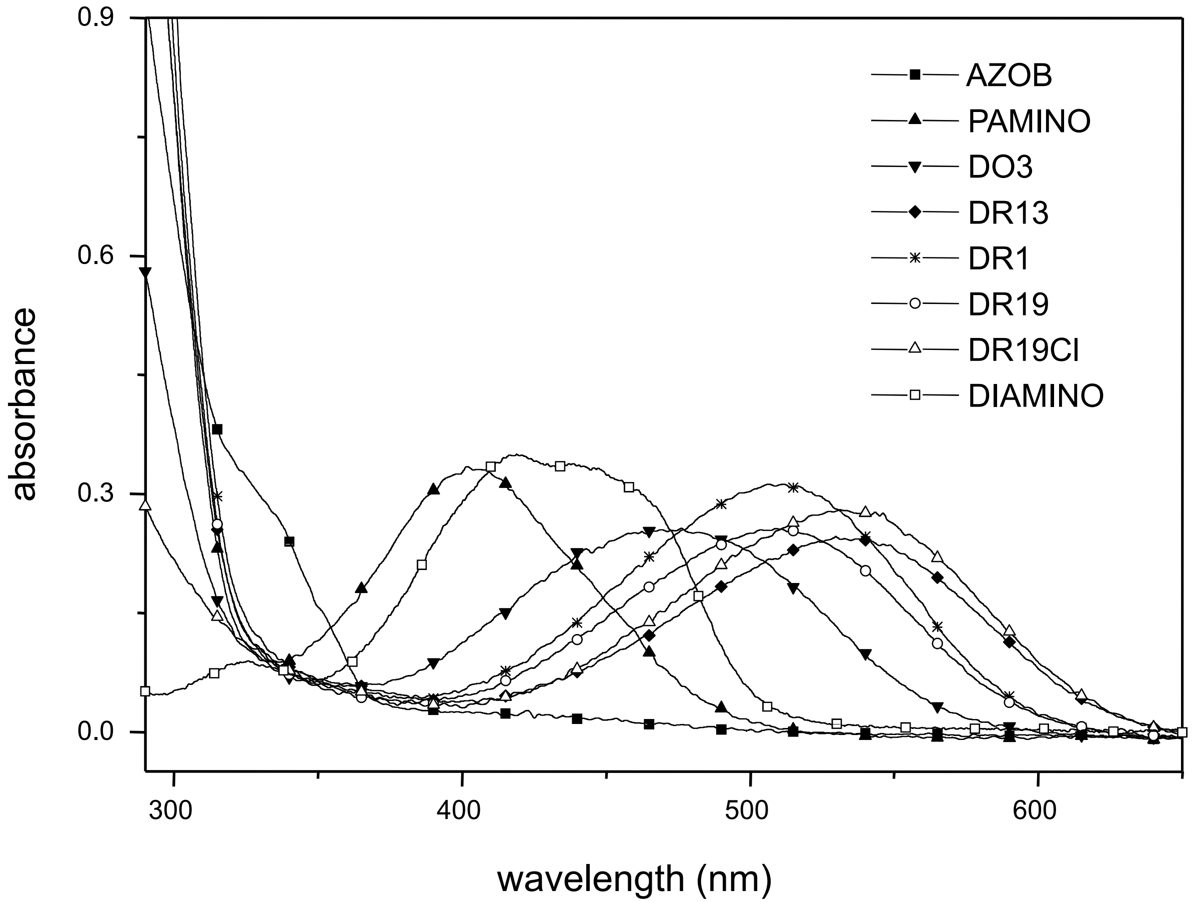


Optically Induced birefringence

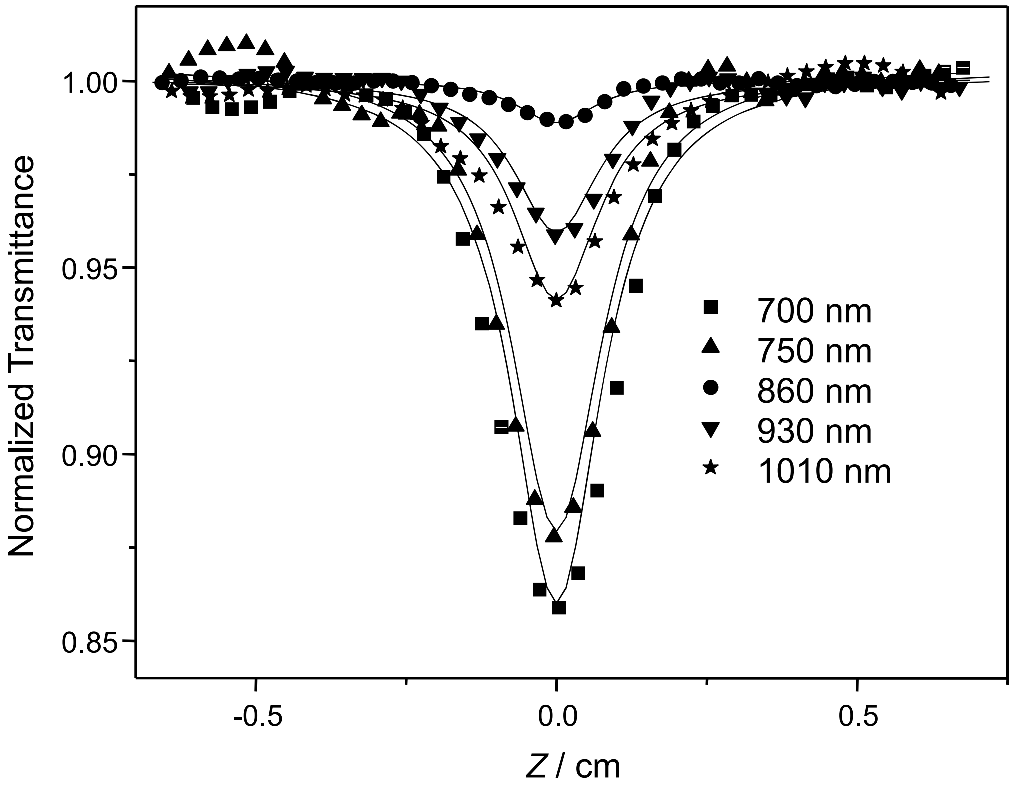


$$n_y > n_x$$

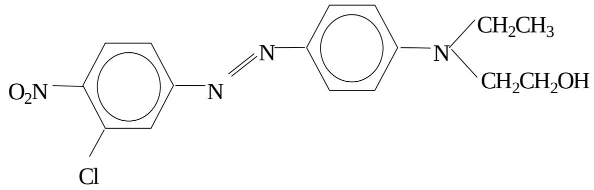
Linear absorption of azoaromatic compounds



Two-photon absorption



DR13

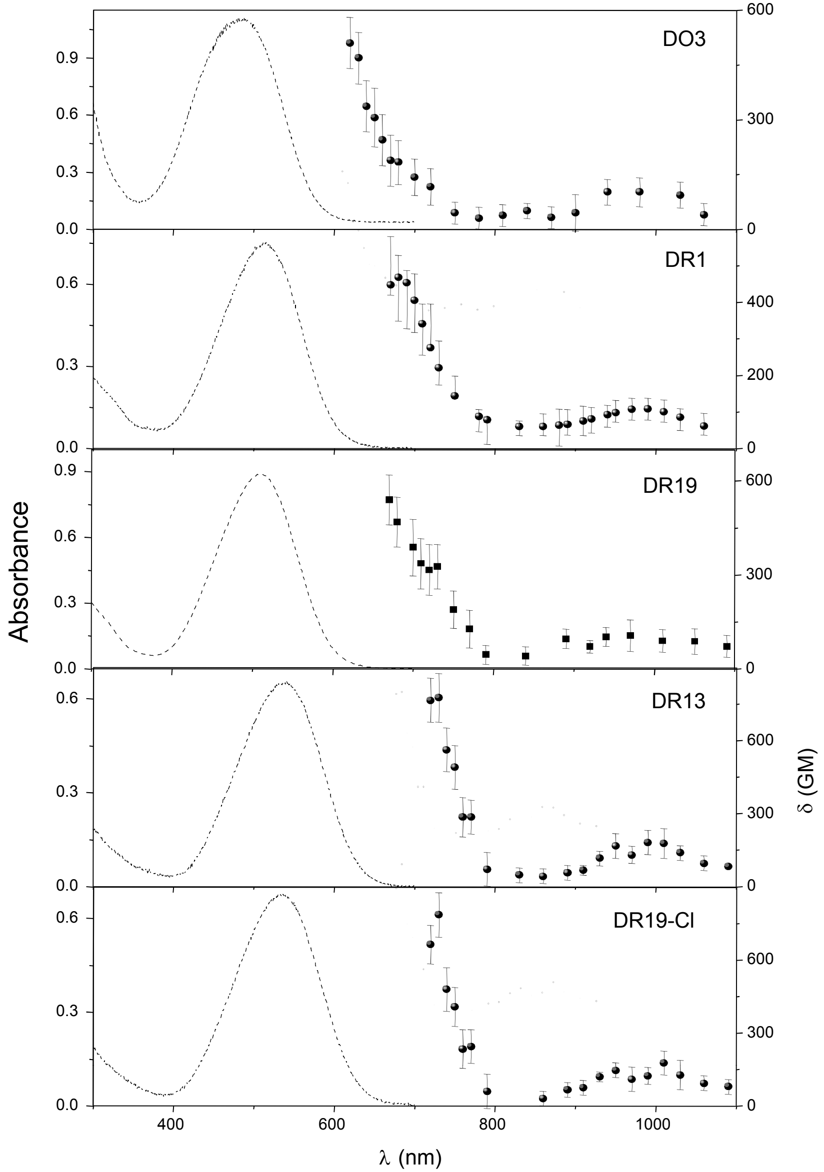


$$T(z) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}}$$

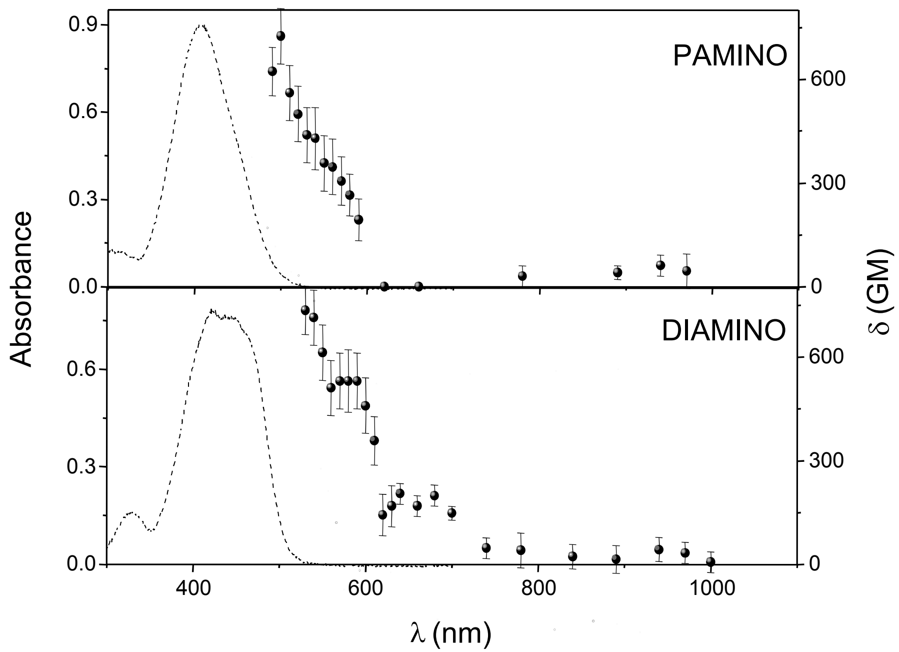
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

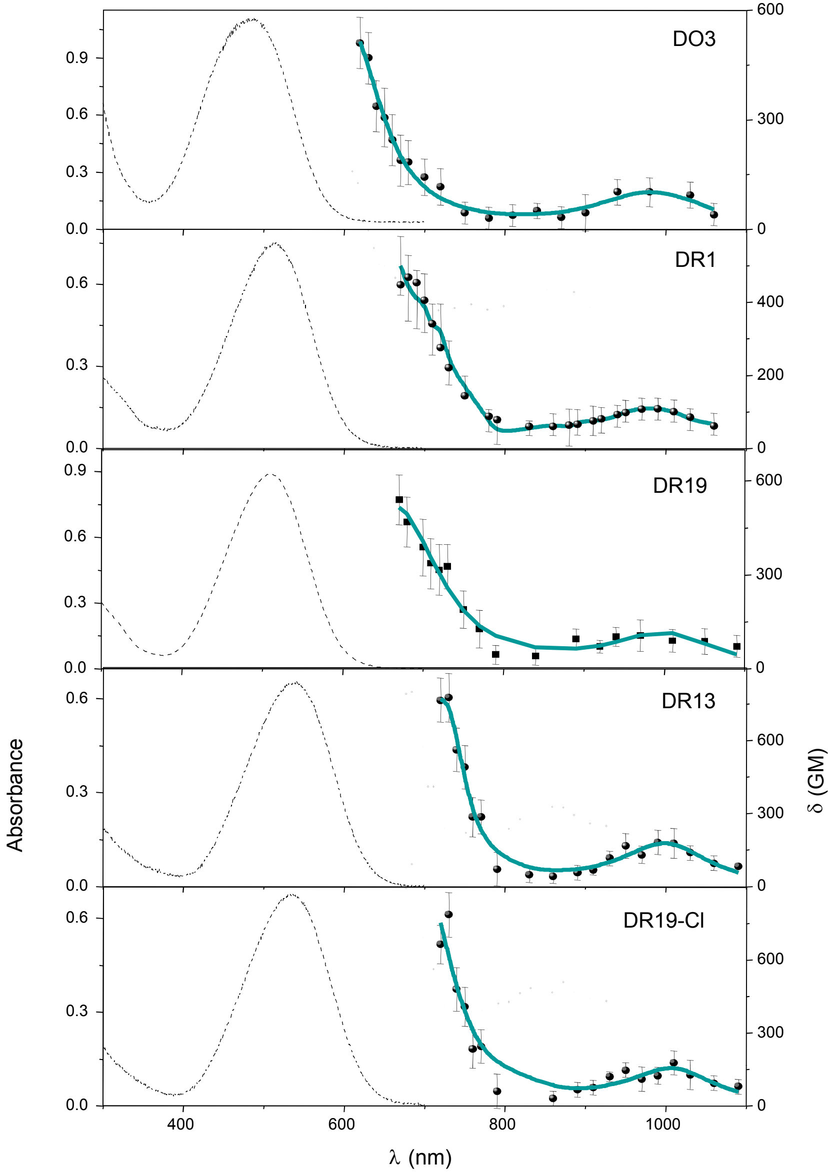
Pseudostilbenes



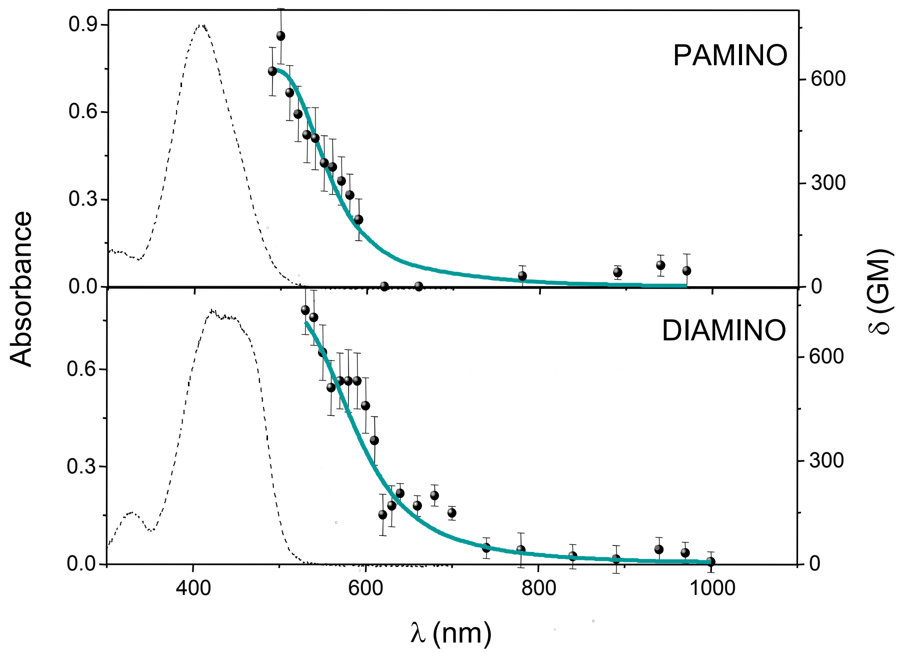
Aminoazobenzenes



Pseudostilbenes



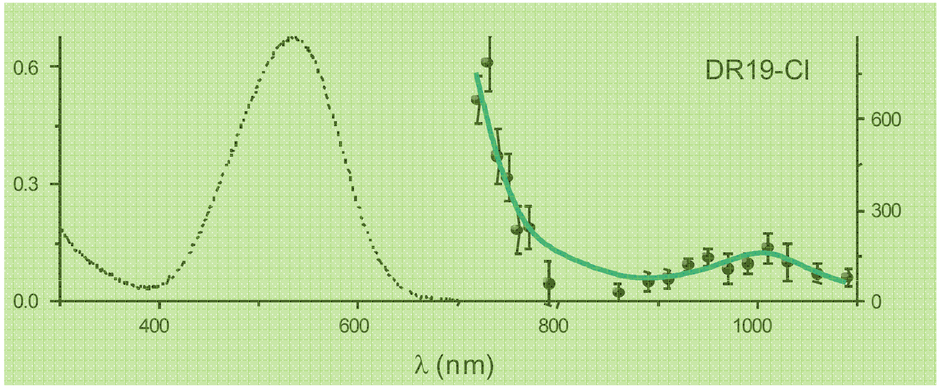
Aminoazobenzenes

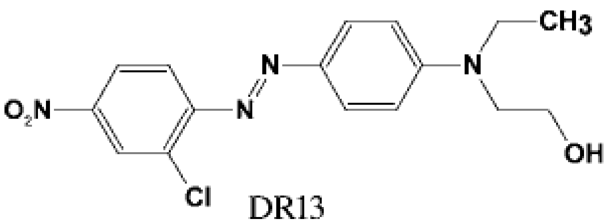


$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0}-\nu)^2+\Gamma_{i0}^2}\left[\frac{A_1}{(\nu_{f_1 0}-2\nu)^2+\Gamma_{f_1 0}^2}+\frac{A_2}{(\nu_{f_2 0}-2\nu)^2+\Gamma_{f_2 0}^2}\right]$$

two-photon absorption – selection rules

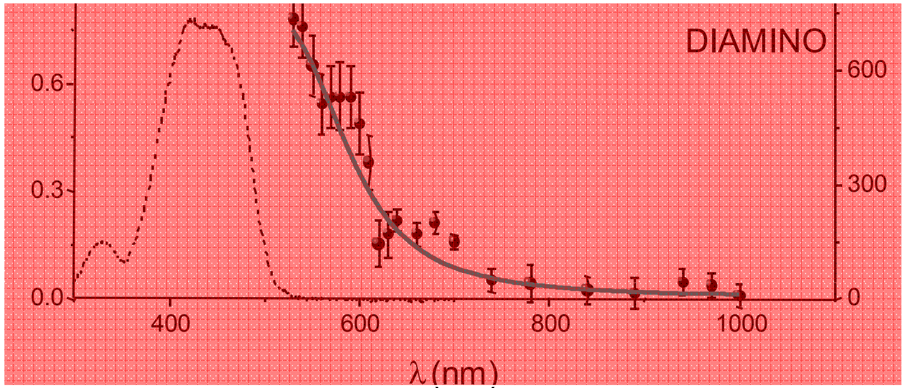
asymmetric

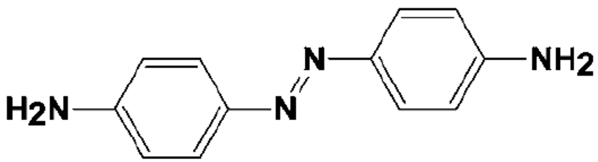




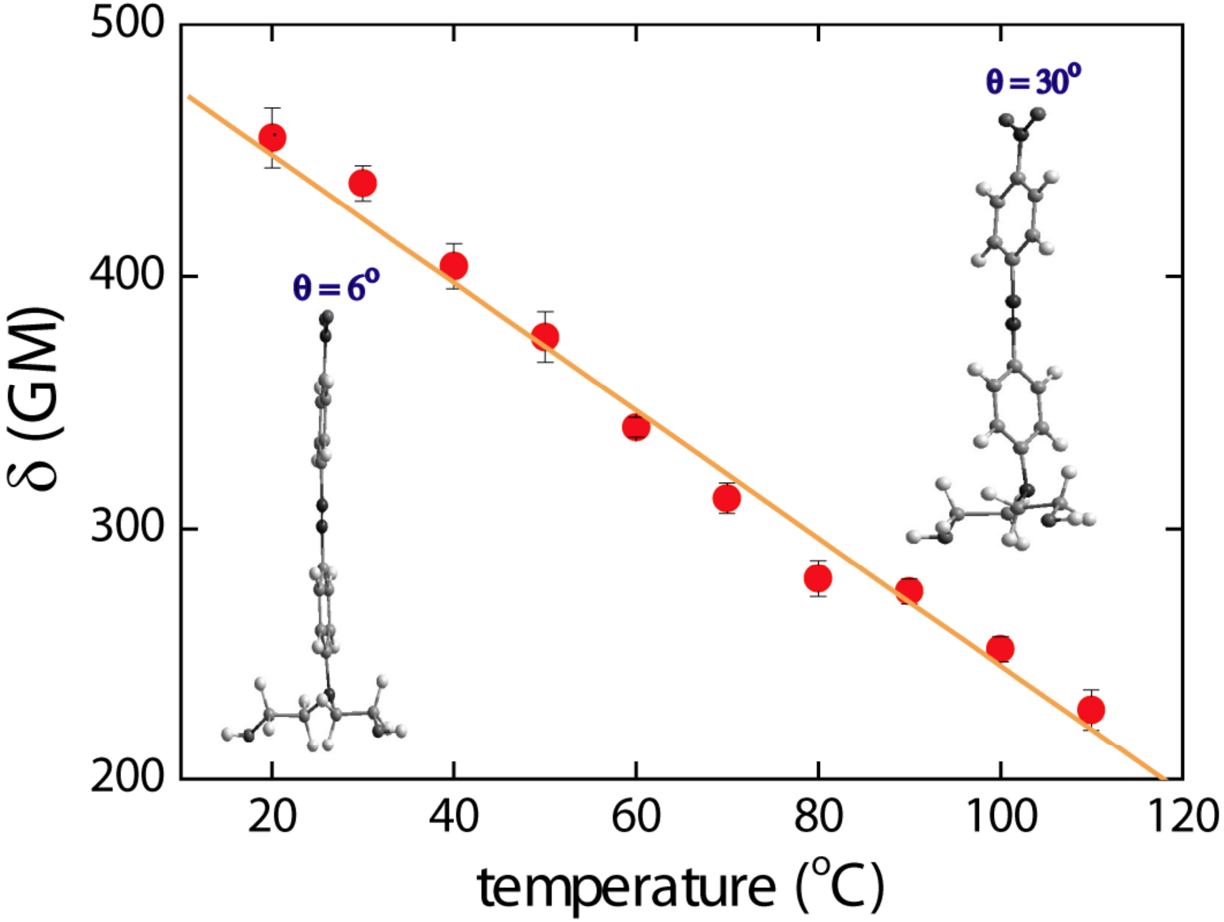
DR13

symmetric





Planarity of the π-bridge



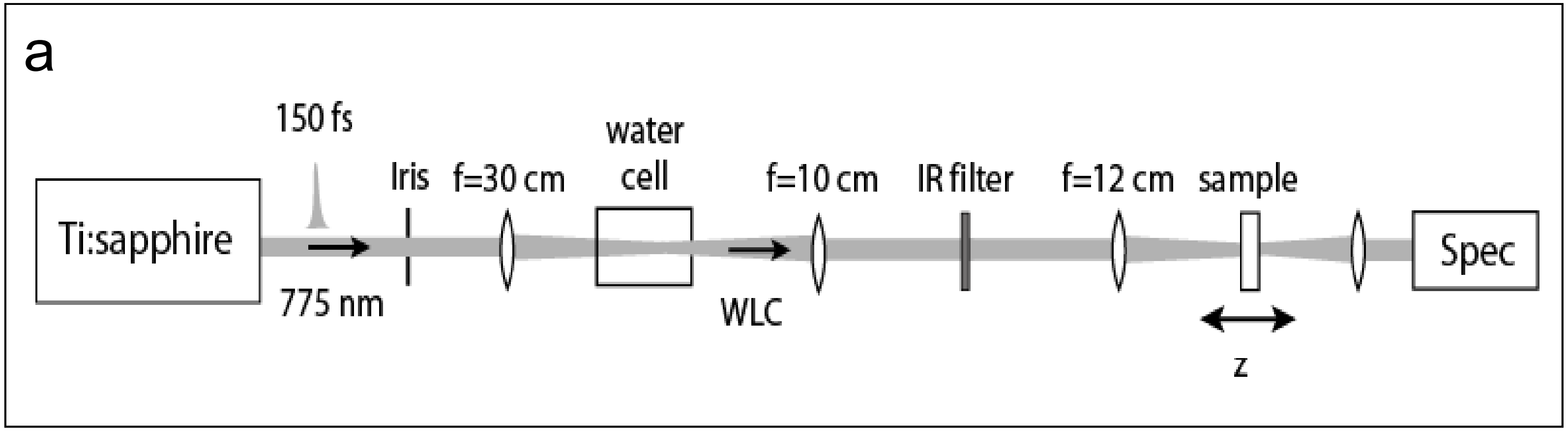
Thermally induced torsion in
the molecular structure

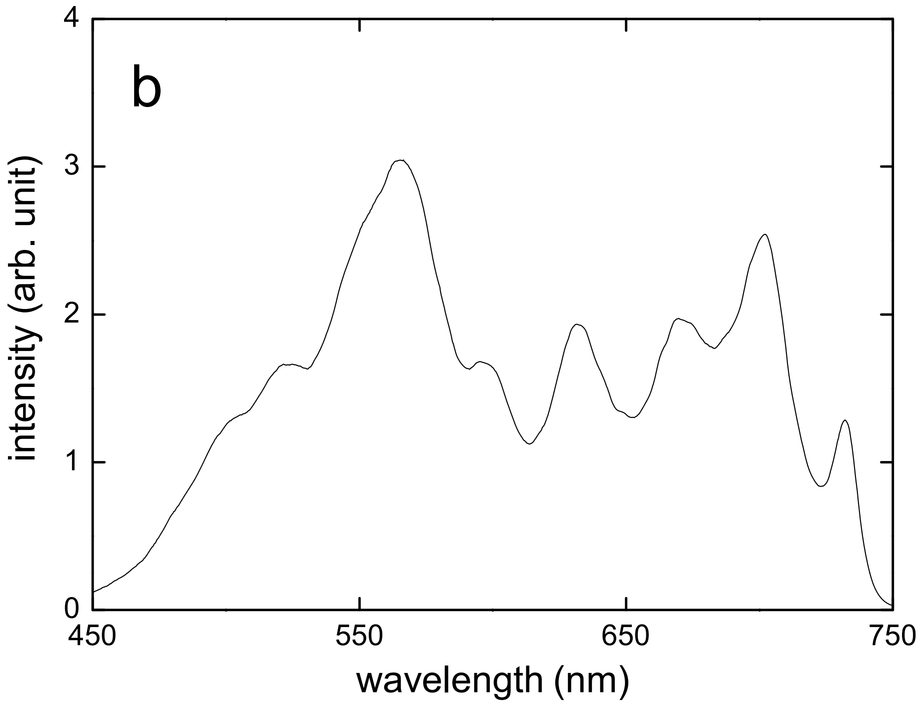
$$d\delta/dT = -2.5GM/°C$$

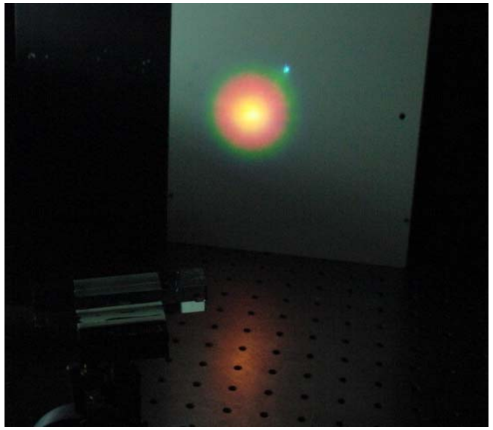
Molecular design strategy

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

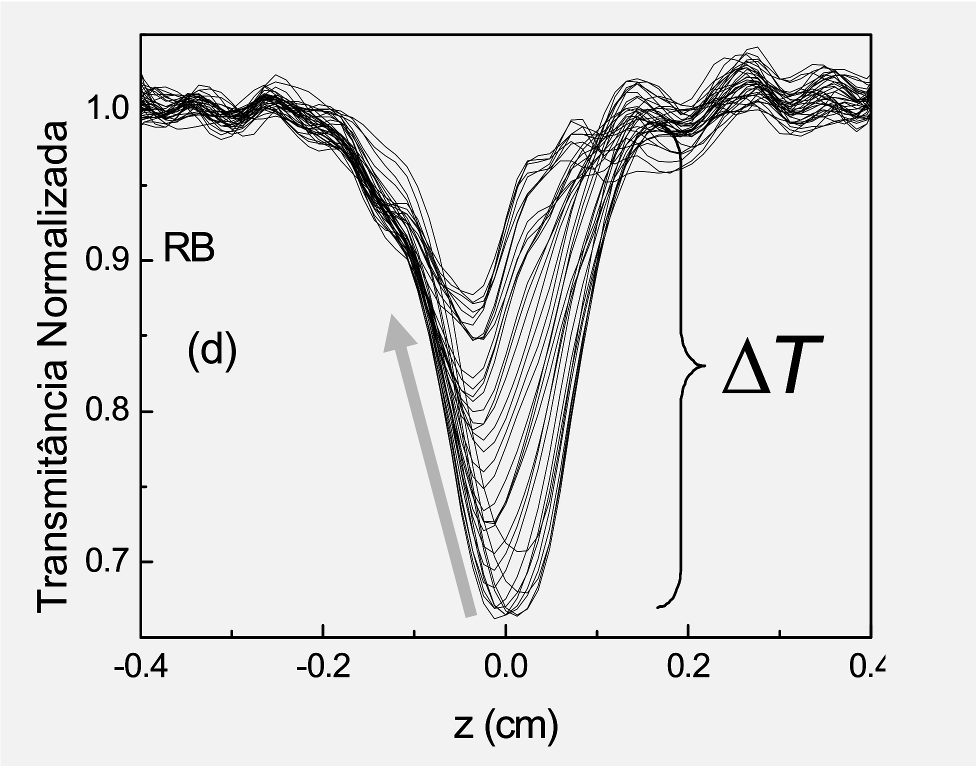
White light continuum Z-scan

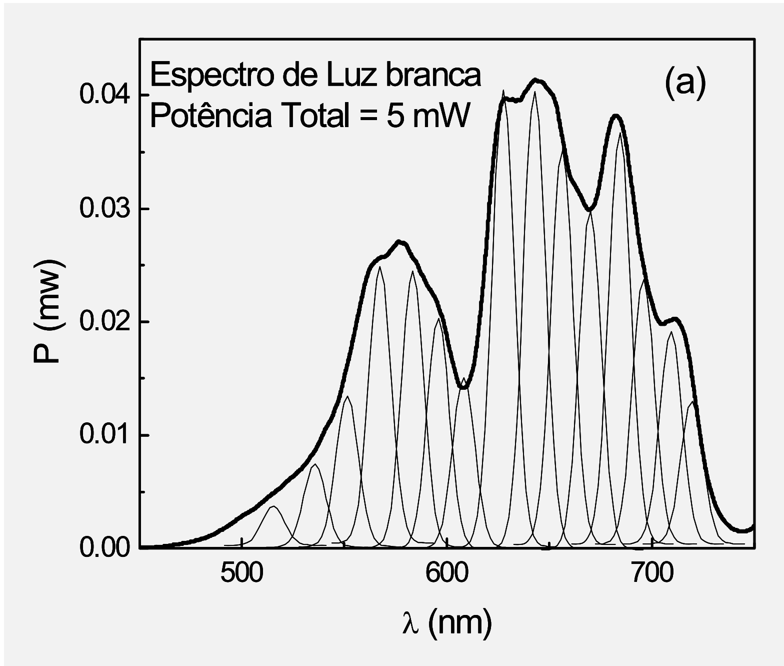




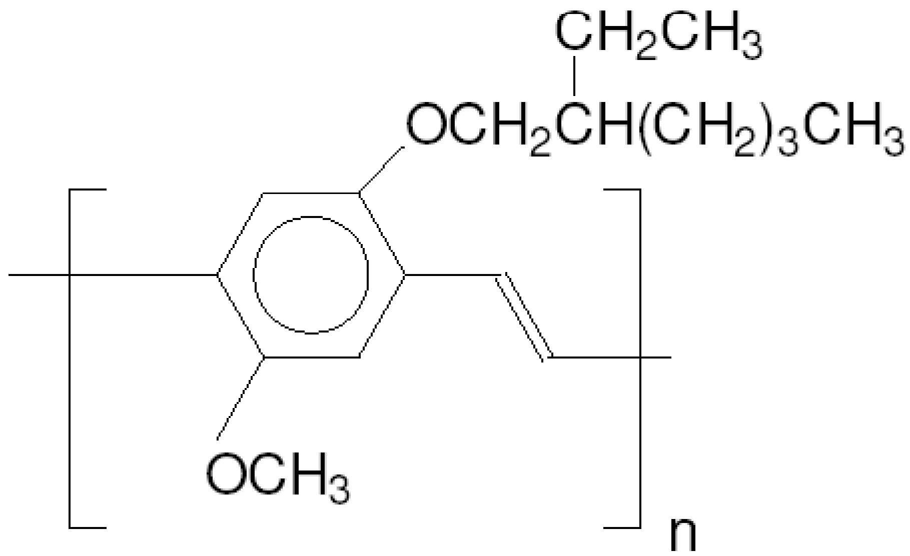


White light continuum Z-scan



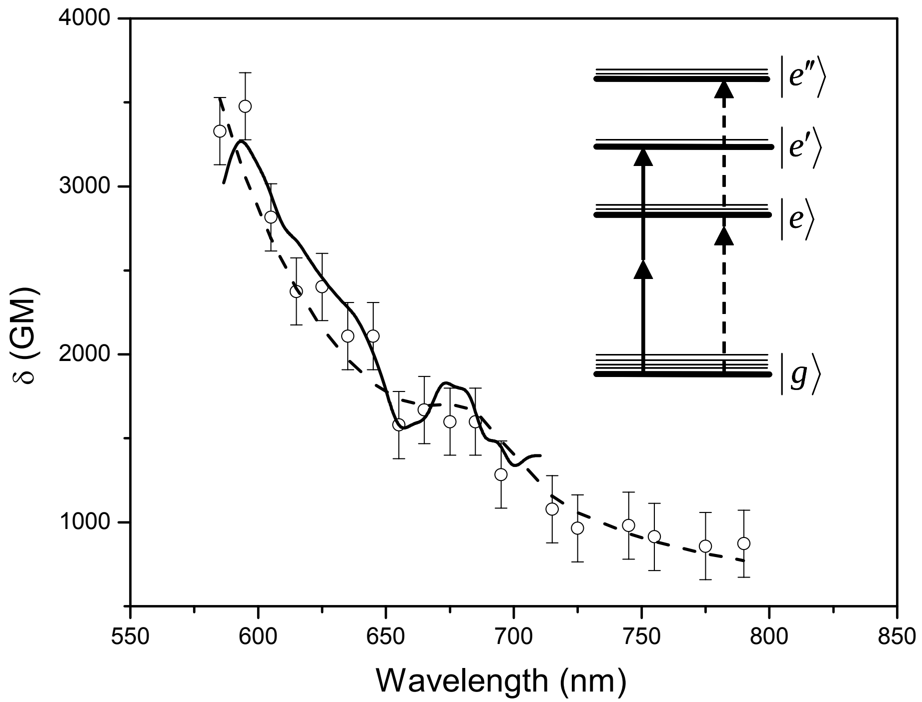


MEH-PPV



- Fluorescence
- Electro Luminescent
- Conductive

White light continuum Z-scan



Two-photon absorption

MEH-PPV

Solid line: Degenerate two-photon absorption cross-section spectra obtained from WLC Z-scan

Circles : discrete Z-scan measurements

Dashed line: theoretical model

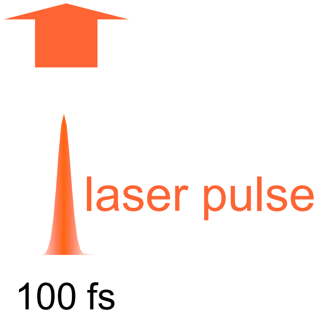
Two-photon microfabrication

Fabrication of 3D microstructures containing organic compounds

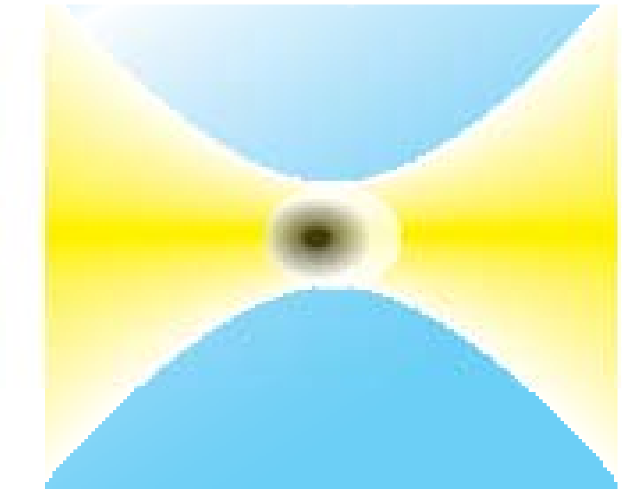
Optical Active Microstructures

Two-photon polymerization

Monomer + Photoinitiator $\rightarrow$ *Polymer*



Two-photon polymerization

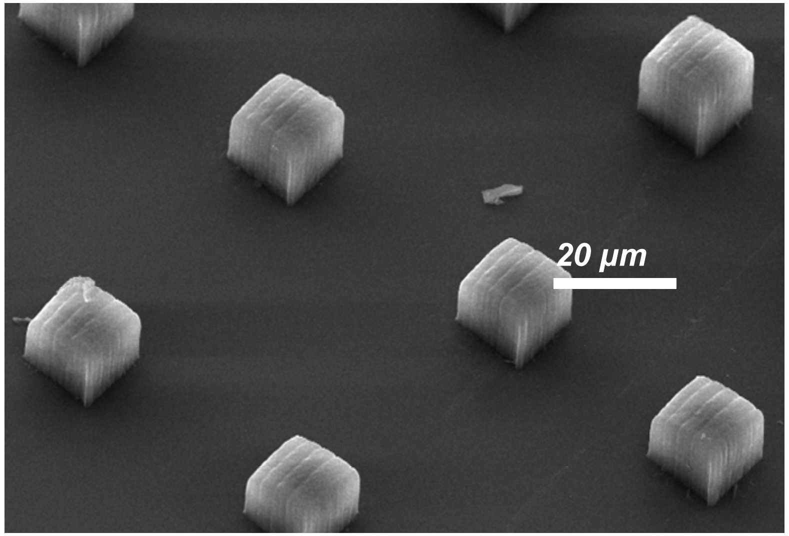


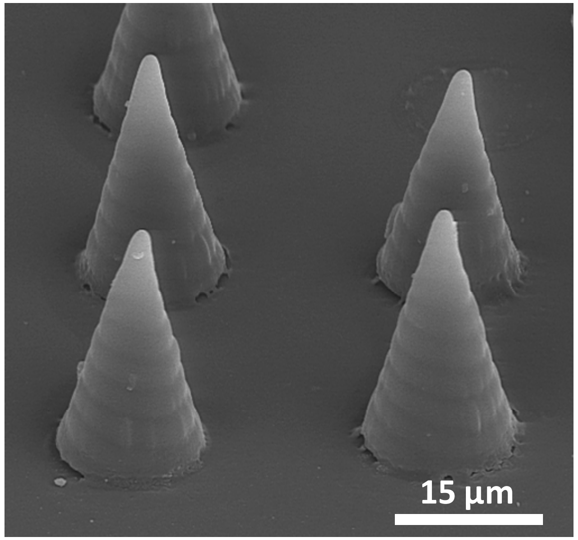
The polymerization is confined to the focal volume.

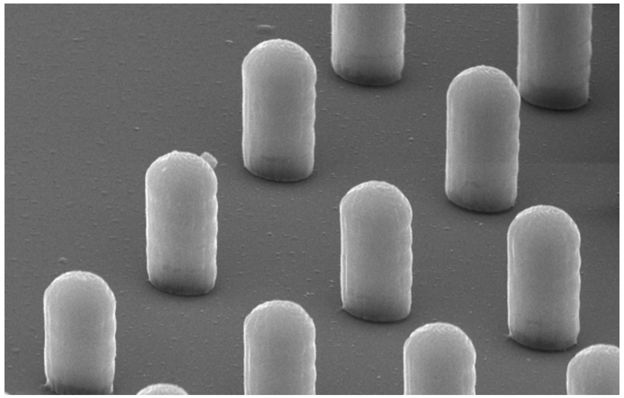
High spatial resolution

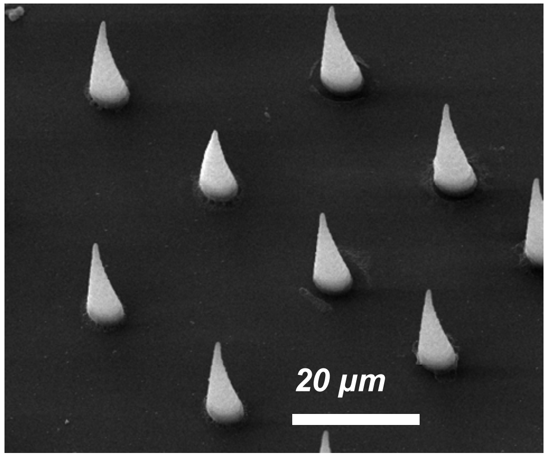
Two-photon polymerization

Microstructures fabricated by two-photon polymerization



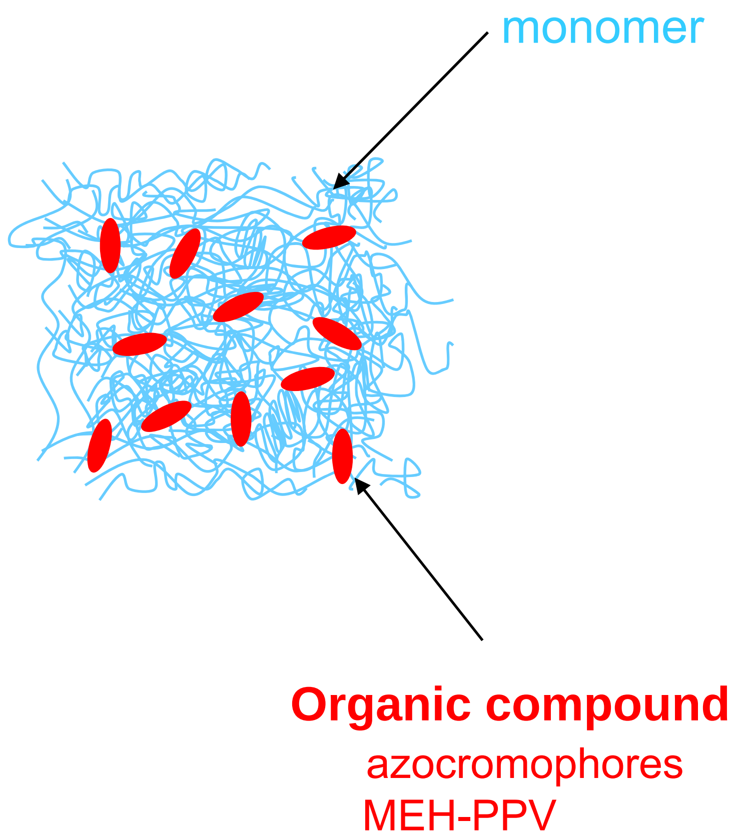






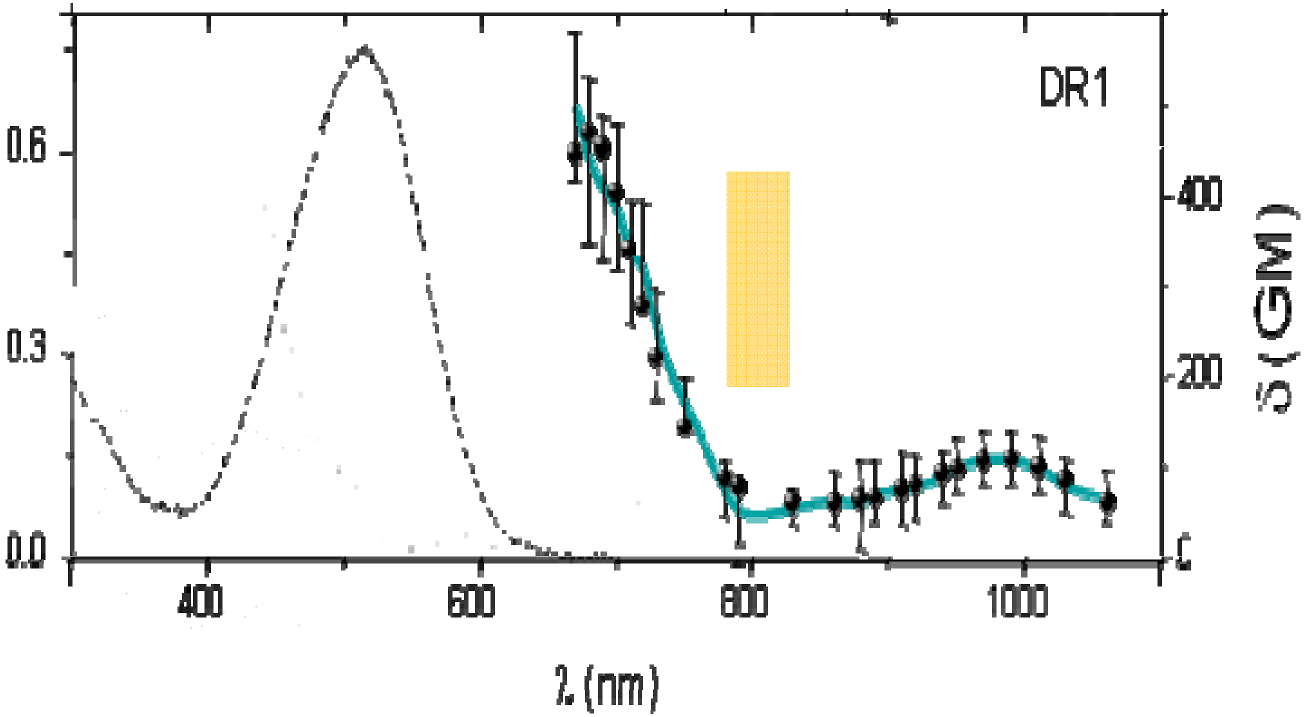
Two-photon polymerization

Microstructures containing active compounds



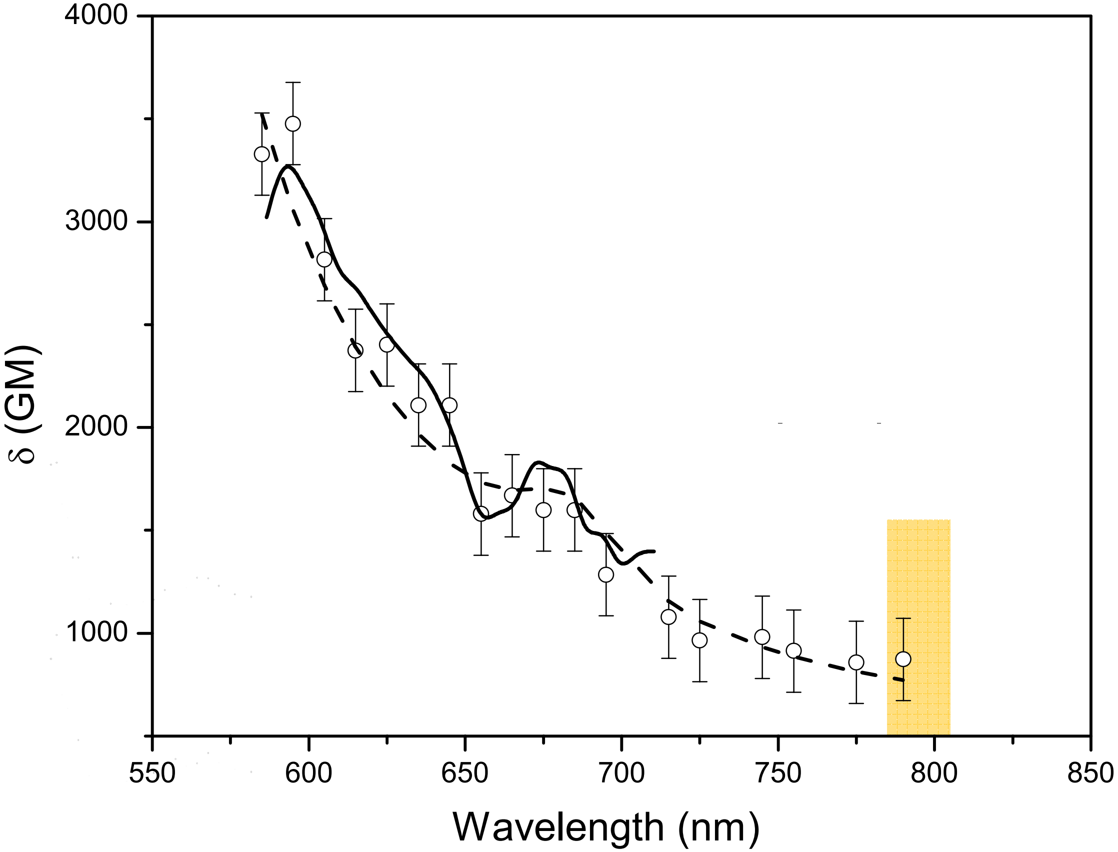
Two-photon polymerization

Azochromophores – DR1

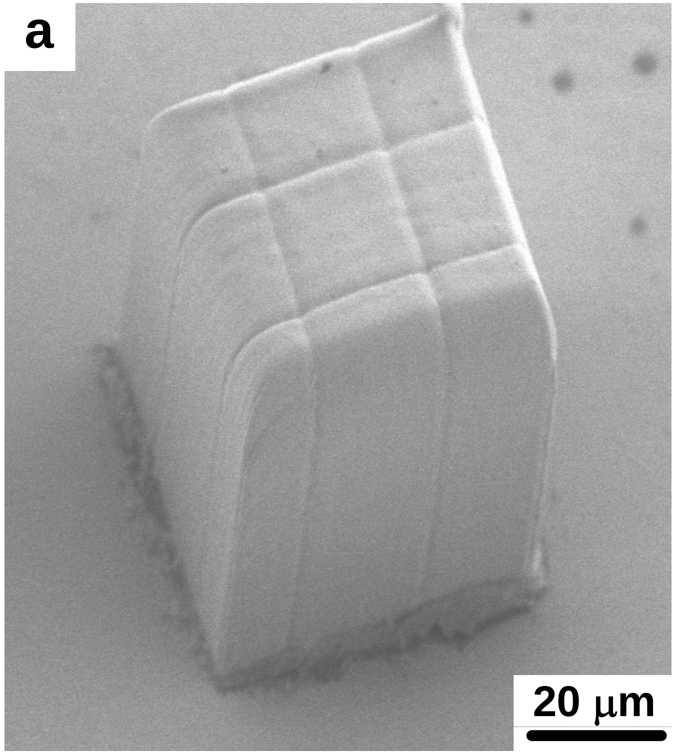


Two-photon polymerization

MEH-PPV



Micro-optical storage



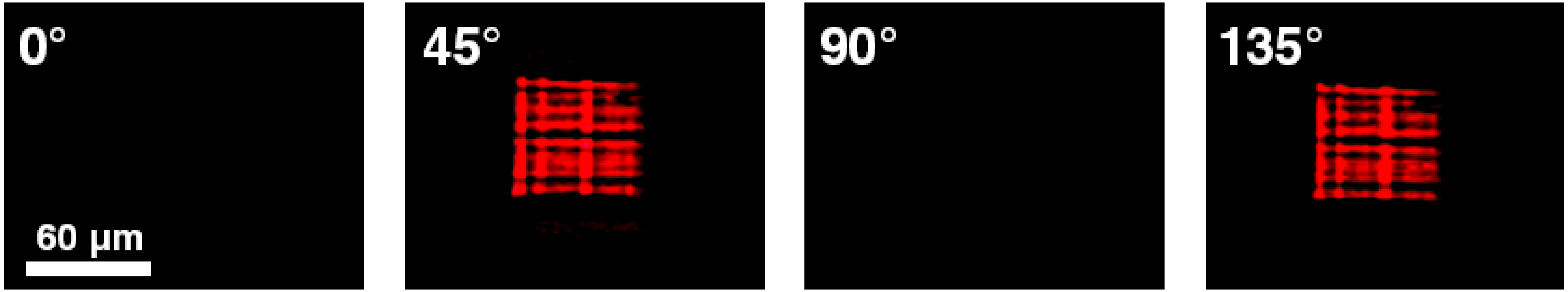
Birefringent microstructures

Ar+ ion laser irradiation

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

Micro-optical storage

The structure is visible when the angle between the birefringence axis and the polarizer is an odd multiple of 45°

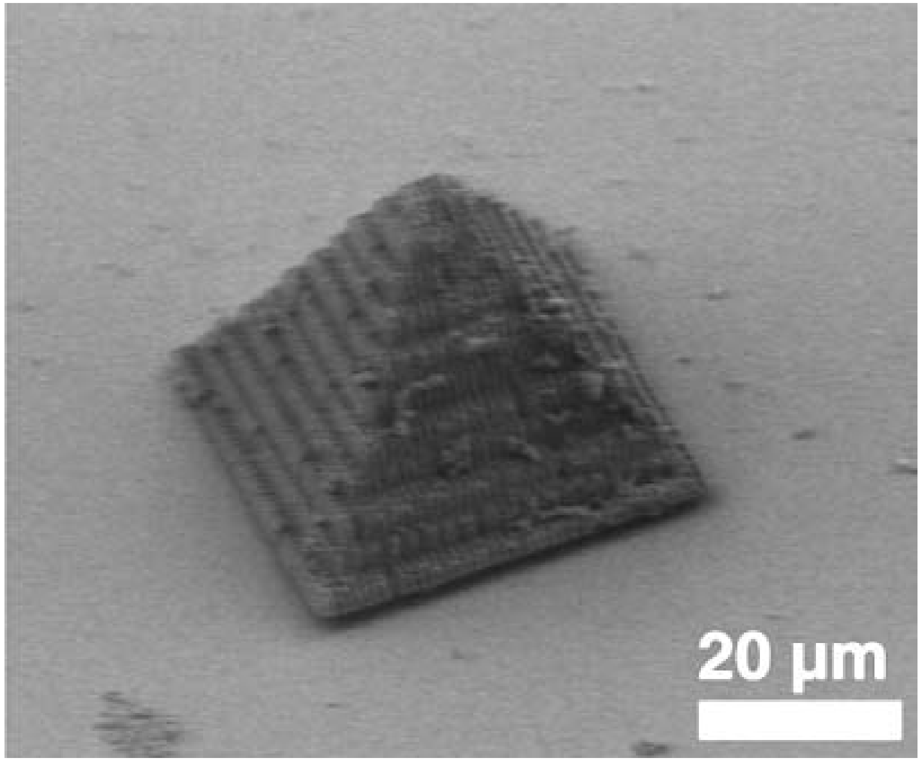


$\Delta n = 5x10^{-5}$

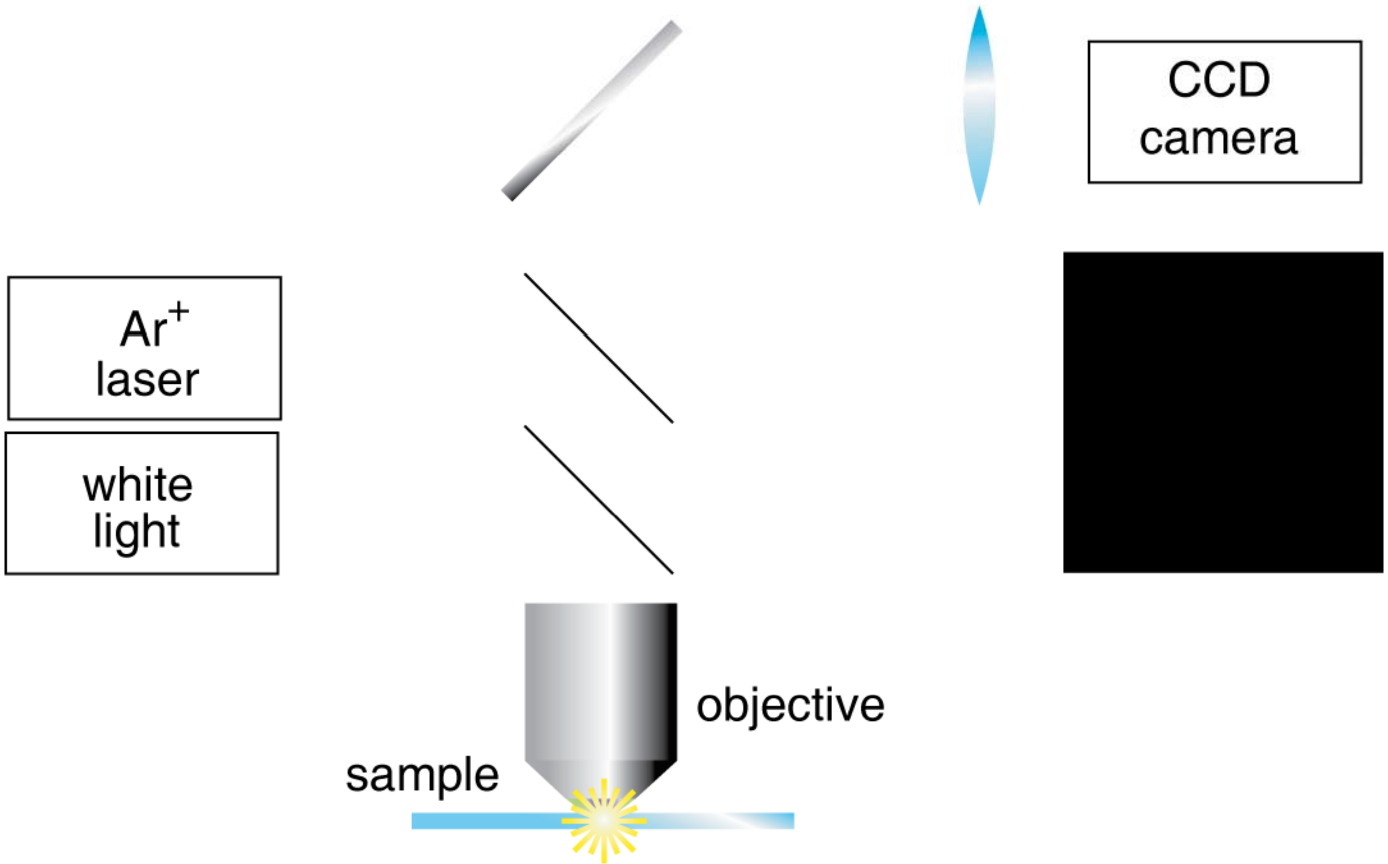
This birefringence can be completely erased by irradiating the sample with circularly polarized light.

Applications: micro-optical switch, micro-optical storage

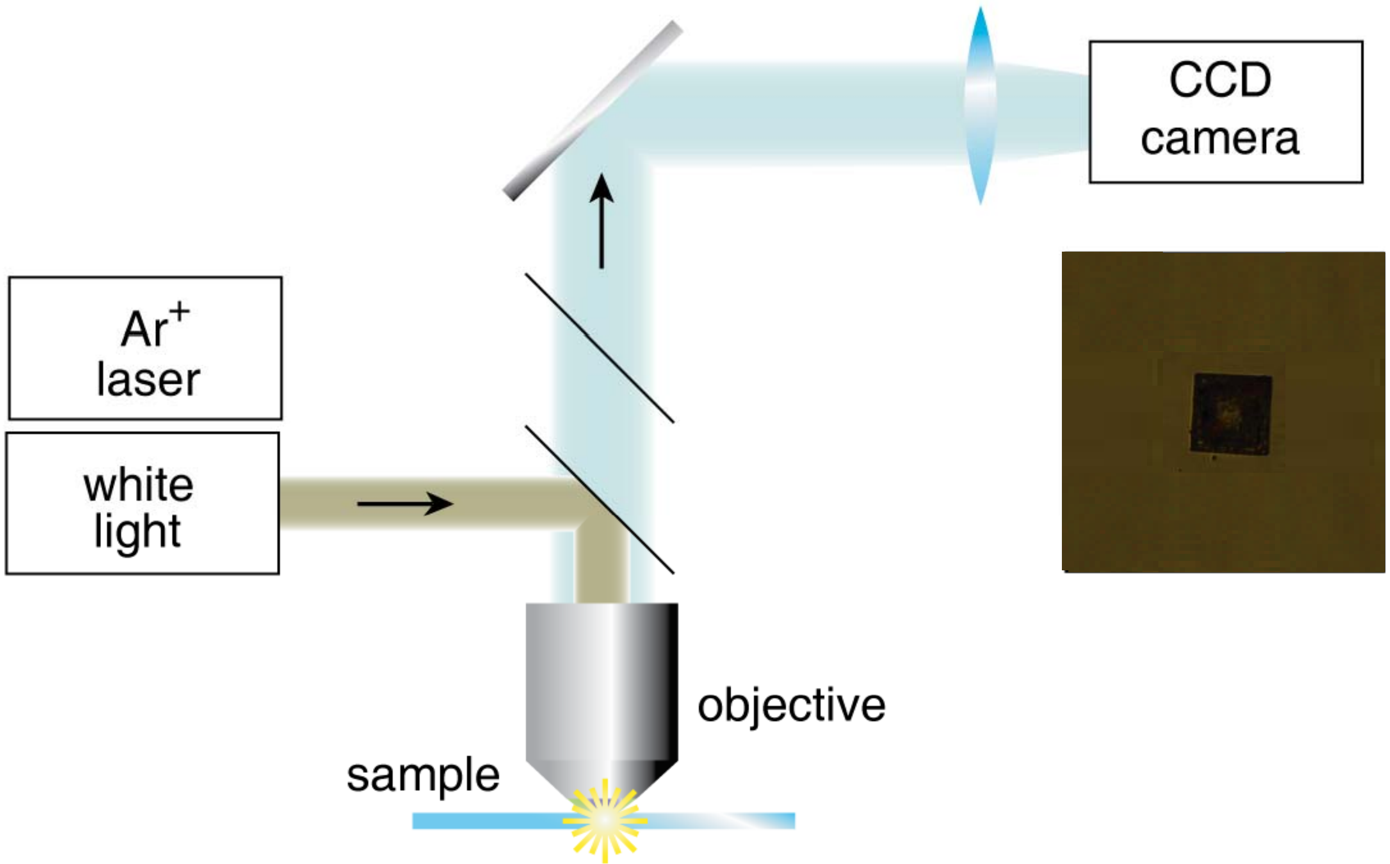
Microstructure containing MEH-PPV



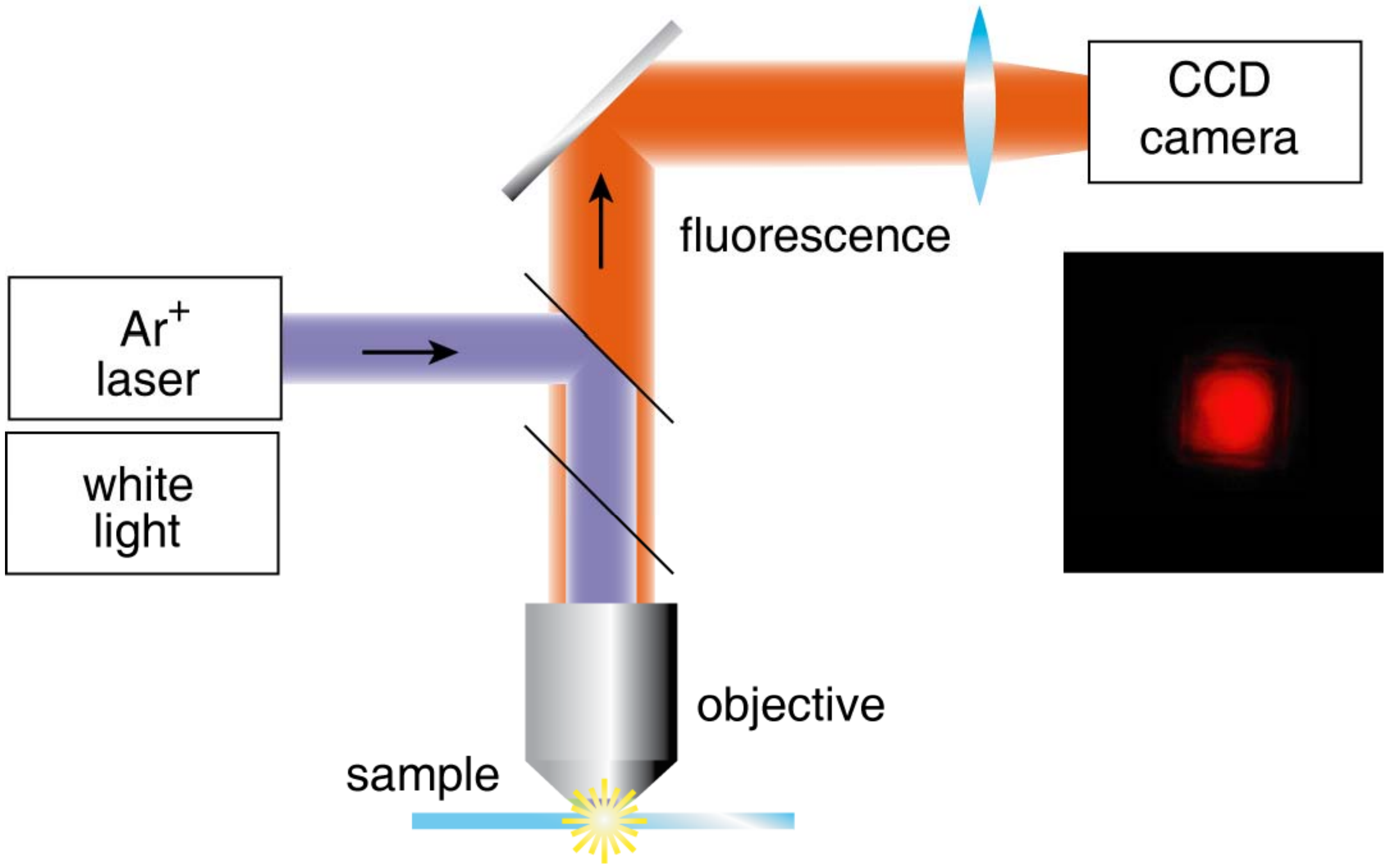
Microstructure containing MEH-PPV



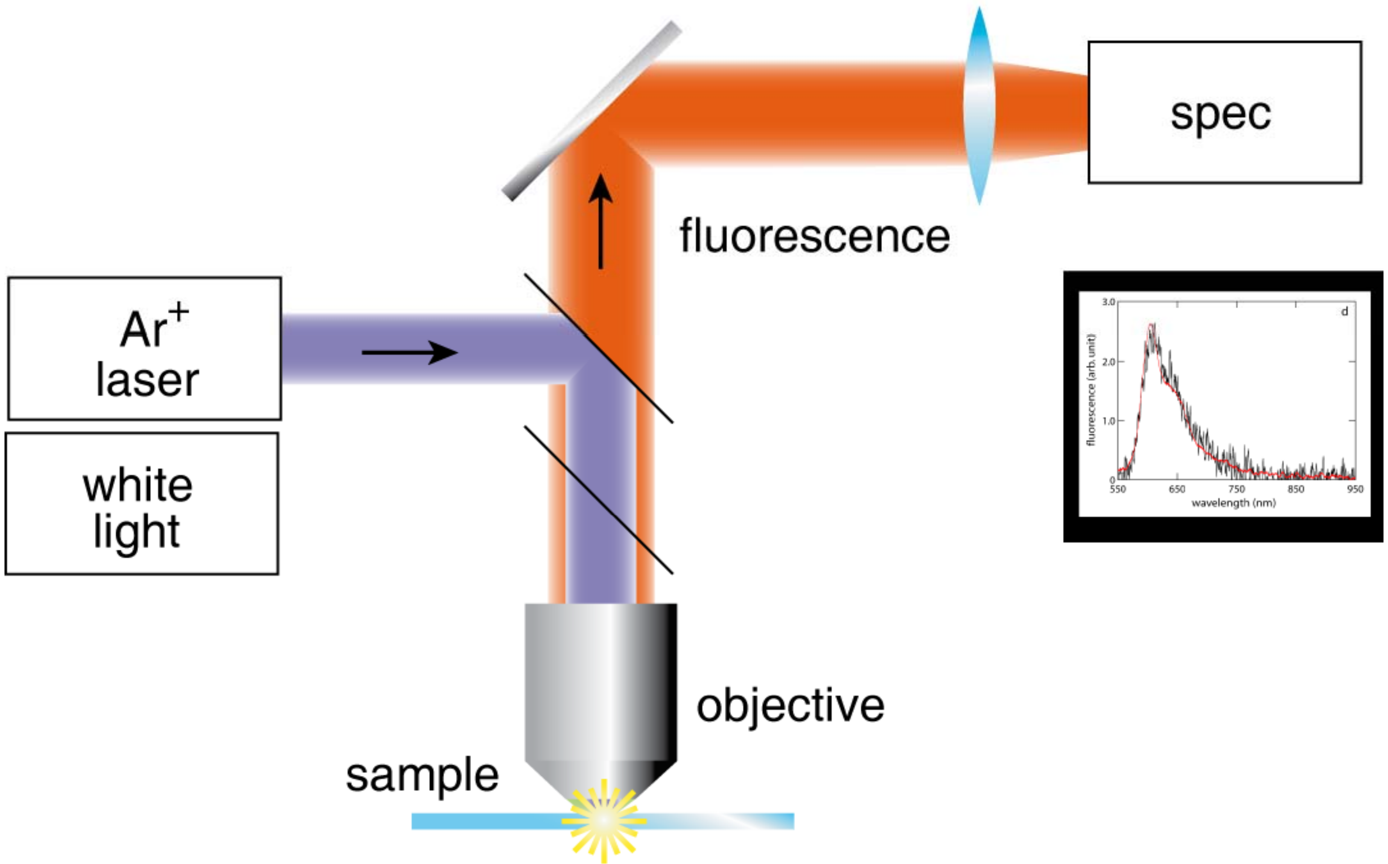
Microstructure containing MEH-PPV



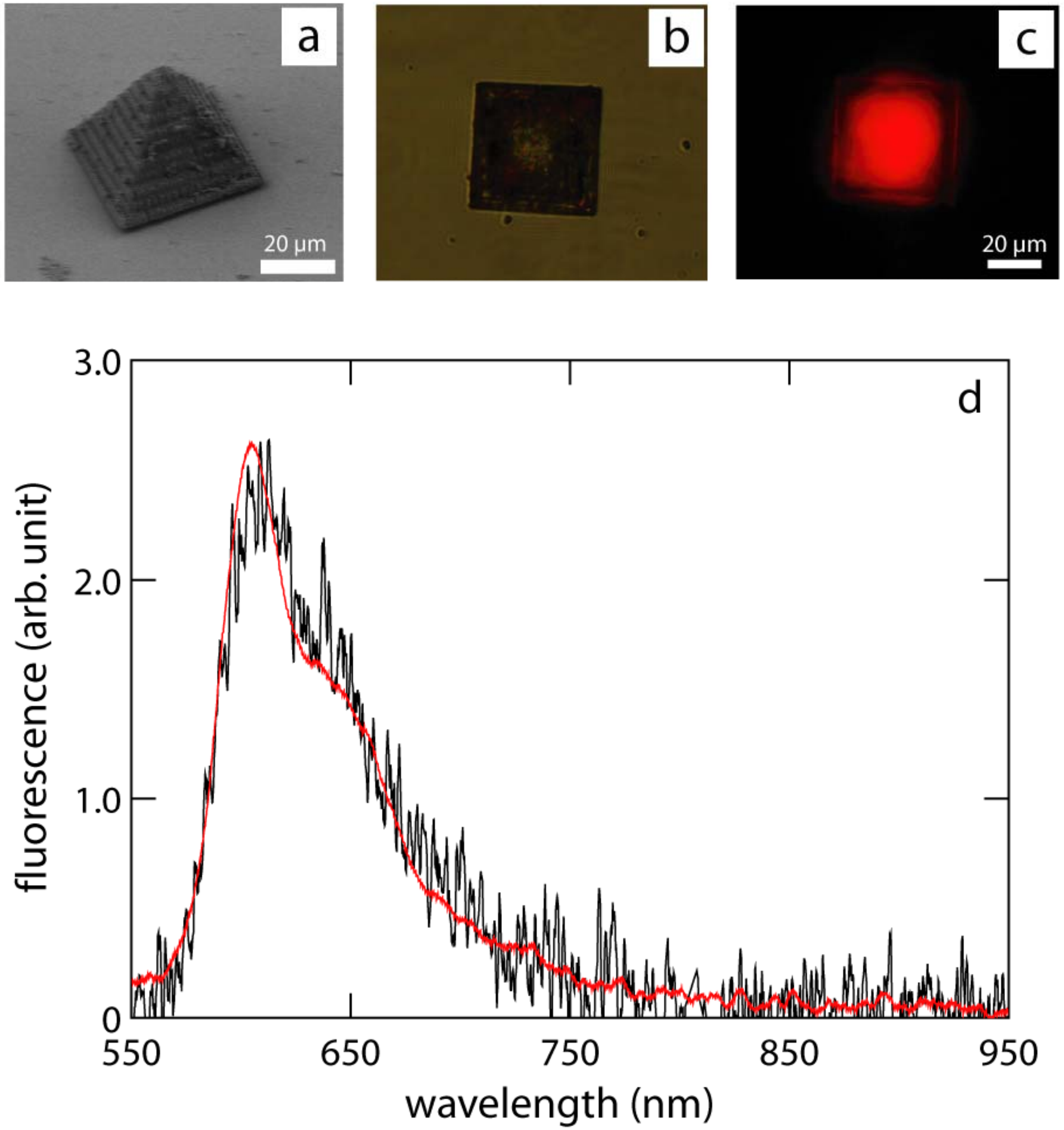
Microstructure containing MEH-PPV



Microstructure containing MEH-PPV



Microstructure containing MEH-PPV



(a) Scanning electron microscopy

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

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

Acknowledgments

- FAPESP
- CAPES
- CNPq
- AFOSR

Thank you !

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