Optical nonlinearities in organic materials

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Outline

introduction to nonlinear optics

nonlinear optics in organic materials

experimental methods

examples of some results

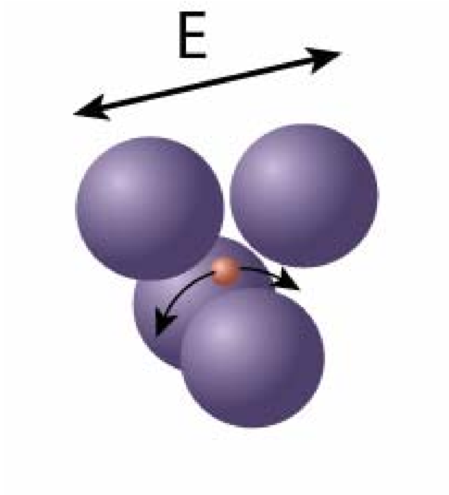
Linear optics vs Nonlinear optics

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

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

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

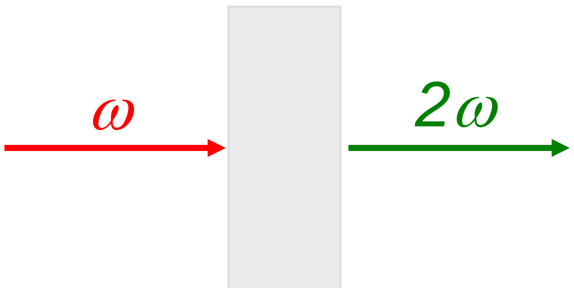
SHG

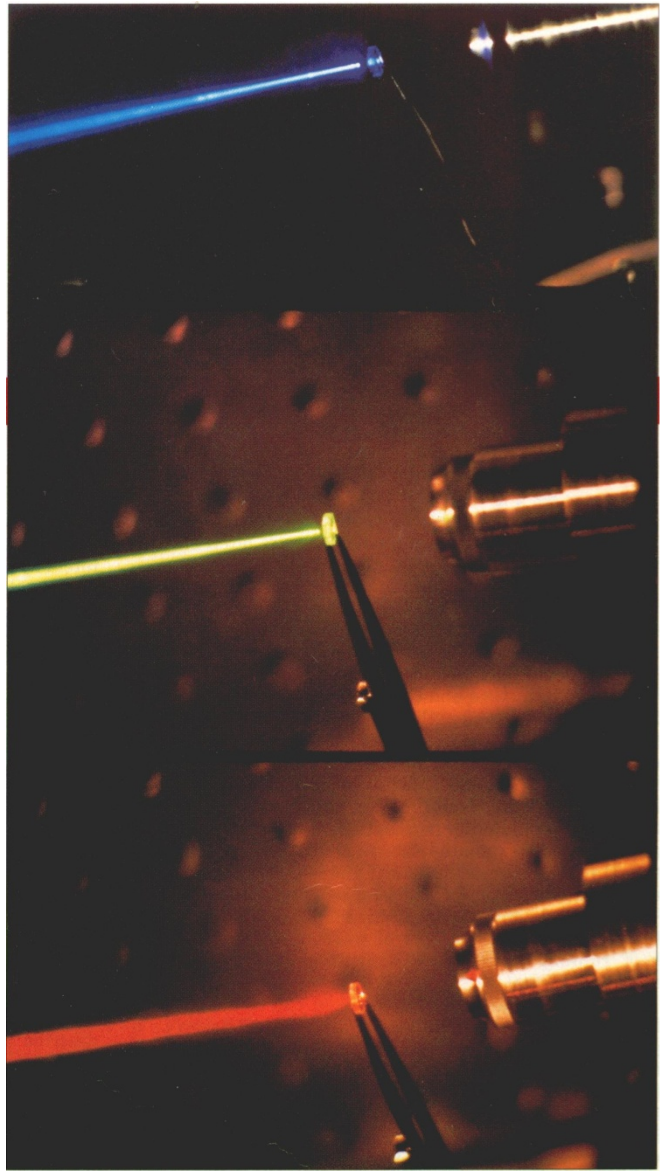
THG
Kerr effect

Nonlinear Optics

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

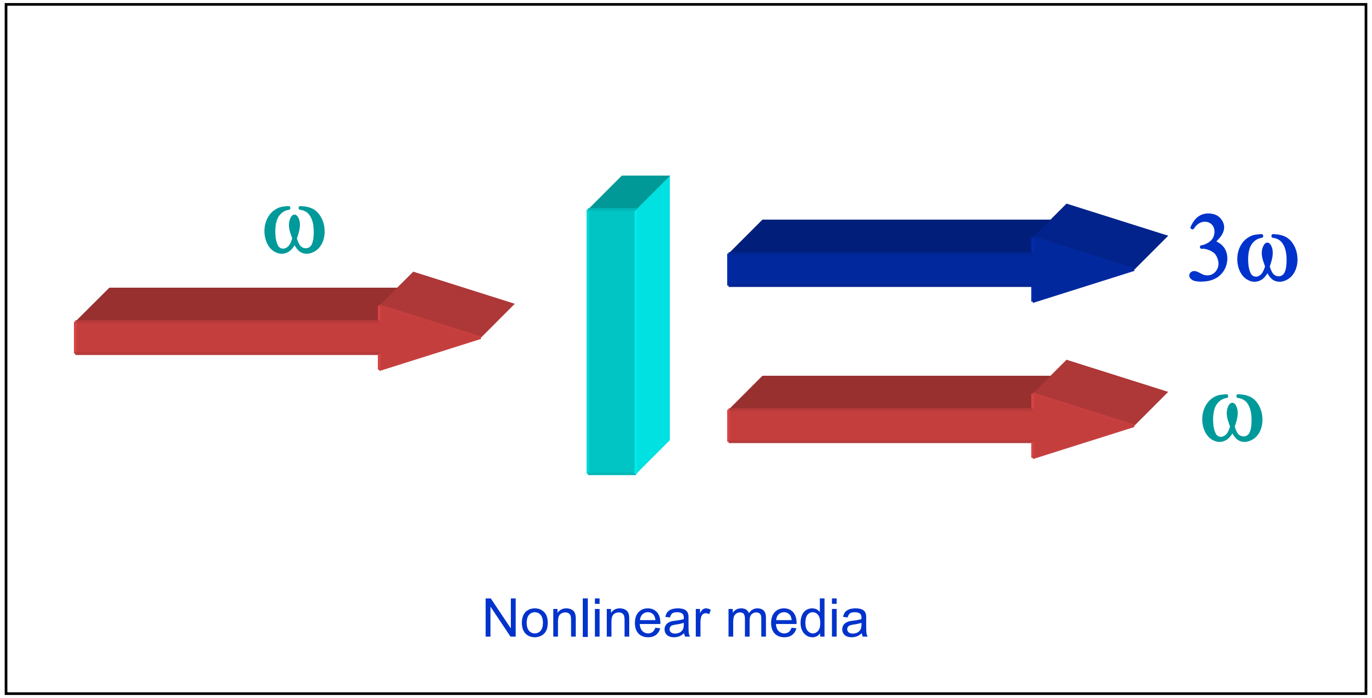
Second Harmonic Generation





Nonlinear Optics

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



Nonlinear Optics

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

Kerr media:

$$n = n_0 + n_2 I$$

Index of refraction depends on the light intensity

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

Self phase modulation

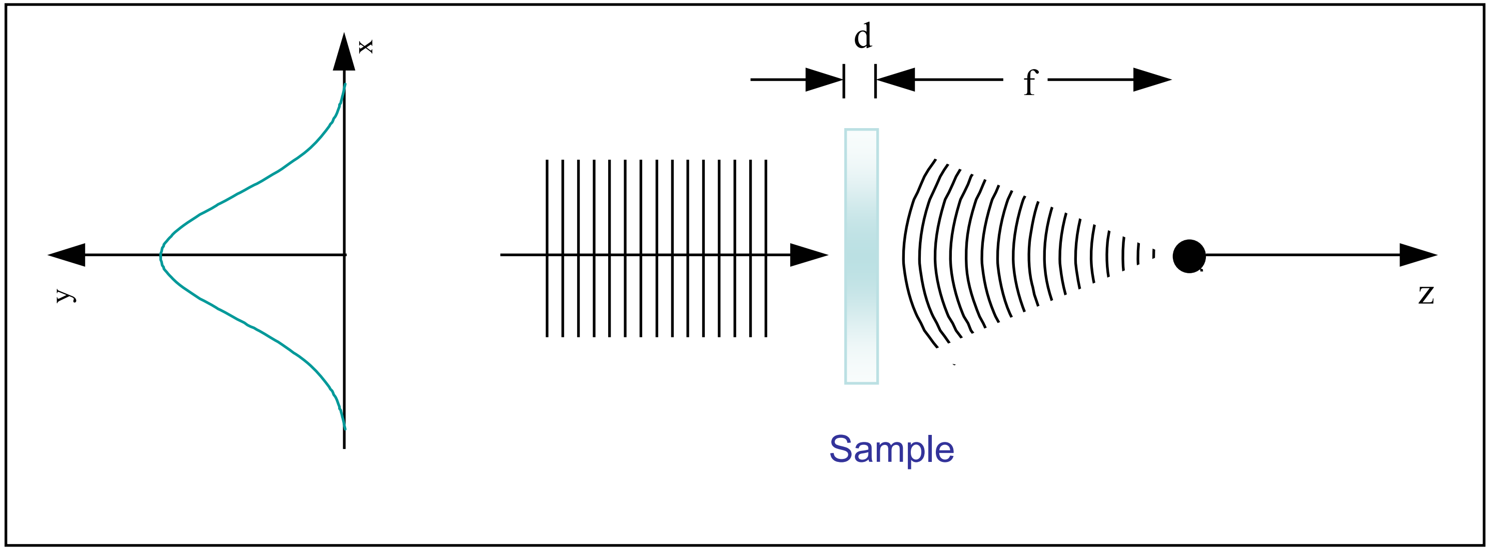
Kerr media:

$$n = n_0 + n_2 I$$

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

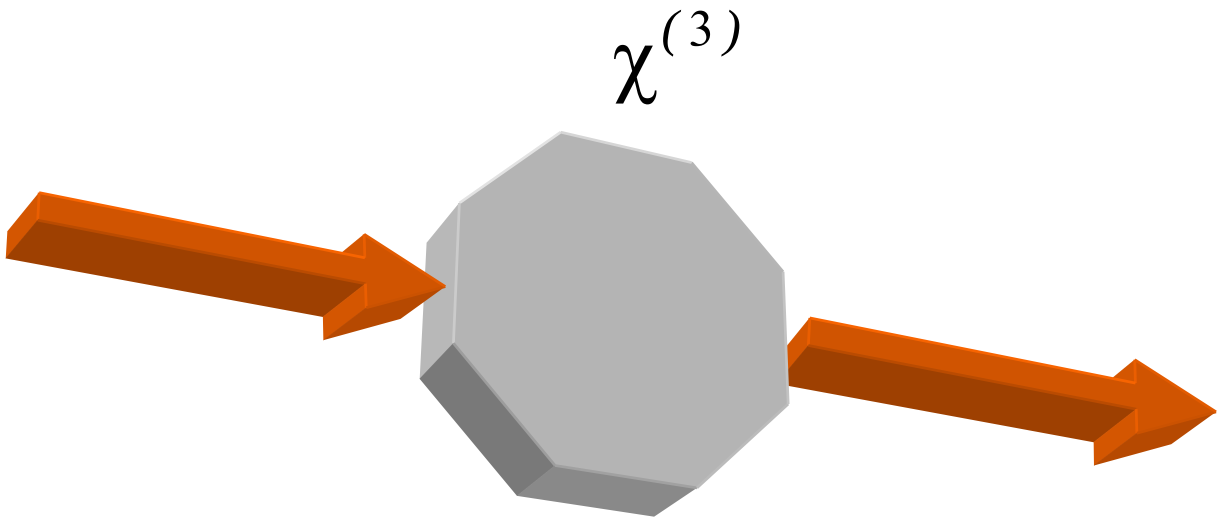
$$P_{NL} = \chi^{(3)} E^3$$

$n_2 > 0$ Material behaves as a convergent lens



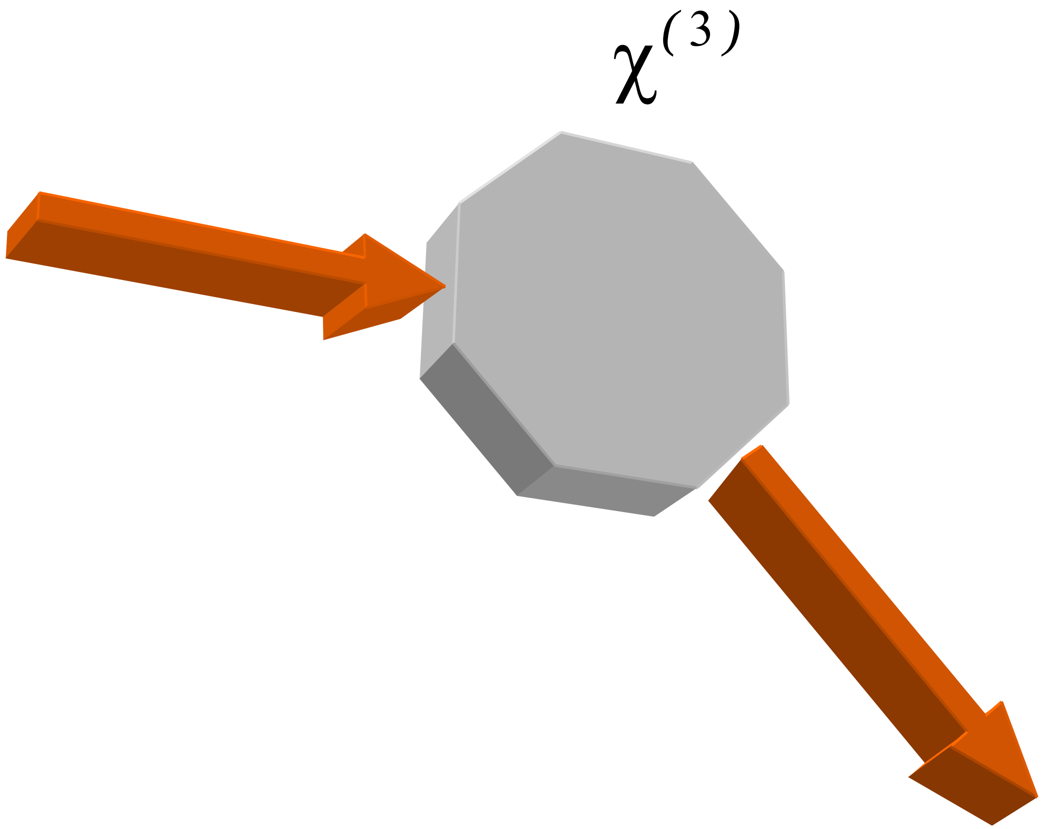
Optical switching

• low intensity



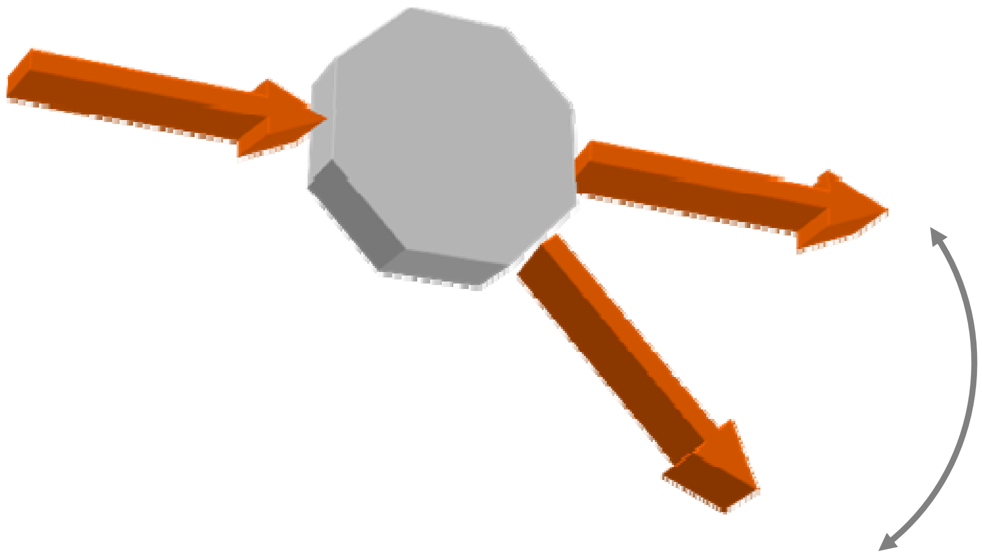
Optical switching

• high intensity



Self action process

Optical switching



response time: 10^{-15} s

response time 1×10^{-9} 1×10^{-15}

1GHz → 1 THz

1 million times faster

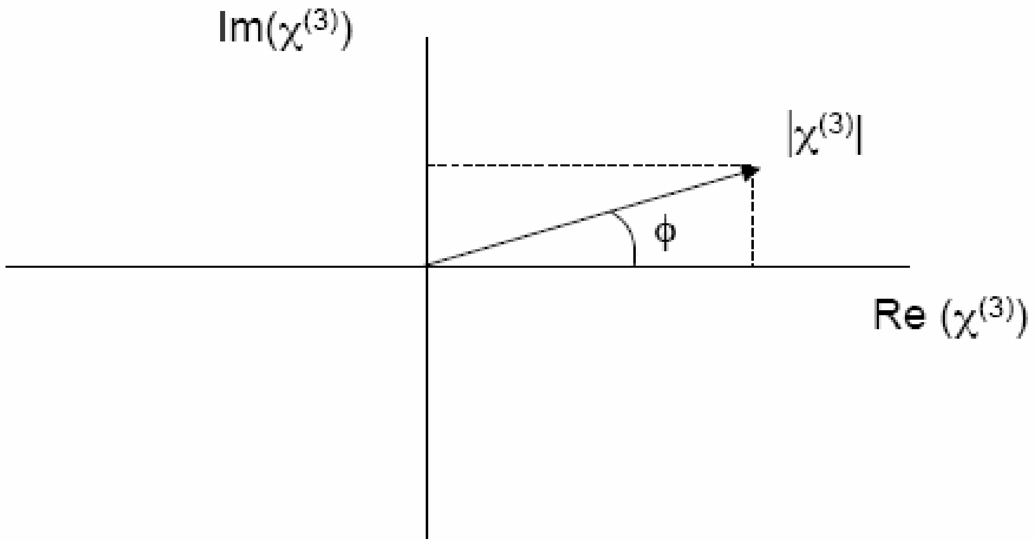
Nonlinear Optics

$\chi^{(3)}$ 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

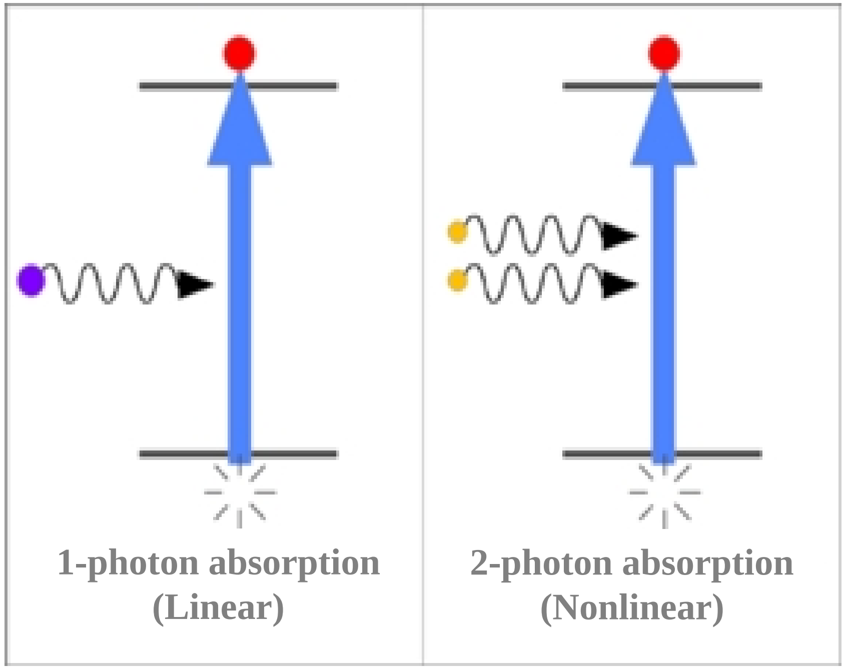
Absorptive process:

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

- nonlinear absorption
- two-photon absorption

Two-photon absorption (2PA) process

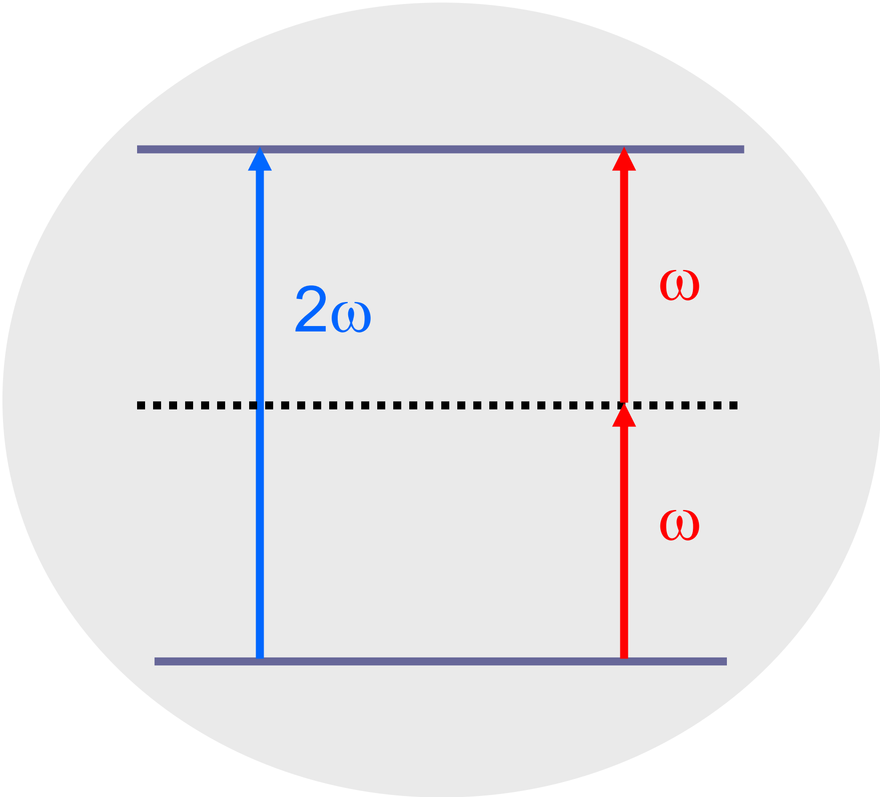
Phenomenon does not described for the Classical Physics and does not observed until the development of the Laser.



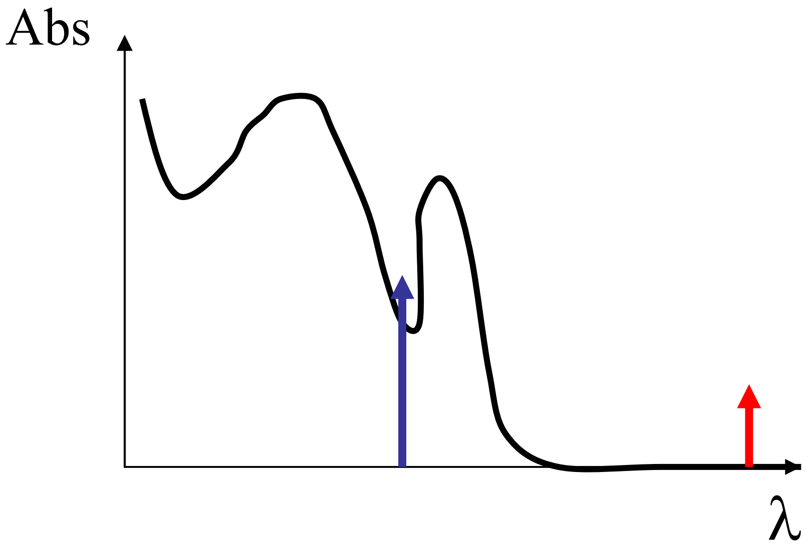
Theoretical model: Maria Göppert-Mayer, 1931

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

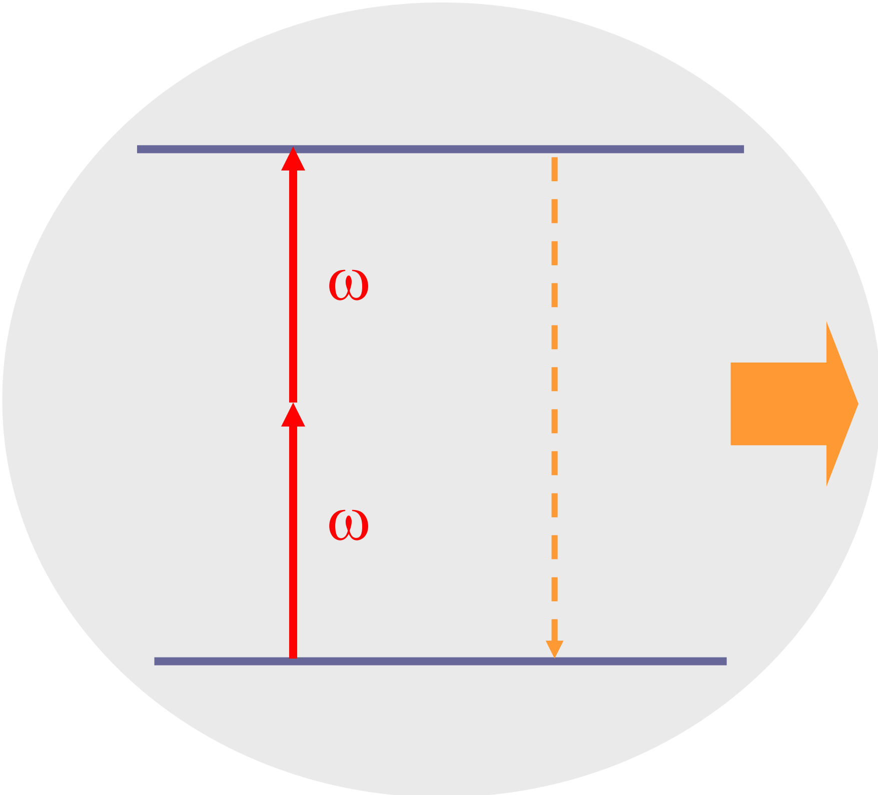
microfabrication

optical limiting

To protect eye and sensors from intense laser pulses

two-photon fluorescence

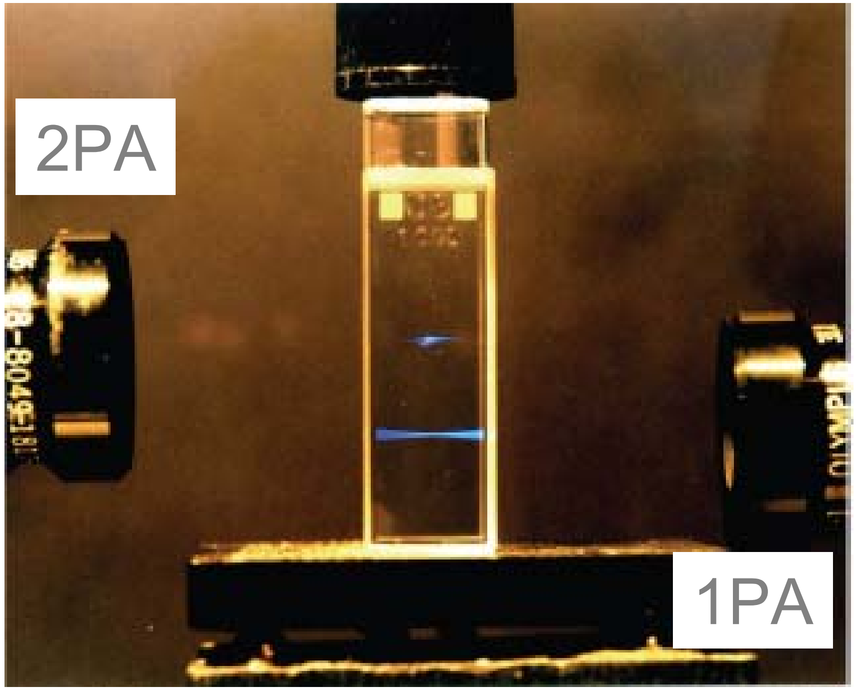
$$\alpha = \alpha_0 + \beta I$$

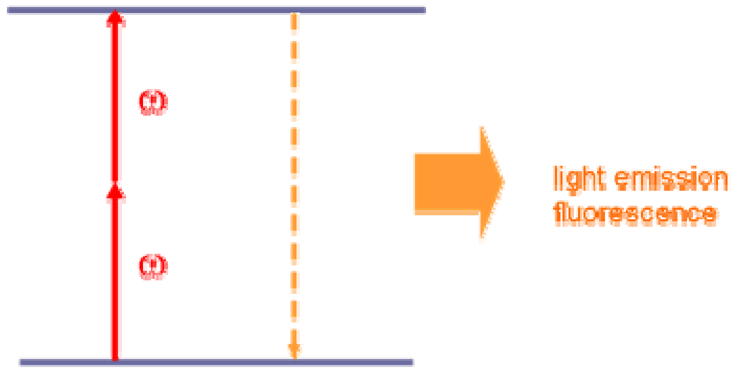


TPA rate constant $\propto \delta I^2$

localization of the excitation with 2PA

dilute solution of fluorescent dye





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

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

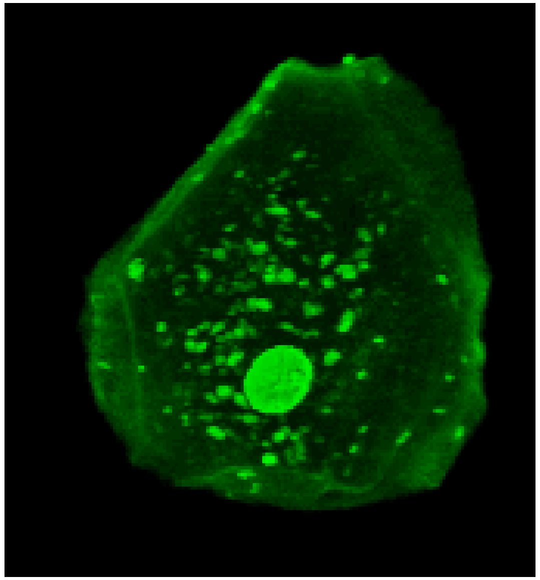
$$\Rightarrow TPA \sim \frac{1}{z^4}$$

spatial confinement of excitation

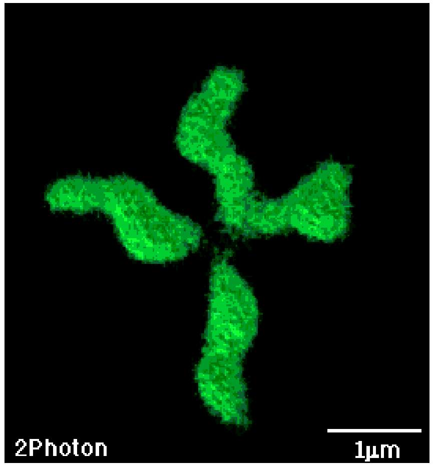
two-photon fluorescence microscopy

- Microscopy by two-photon fluorescence

3D image of a cell



Laboratory for Optics and Biosciences
Ecole polytechnique

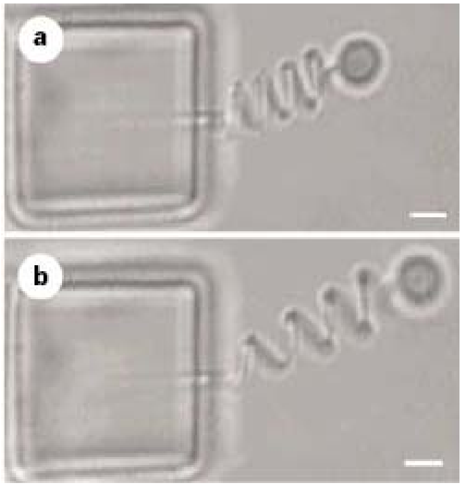


Human chromosome

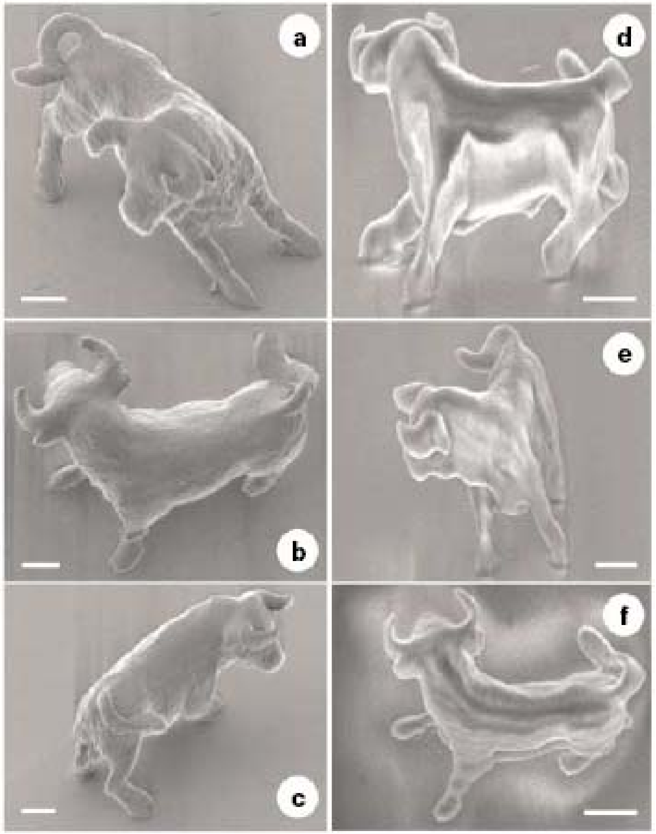
microfabrication

- **Two-photon polymerization**

Nature 412, 697-698 (2001)



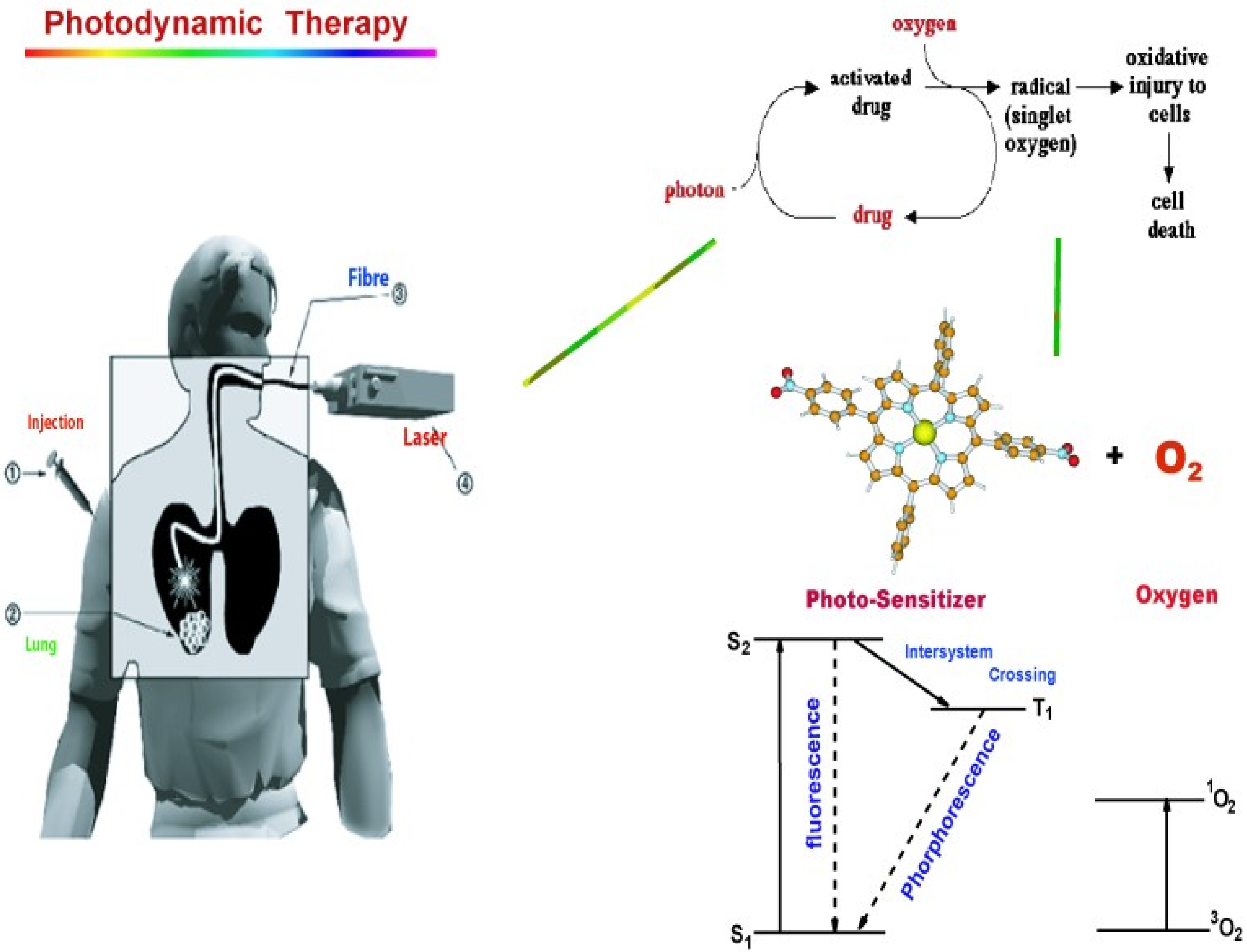
oscillator



Bull

two-photon photodynamic therapy

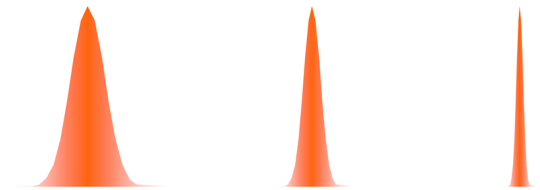
- PDT via dois fótons



Real applications in nonlinear optics

Very intense light: femtosecond pulses

Ti:Sapphire lasers



100 fs   50 fs   20 fs

1 fs = 10^{-15} s

Laser intensities ~ *100 GW/cm^2*

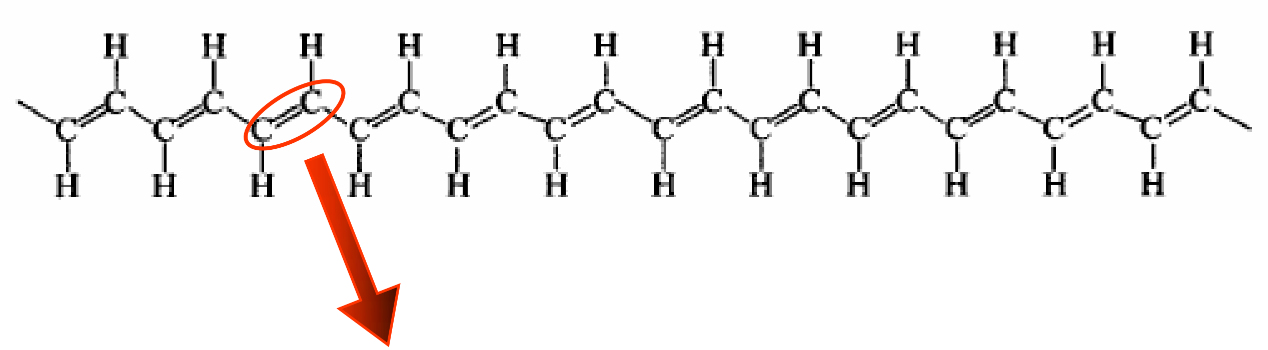
1 x 10^{11}W/cm^2

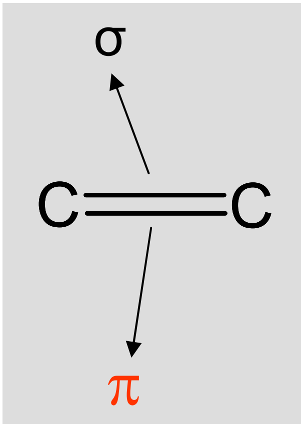
Laser pointer: 1 mW/cm^2 (1 x10^{-3} W/ cm^2)

Organic materials

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

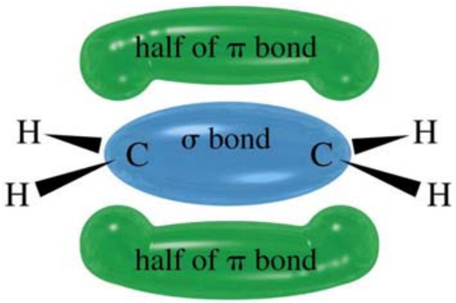
- π-conjugated structures





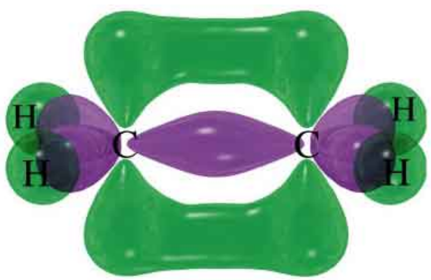
Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation



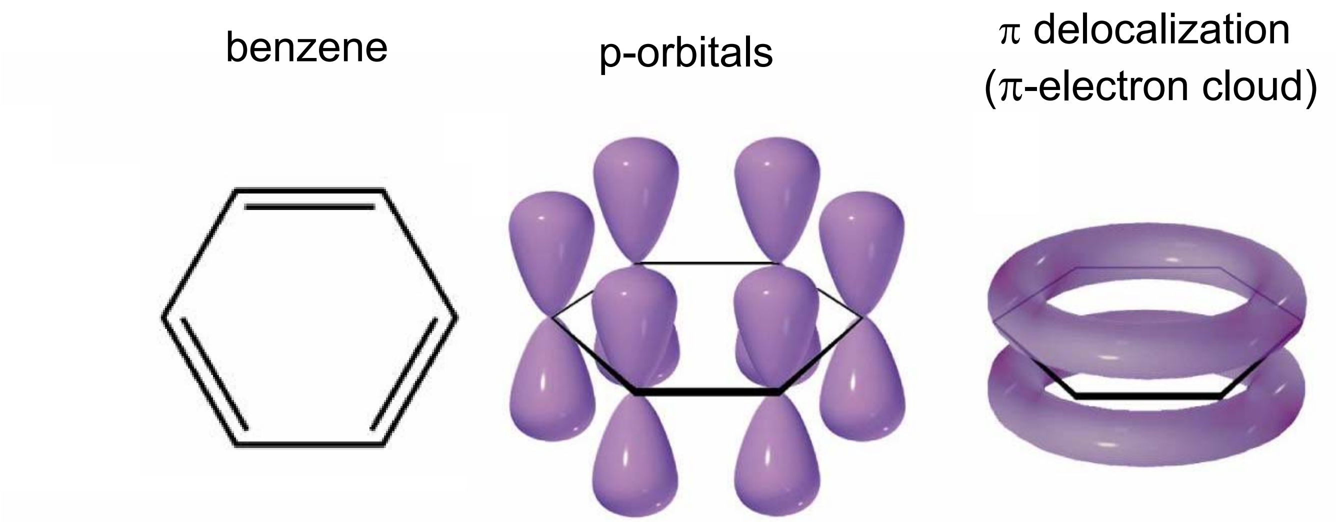
σ bond: forms a strong chemical bond; localized

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



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

π-conjugation



π bond in conjugated system: delocalized electrons

high optical nonlinearities

 $\chi^{(3)}$

Research

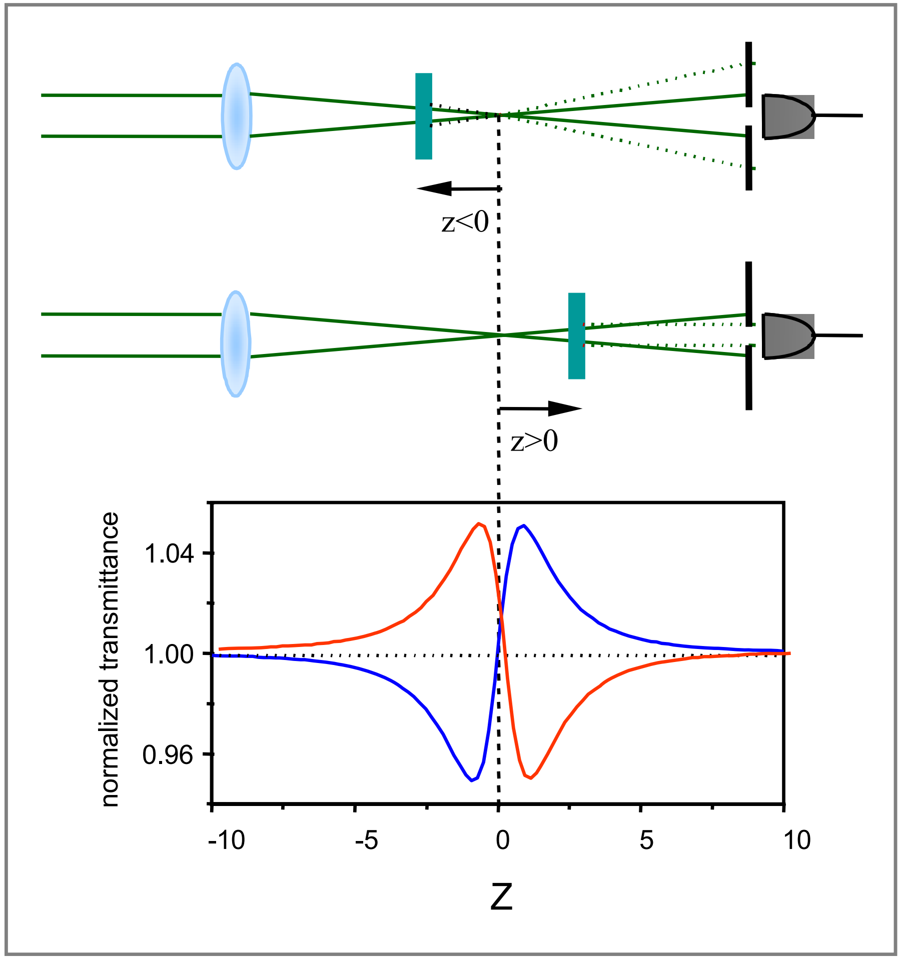
• Understanding the physical principles behind two-photon absorption

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

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

Z-scan

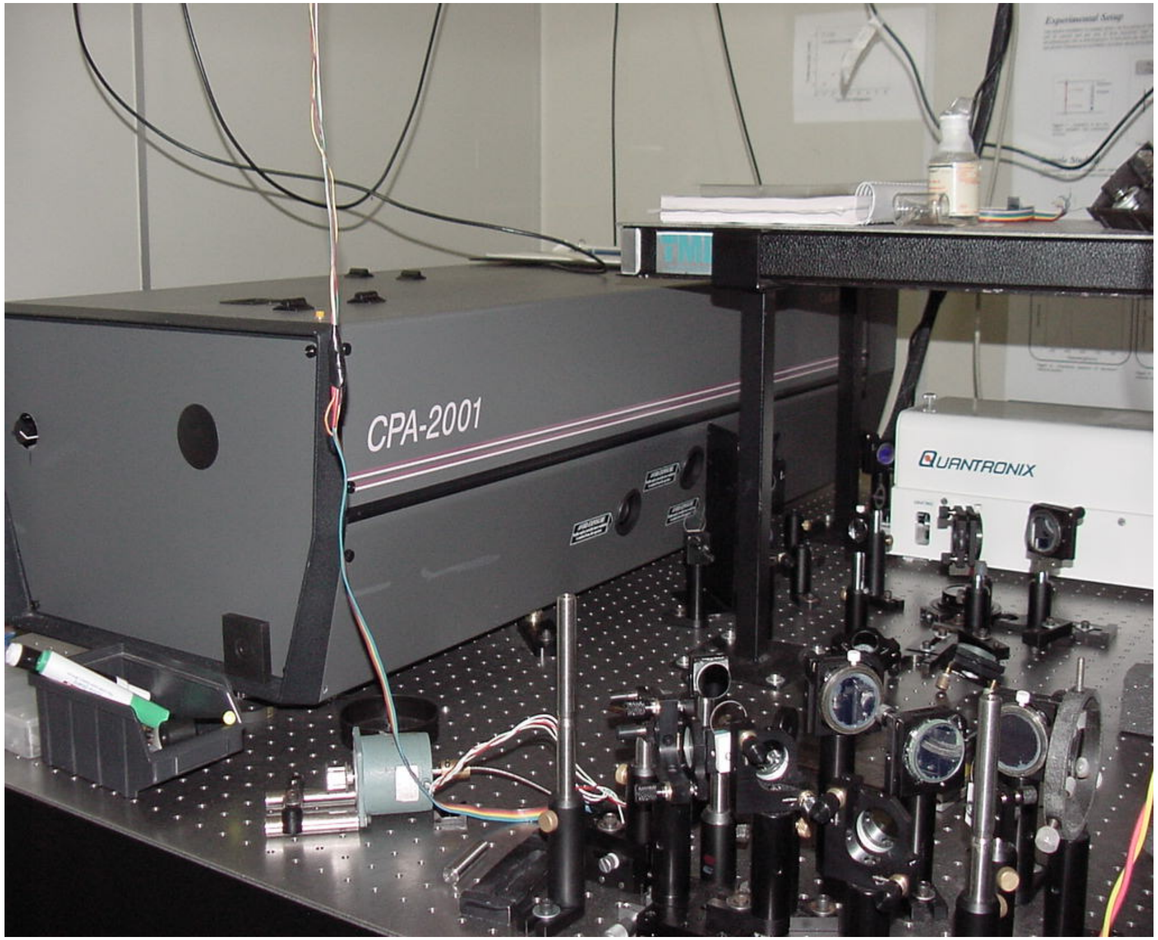
closed aperture Z-scan



$$n = n_0 + n_2 I$$

$$\Delta T \propto n_2 I$$

150 fs laser system



Ti:Sapphire amplifier

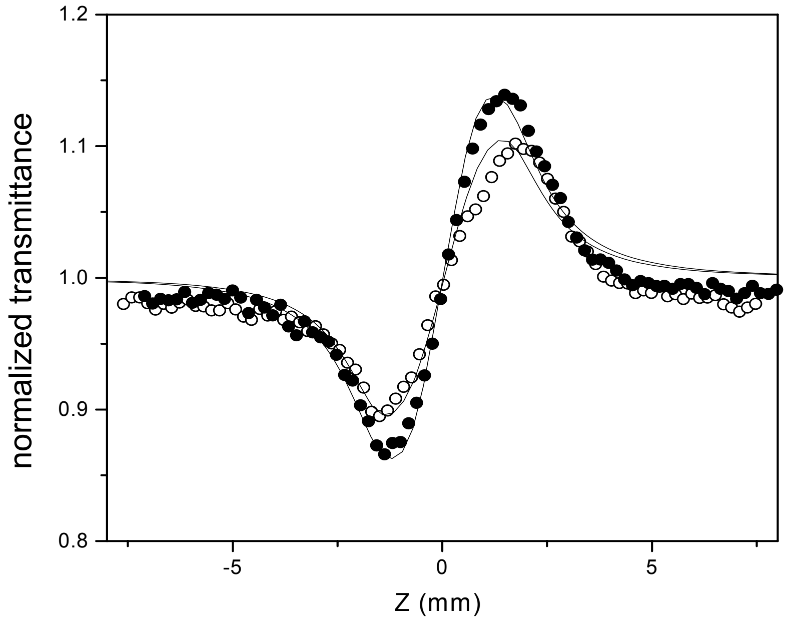
775 nm

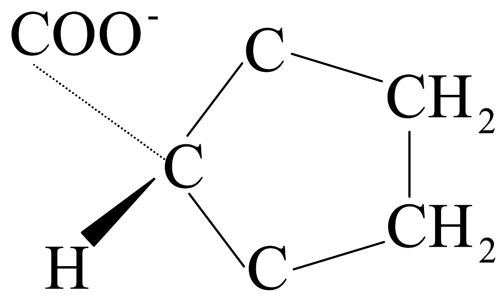
150 fs

800 μJ

Nonlinear refraction

Aminoacids





L-Proline

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

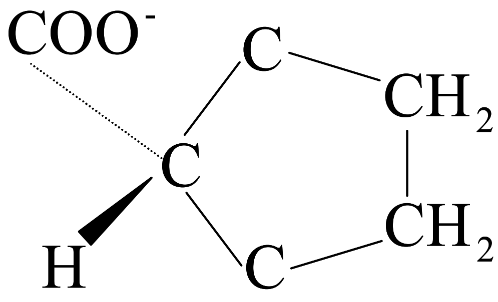
150 fs 100 GW/cm²

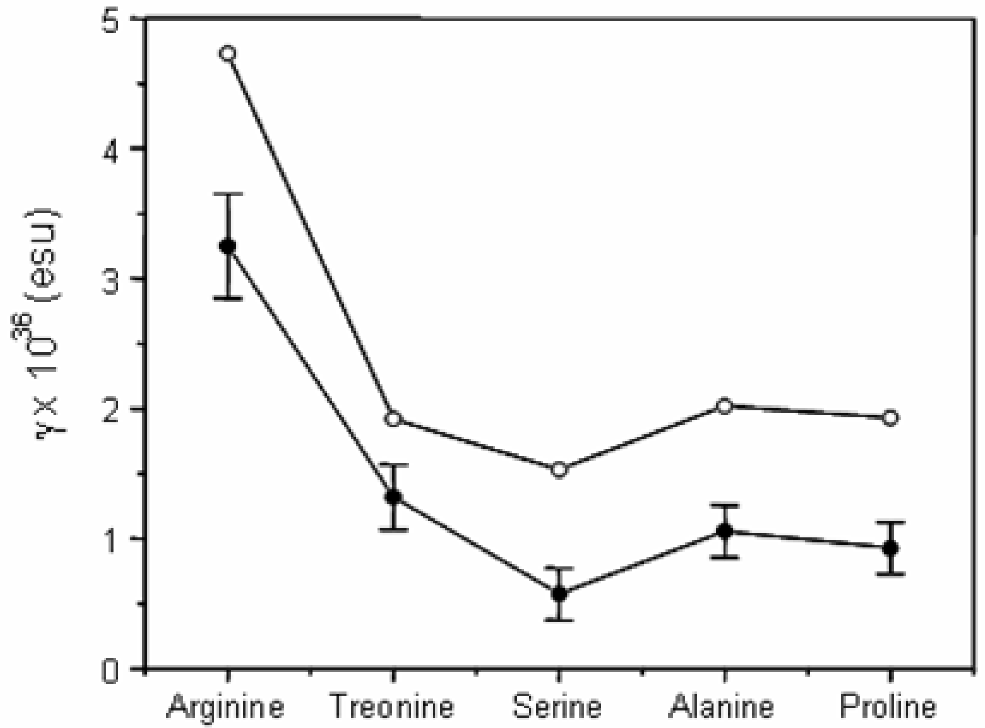
775 nm

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

Nonlinear refraction

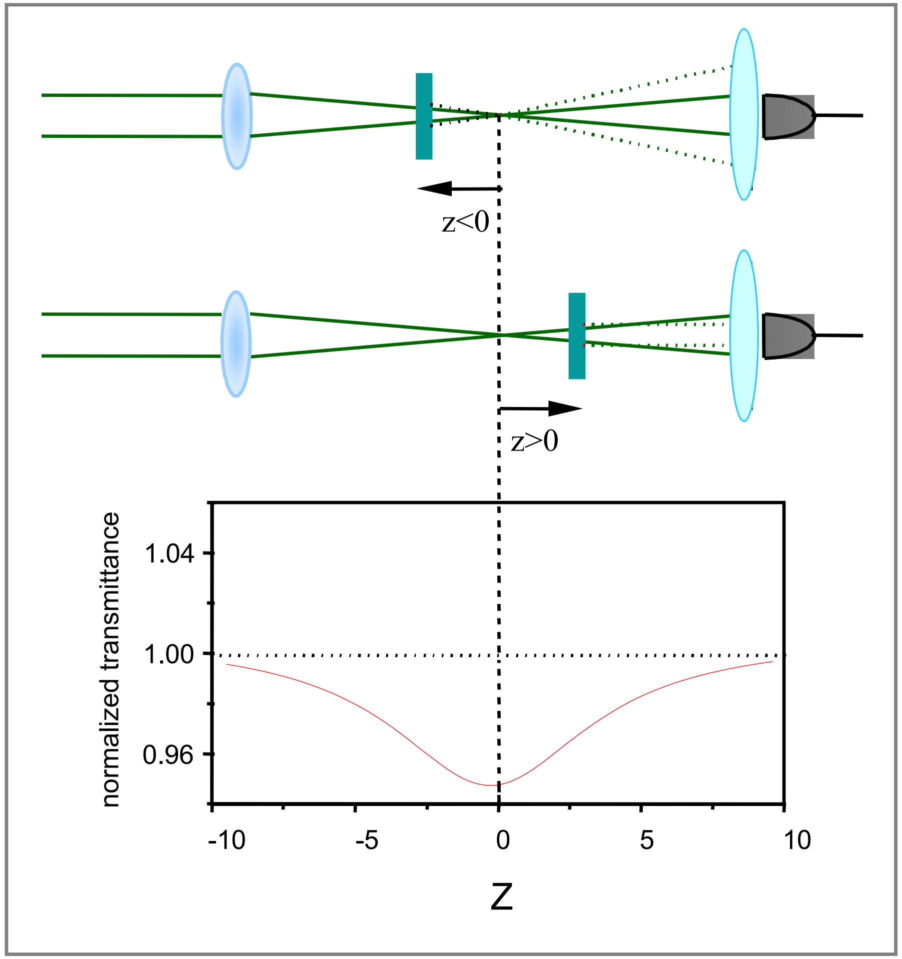
L-Proline





Z-scan (nonlinear absorption)

open aperture Z-scan



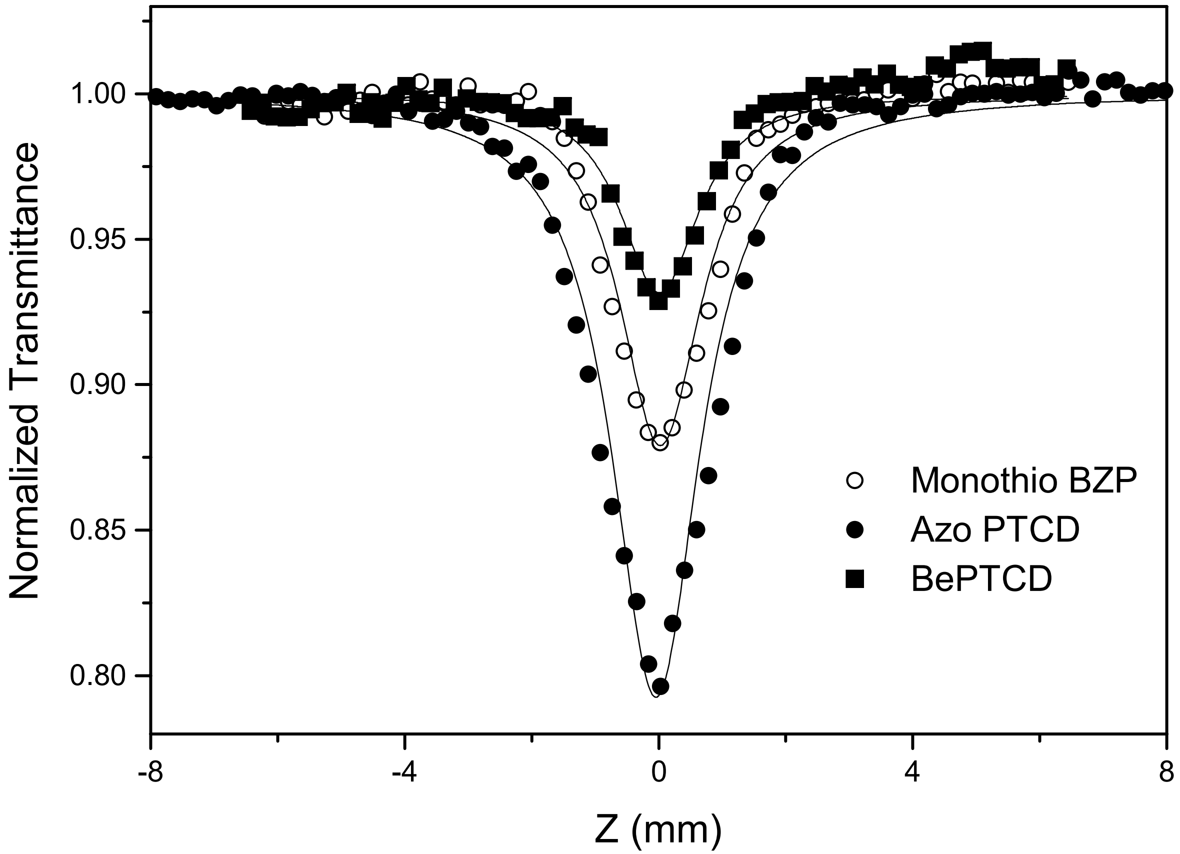
$$\alpha(I) = \alpha_0 + \beta I$$

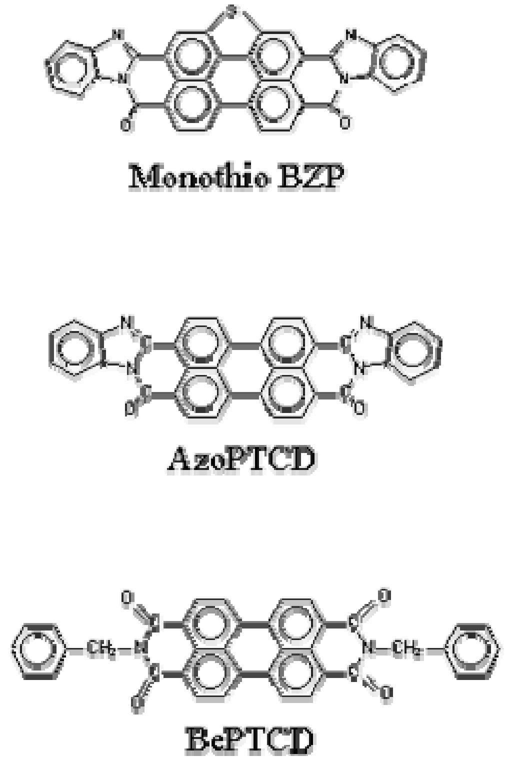
$$\Delta T \propto \beta I$$

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

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

Nonlinear absorption



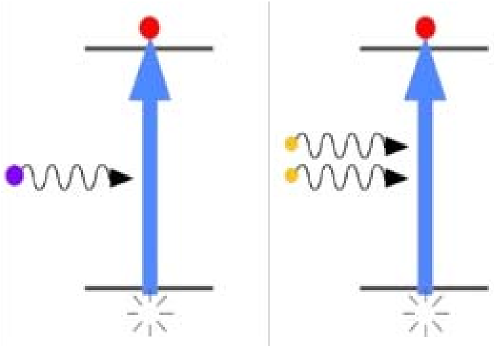


775 nm

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

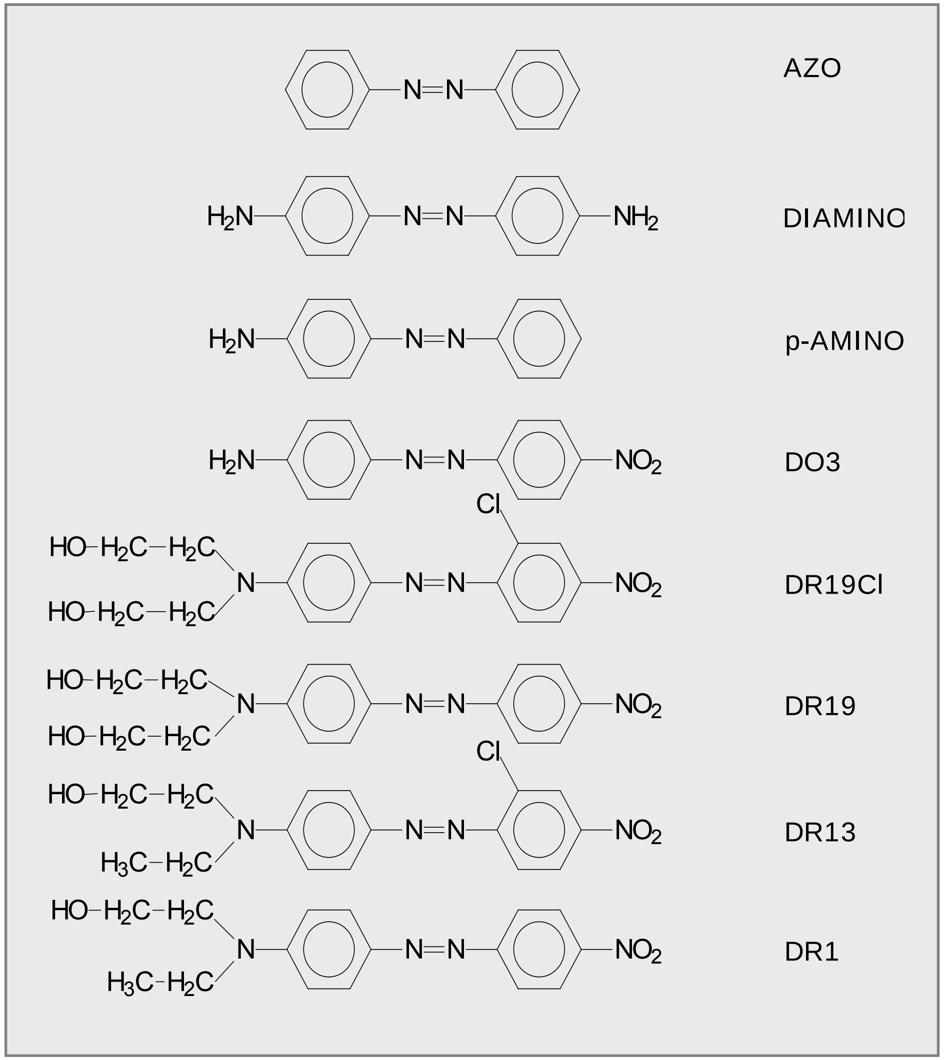
Optical parametric amplifier

460 - 2600 nm

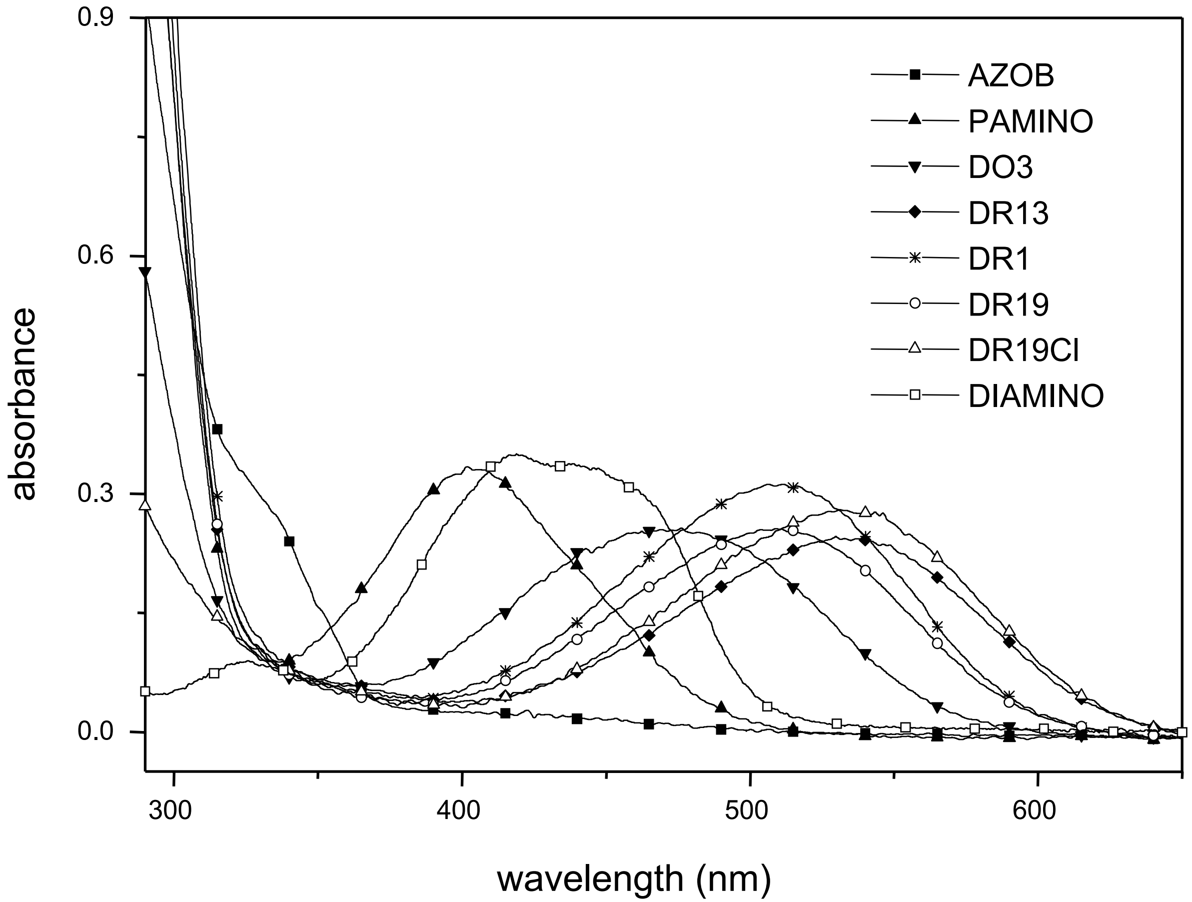
≈120 fs

20-60 μJ

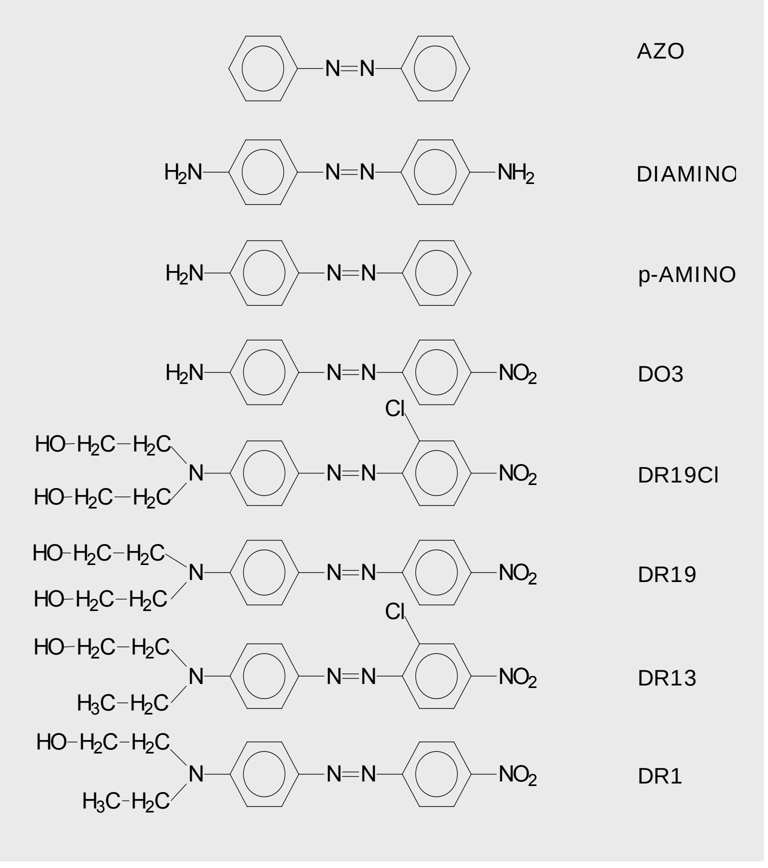
Azoaromatic samples

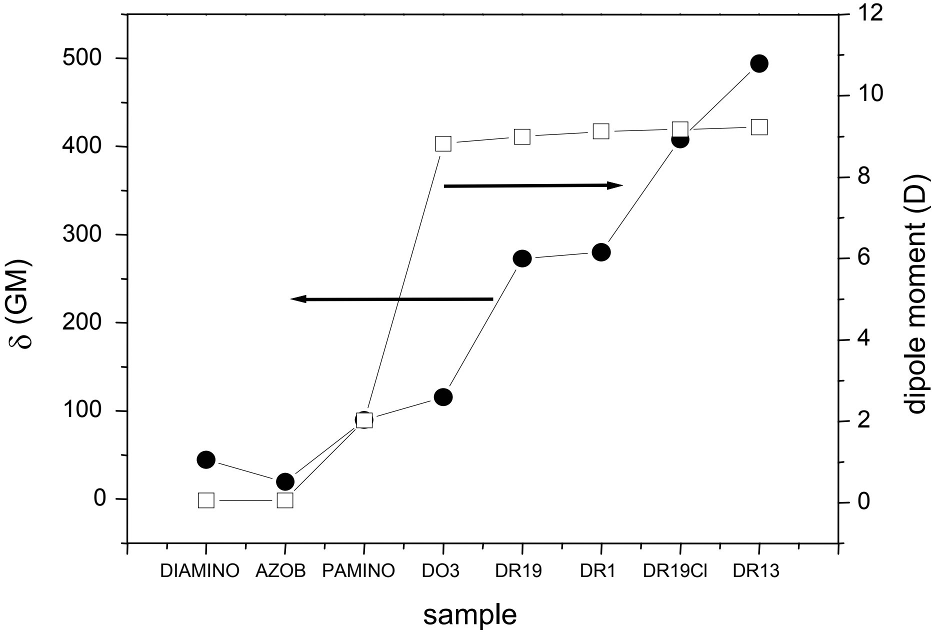


Linear absorption of azoaromatic compounds



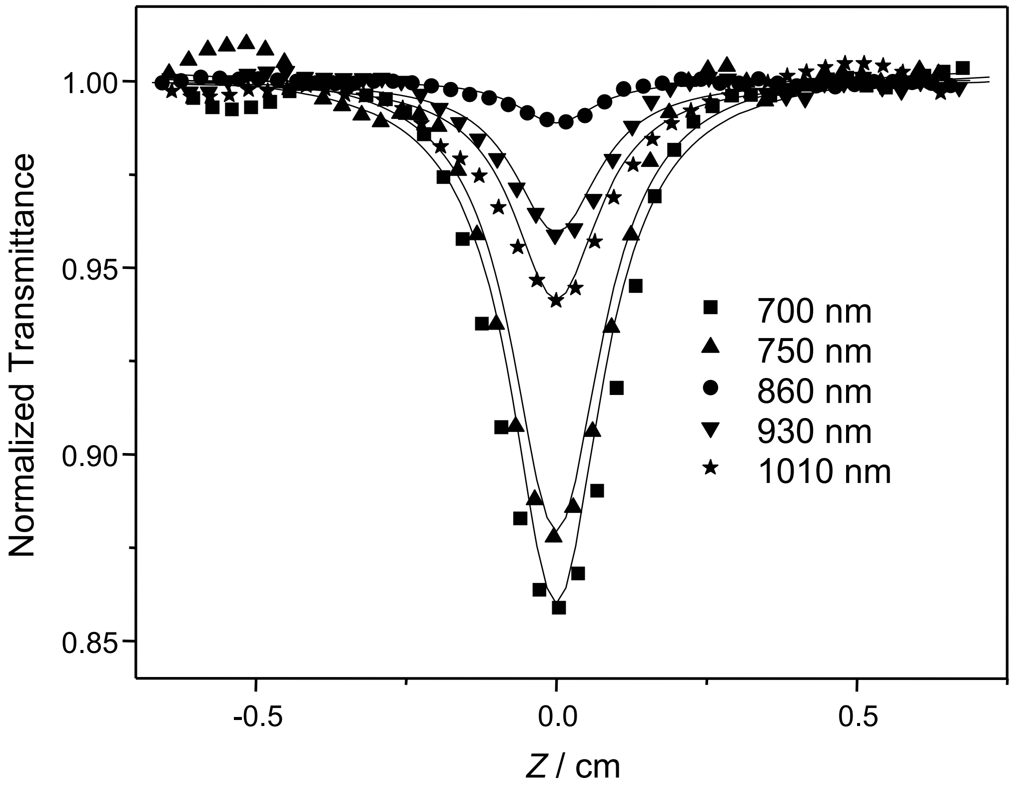
Two-photons absorption





775 nm

Two-photon absorption



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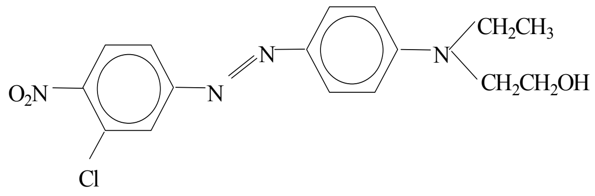
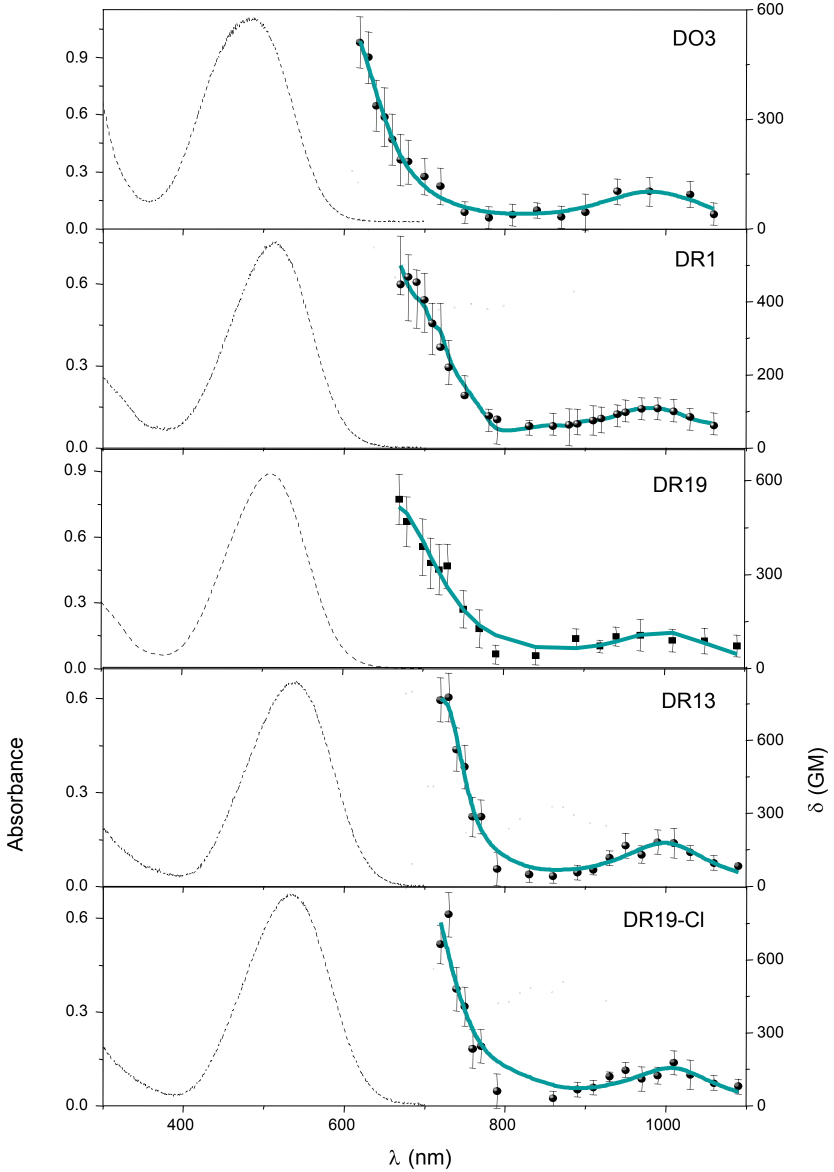


$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}$$

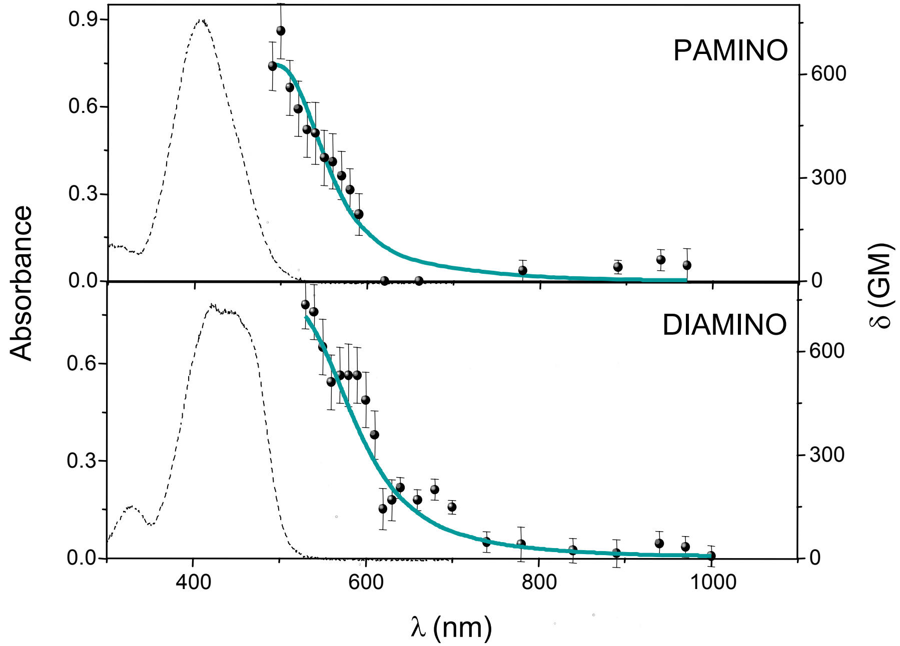
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

Psuedostilbenos

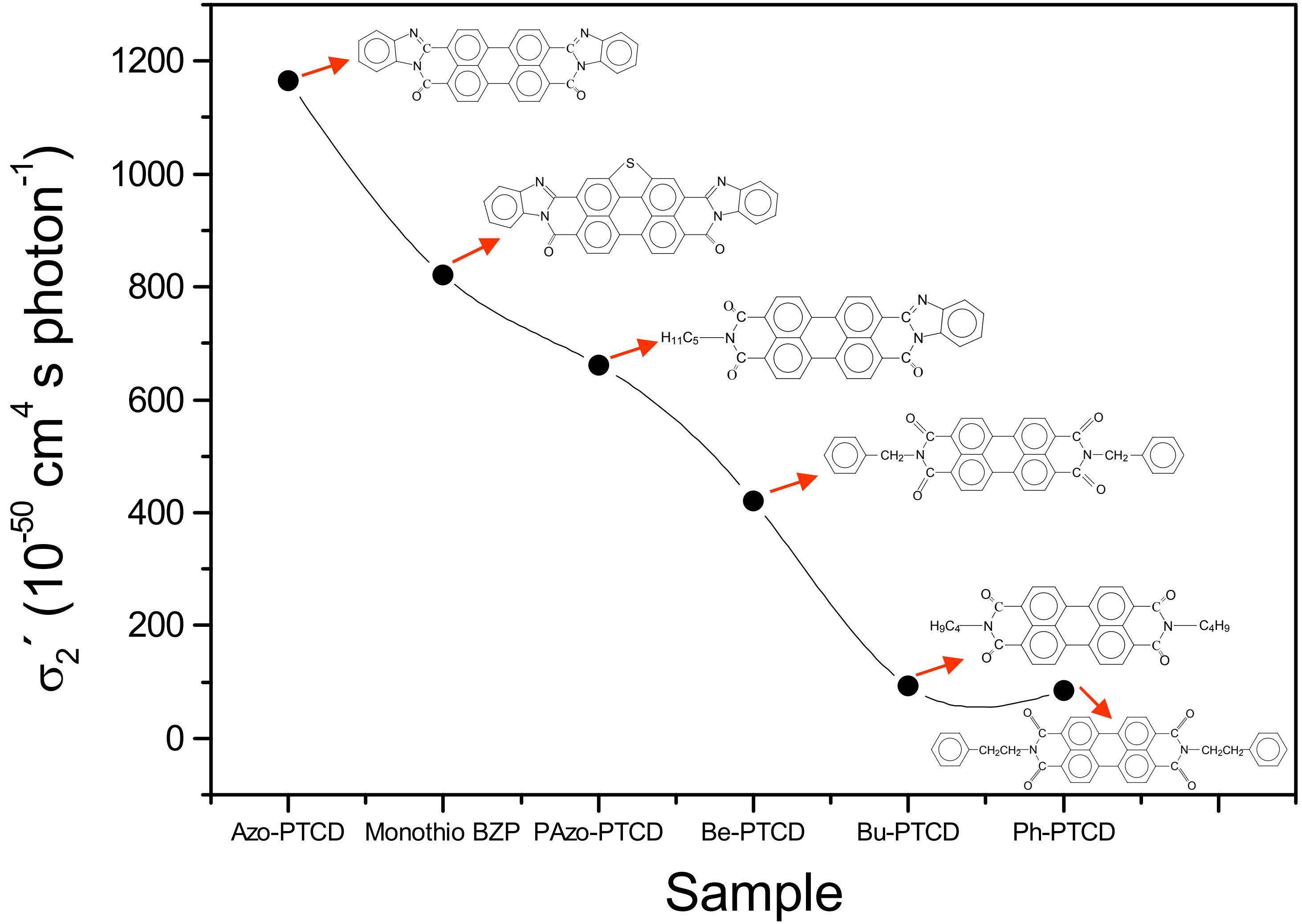


Aminoazobenzenos



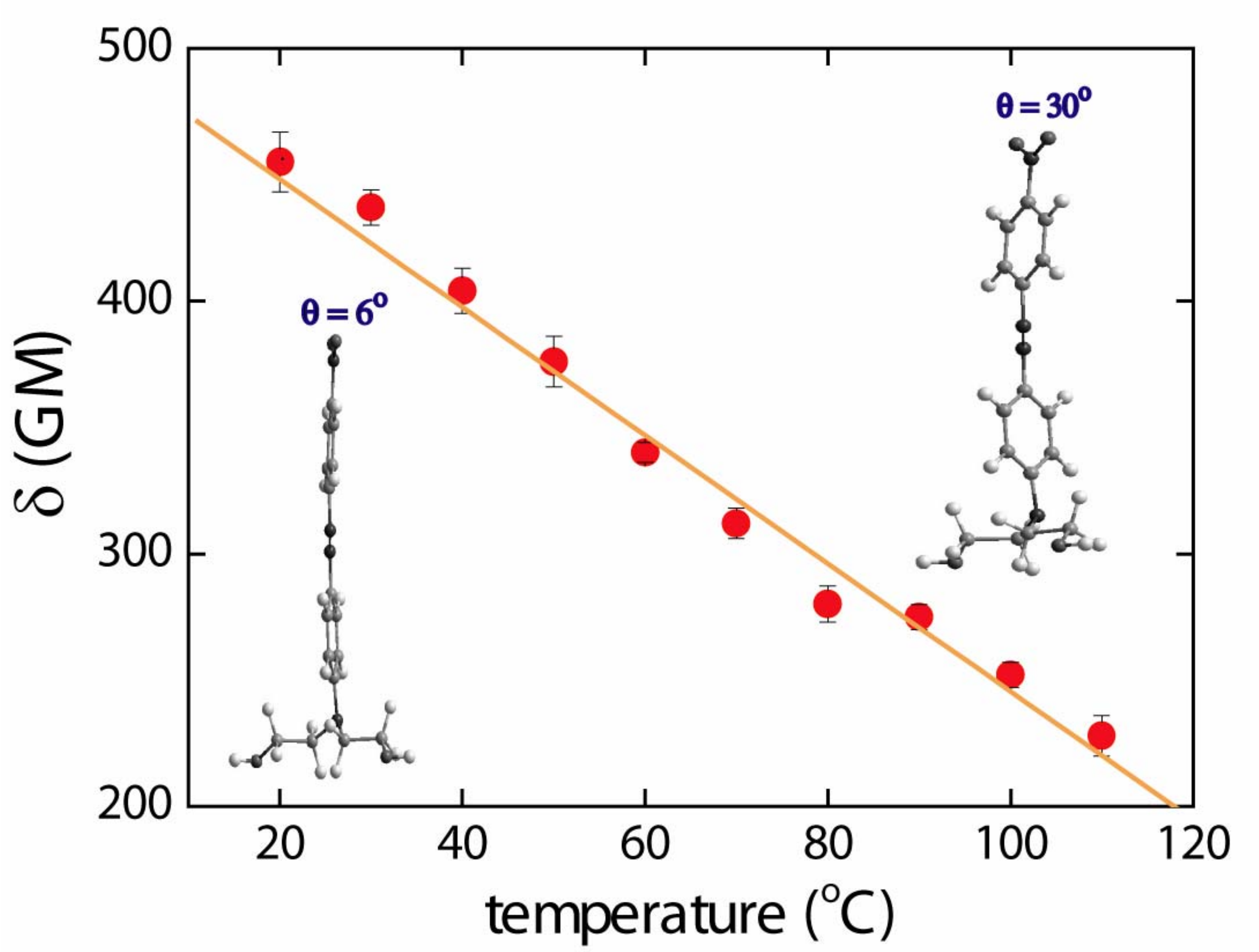
$$\delta(\nu) \propto \frac{\nu^2}{(\nu_{i0}-\nu)^2+\Gamma_{i0}^2}\left[\frac{A_1}{(\nu_{f_1 0}-2\nu)^2+\Gamma_{f_1 0}^2}+\frac{A_2}{(\nu_{f_2 0}-2\nu)^2+\Gamma_{f_2 0}^2}\right]$$

Two-photon absorption of perylenes



Correlation between molecular structure and the nonlinear response

Planarity of the π-bridge

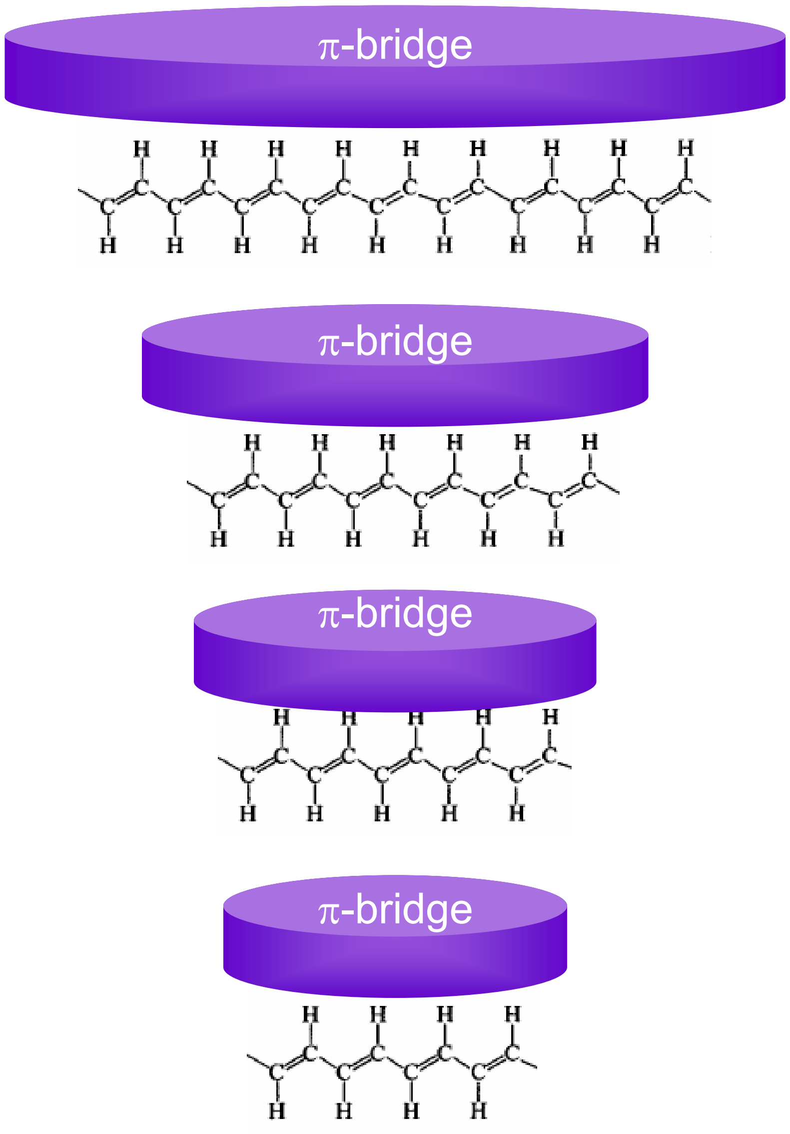


Thermally induced torsion in the molecular structure

Molecular design strategy

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

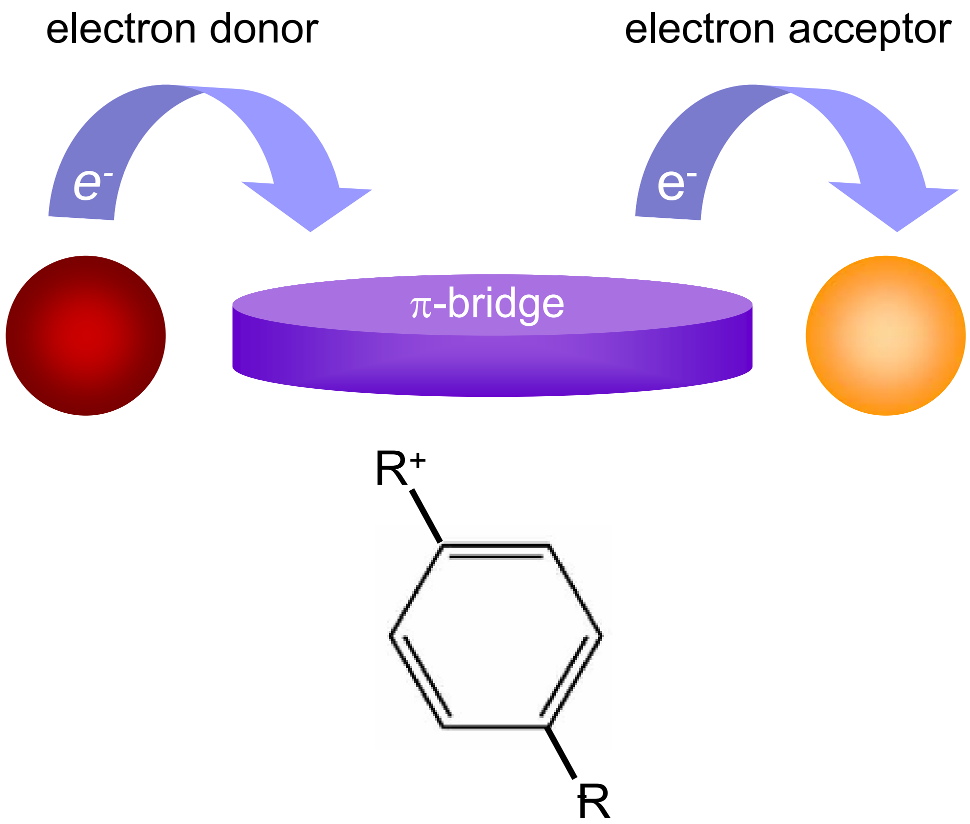
Increasing the conjugation



Increase in the optical nonlinearity

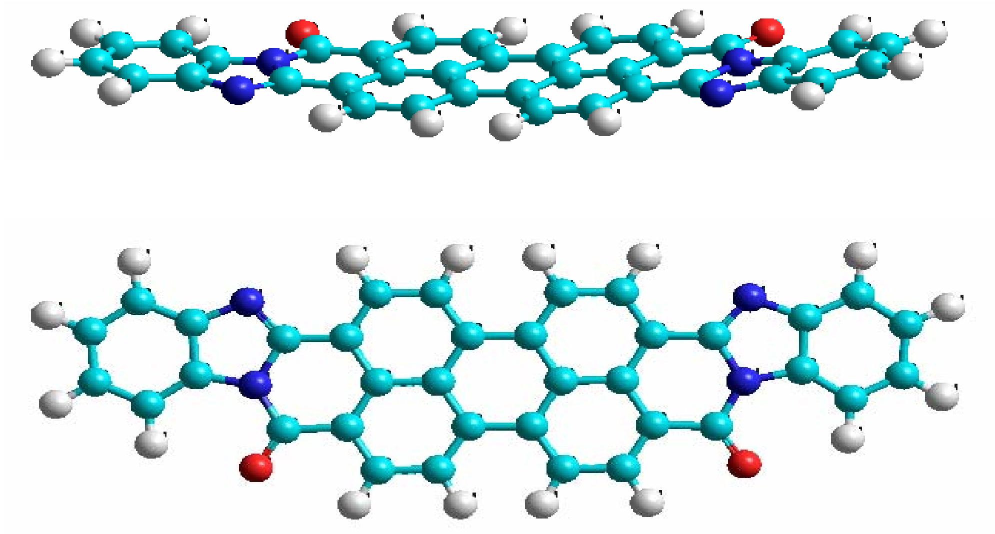
Increasing the π-conjugation

Donor and acceptor groups



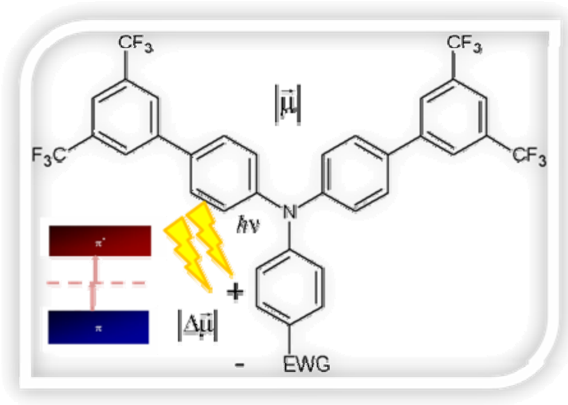
Incorporating electron donor and acceptor groups in a predictable way leads to an enhancement of the optical nonlinearity

Planarity of the π-bridge

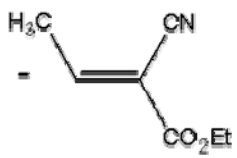


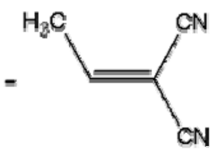
Perylene compounds are very planar molecules, which explains its high optical nonlinearities

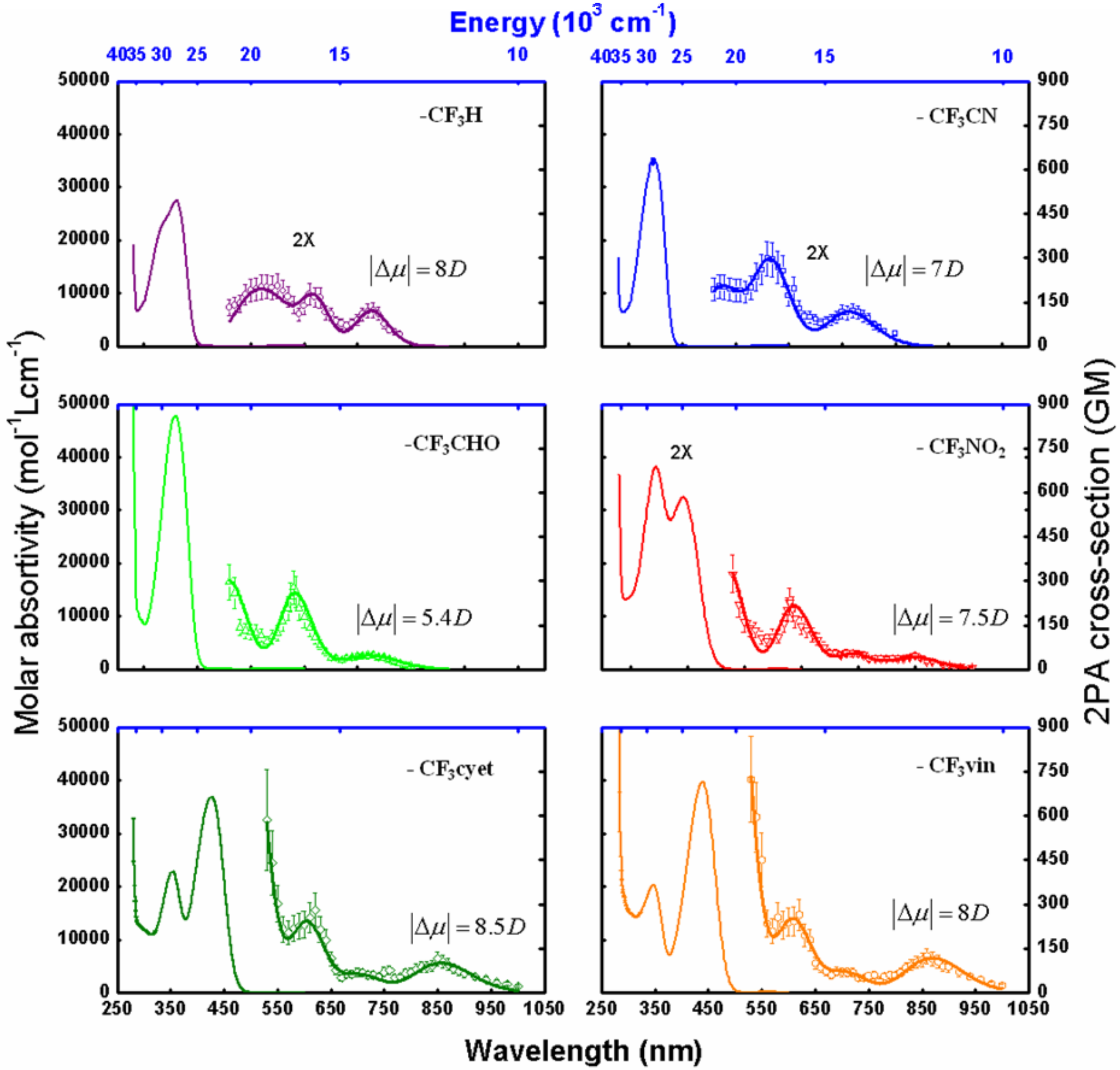
2PA: triarylamine compounds with electron withdrawing substituints



1. -H
2. -CN
3. -CHO
4. $-NO_2$

5. - 

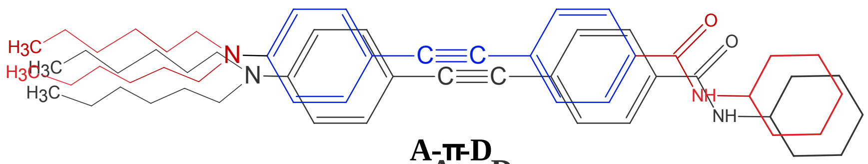
6. - 



Prof. Elena Ishow

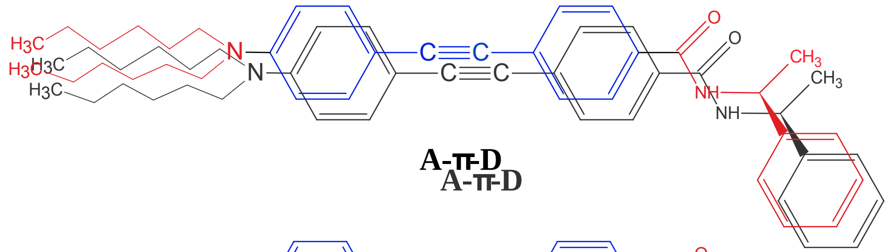
Chiral Compounds

JCM874
JCM874



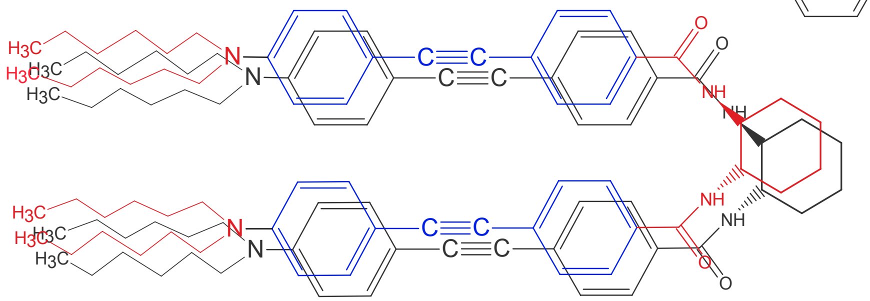
A-π-D
A-π-D

FD43
FD43



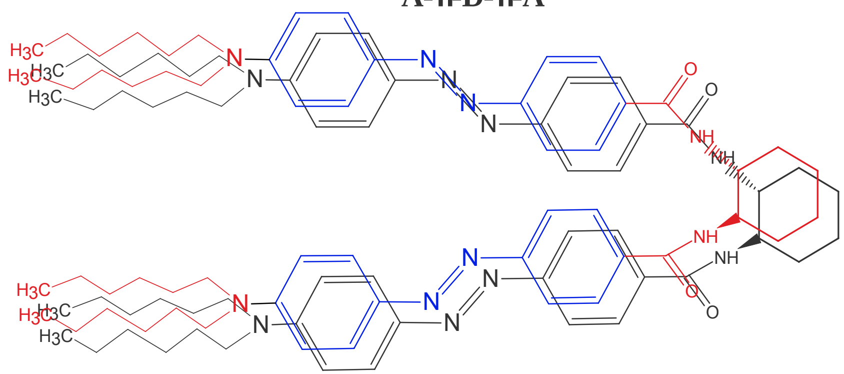
A-π-D
A-π-D

FD48
FD48



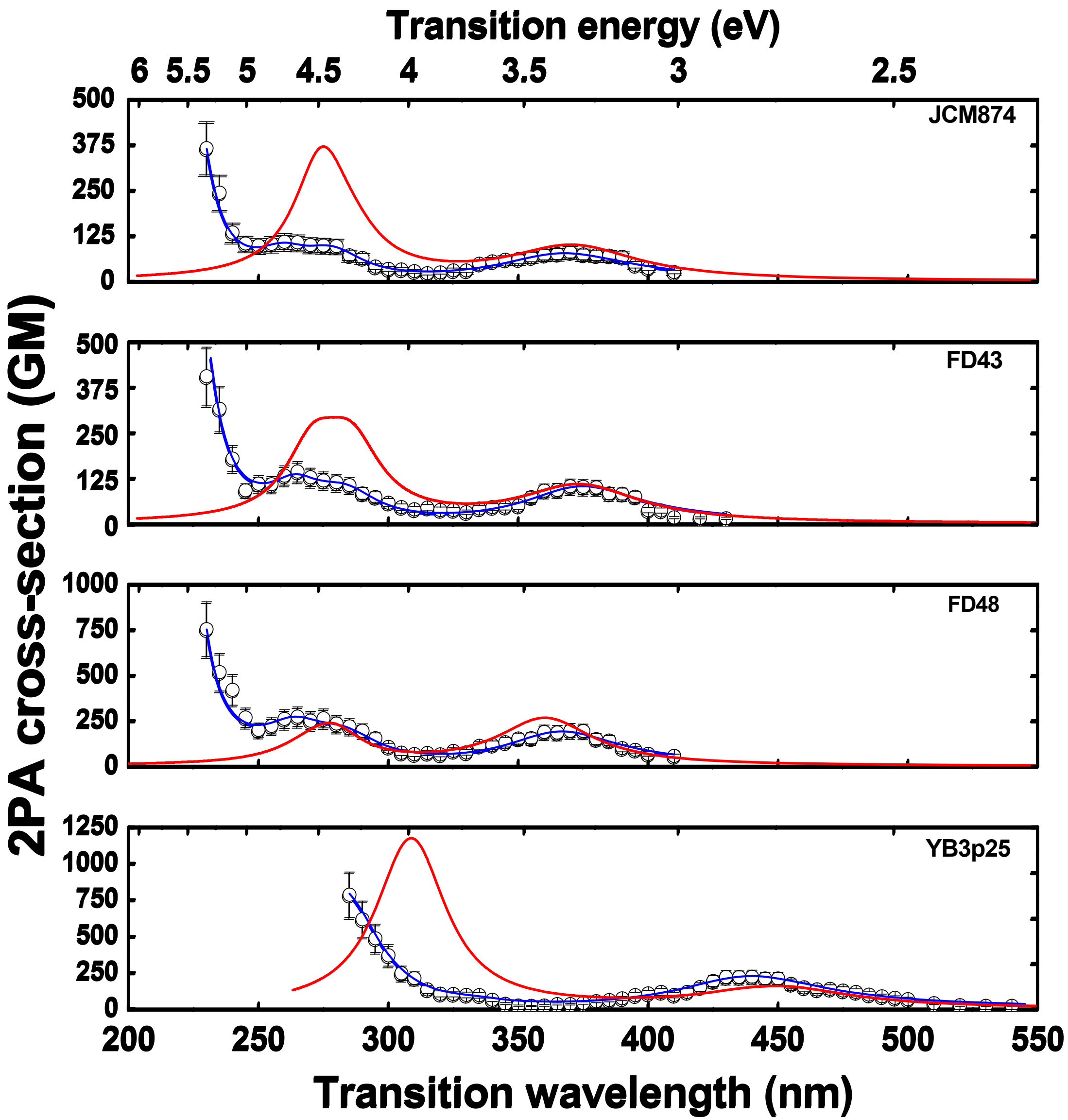
A-π-D-π-A
A-π-D-π-A

YB3p25
YB3p25

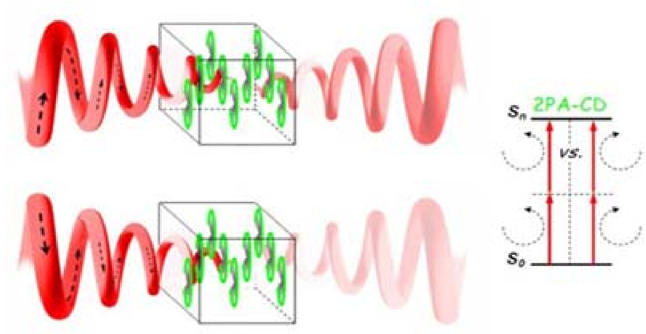


A-π-D-π-A
A-π-D-π-A

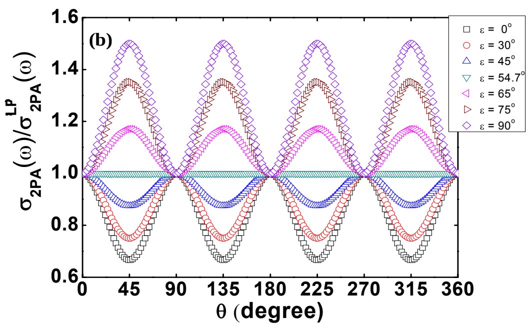
Comparison between experimental and theoretical results



Polarization effect on the 2PA



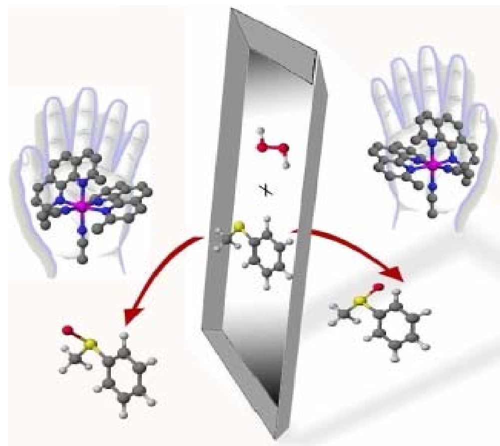
➢ *Recently, the polarization effect on the 2PA properties of organic compounds has drawn great attention from scientific community due the possibility of explore new optical effects.*



➢*For example, 2PA circular-linear provide information about the angle between dipole moments and symmetry of excited states.*

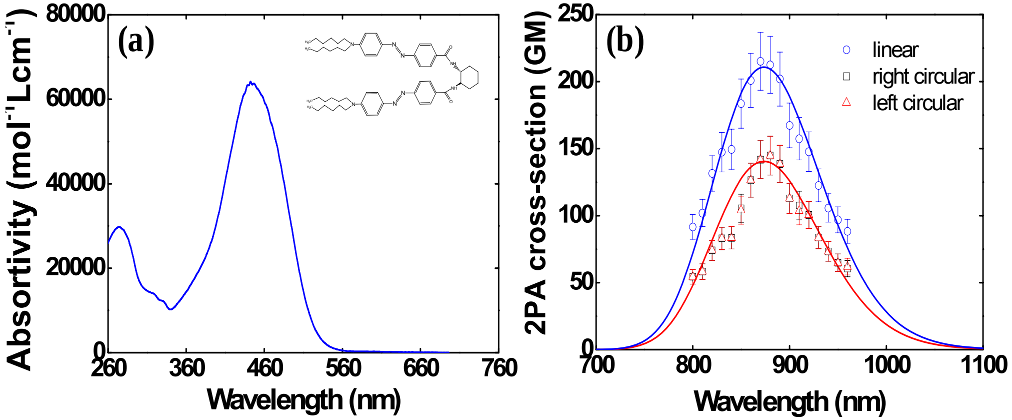
➢*In chiral samples, it allows obtaining information on magnetic-dipole and transition electric-quadrupole moment.*

$$\sigma_{2PA}^{DC}(\omega)=\frac{4}{5}\frac{(2\pi)^5\omega^2}{(ch)^2}\{b_1B_1(\omega)+b_2B_2(\omega)+b_3B_3\}g(2\omega),$$

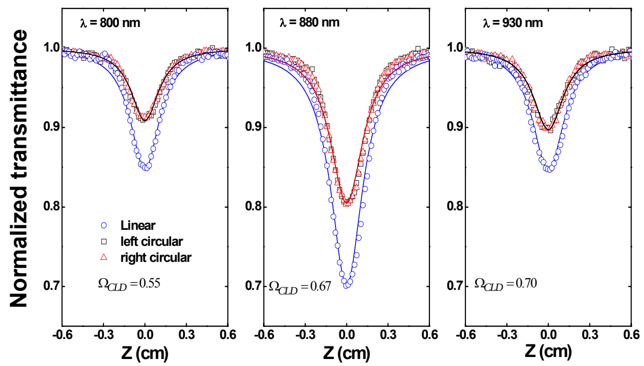


Results: Polarization effect on the 2PA properties

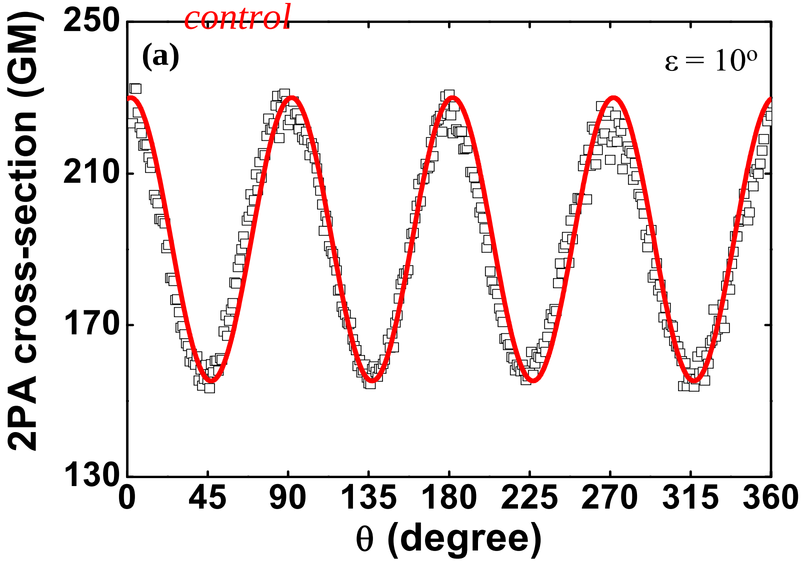
➢*Polarization effect on the 2PA properties of organic compounds YB3p25*



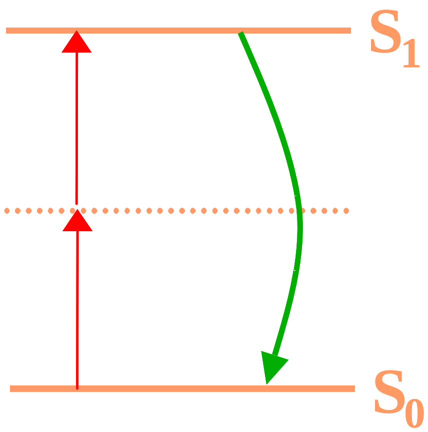
➢*We did not observe differences between 2PA using right and left circularly polarized light*

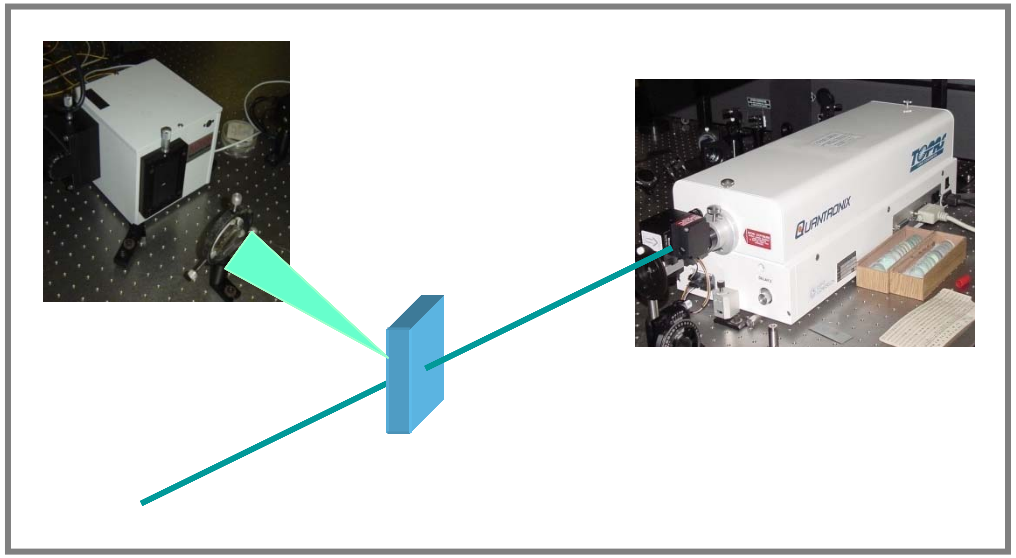


➢*Polarization induced 2PA control*



Two-photon excited fluorescence

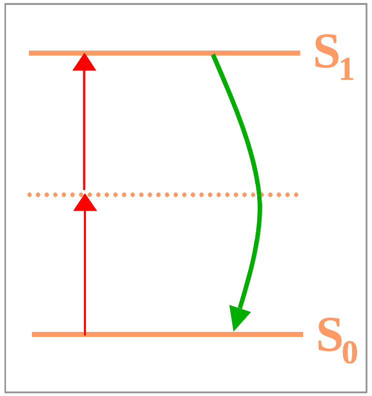




$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

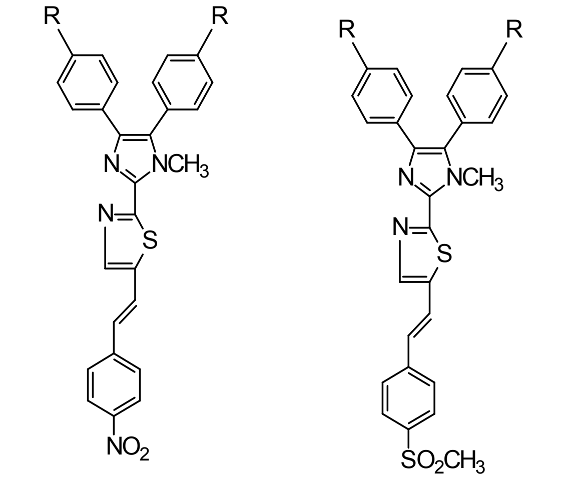
$$F \approx I^2$$

Multi-photon excited fluorescence



$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

$$F \approx I^2$$

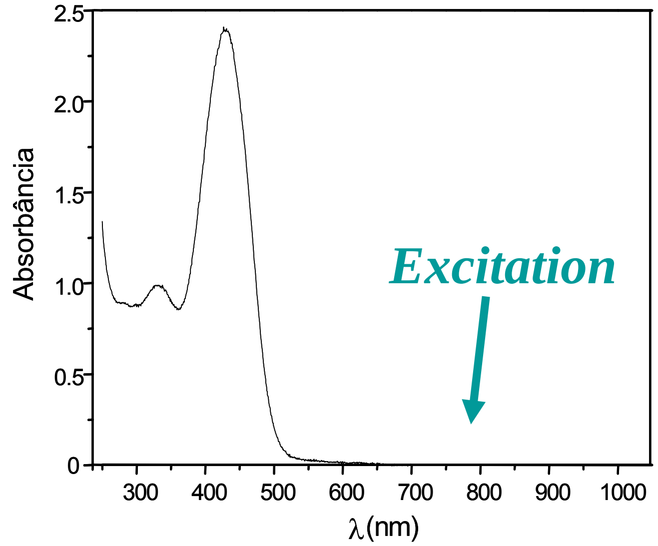


1 **2** **3**
R = H, CH_3, OCH_3

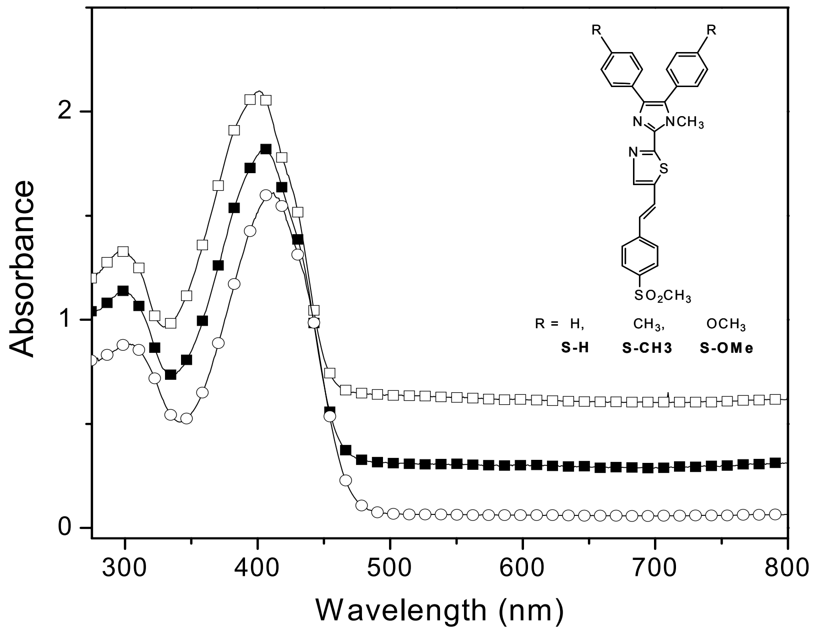
4 **5** **6**
R = H, CH_3, OCH_3

NITRO **SULFONIL**

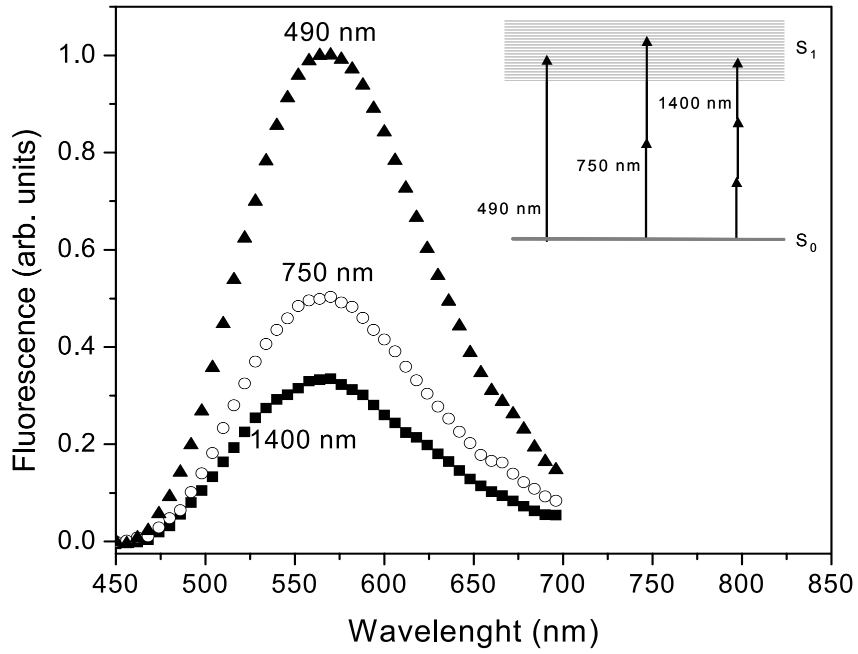
Y-shaped



Fluorescence excited by two and three photons

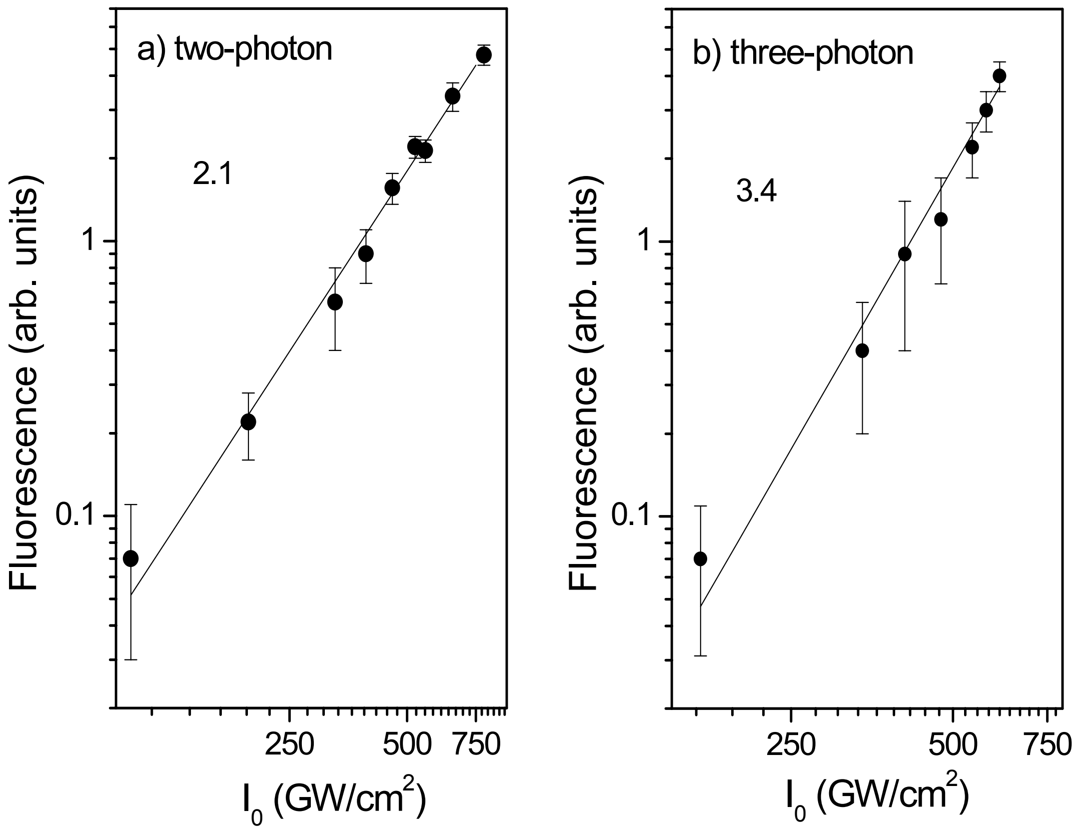


Absorption



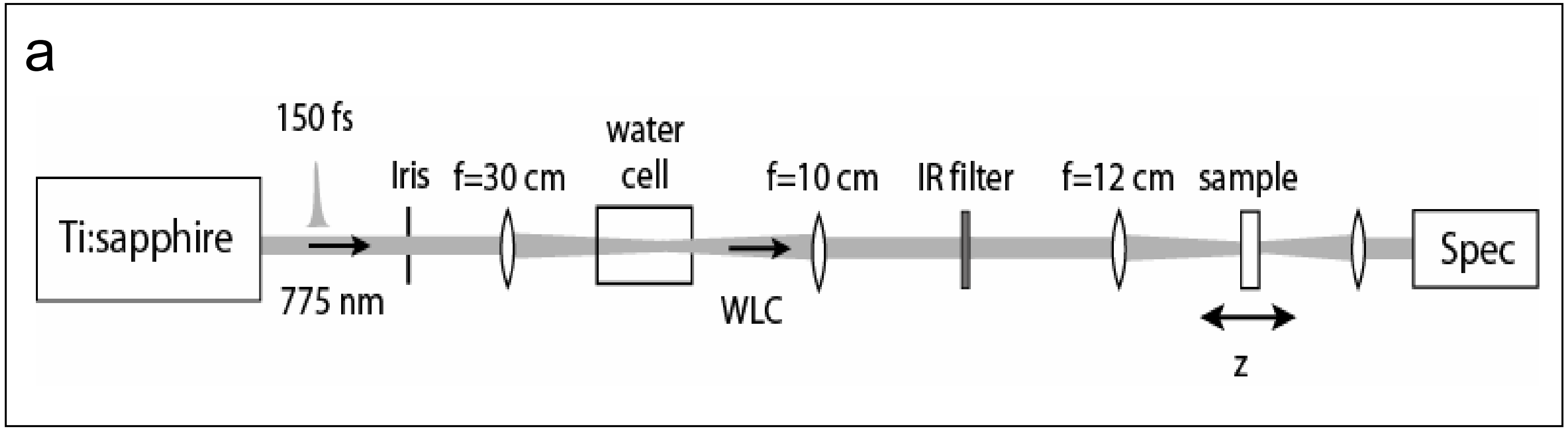
Fluorescence

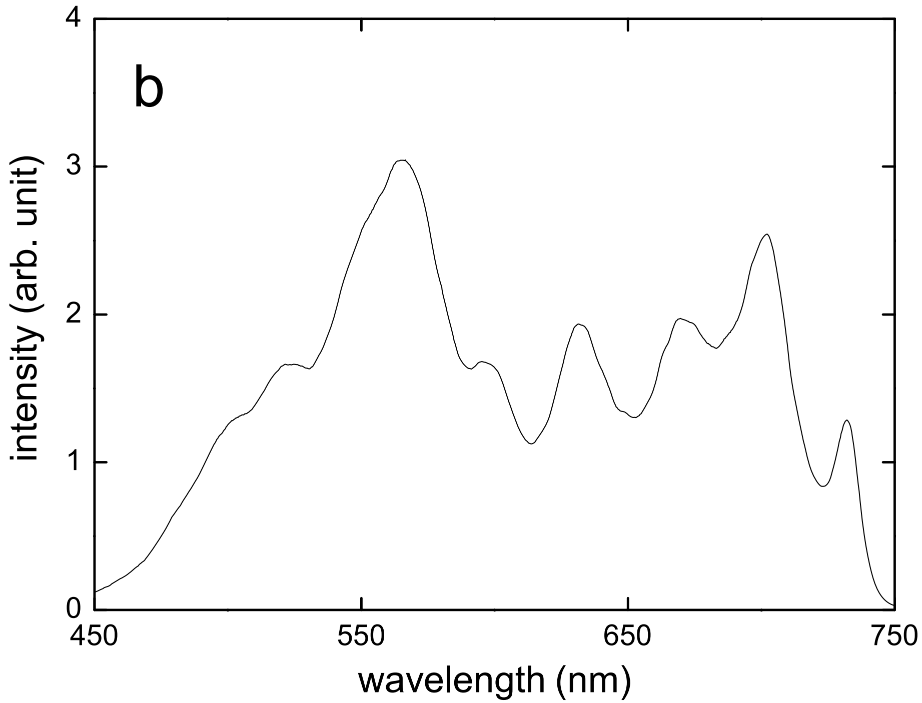
Two-photon excited fluorescence

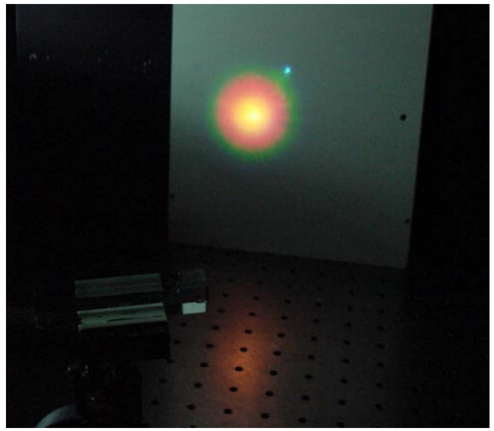


Sample	***N*** *(10^{18} molecules/cm^3)*	*σ_2 (10^{-50} cm^4 s) @ 750 nm*	*σ_3 (10^{-78} cm^6 s^2) @ 1400 nm*
S-H	3.2	500	4.5
S-CH3	2.6	1450	5.6
S-Ome	2.4	1550	7.3

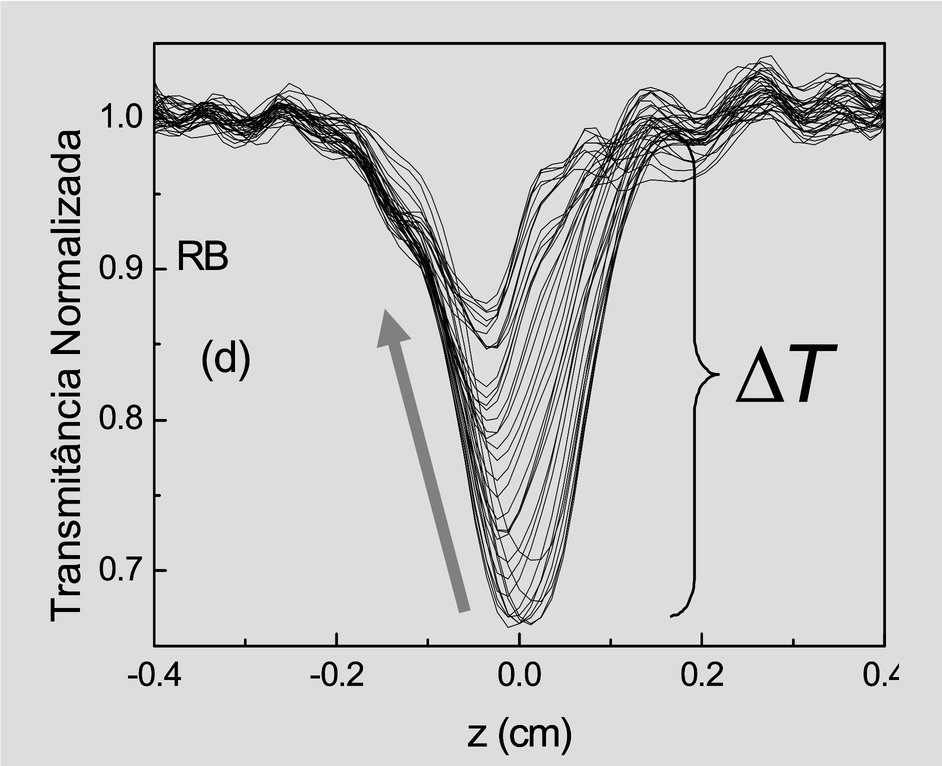
White light continuum Z-scan

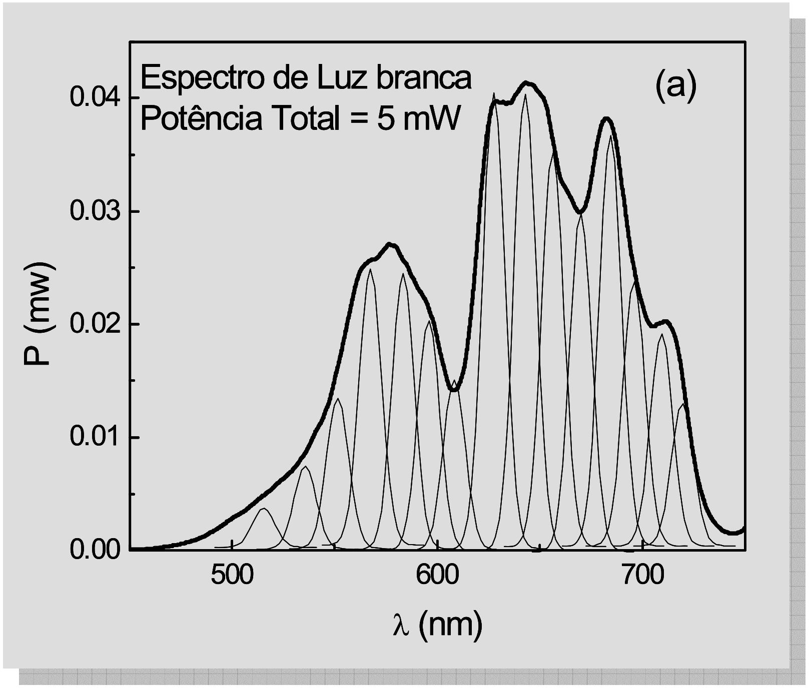




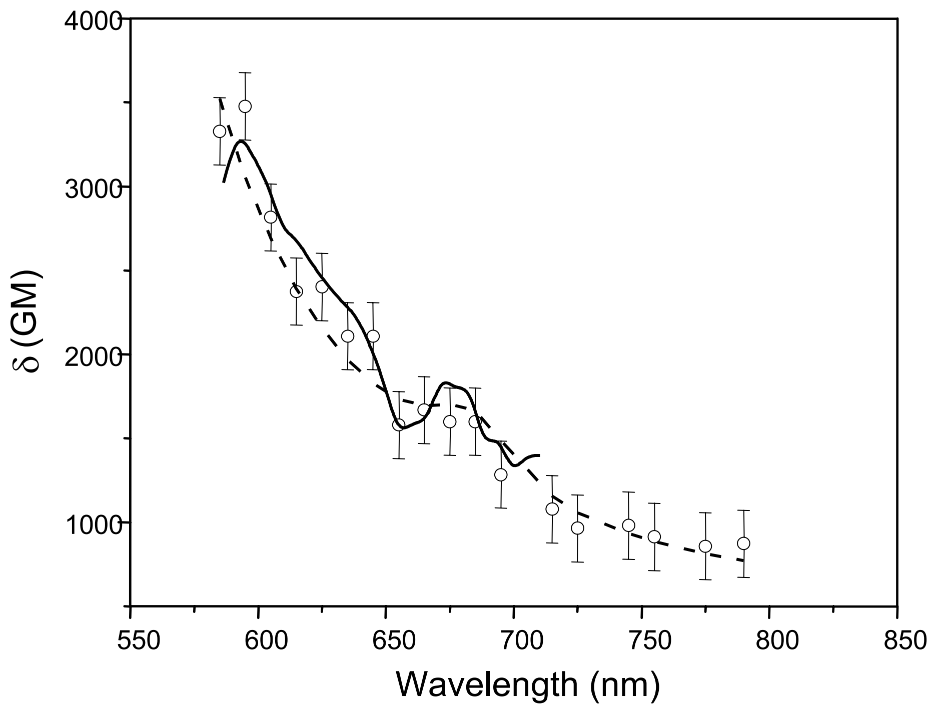


White light continuum Z-scan





White light continuum Z-scan



Two-photon absorption

MEH-PPV

Circles : discrete Z-scan measurements

Dashed line: theoretical model

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

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