Optical nonlinearities in organic materials

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Outline

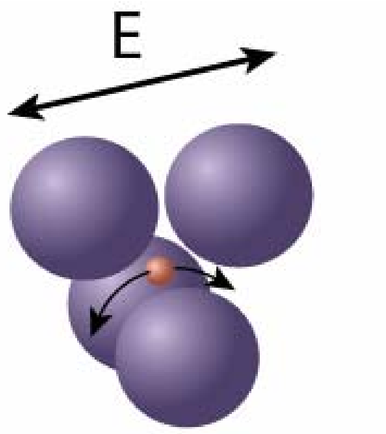
introduction to nonlinear optics

nonlinear optics in organic materials

experimental methods

examples of some results

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

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

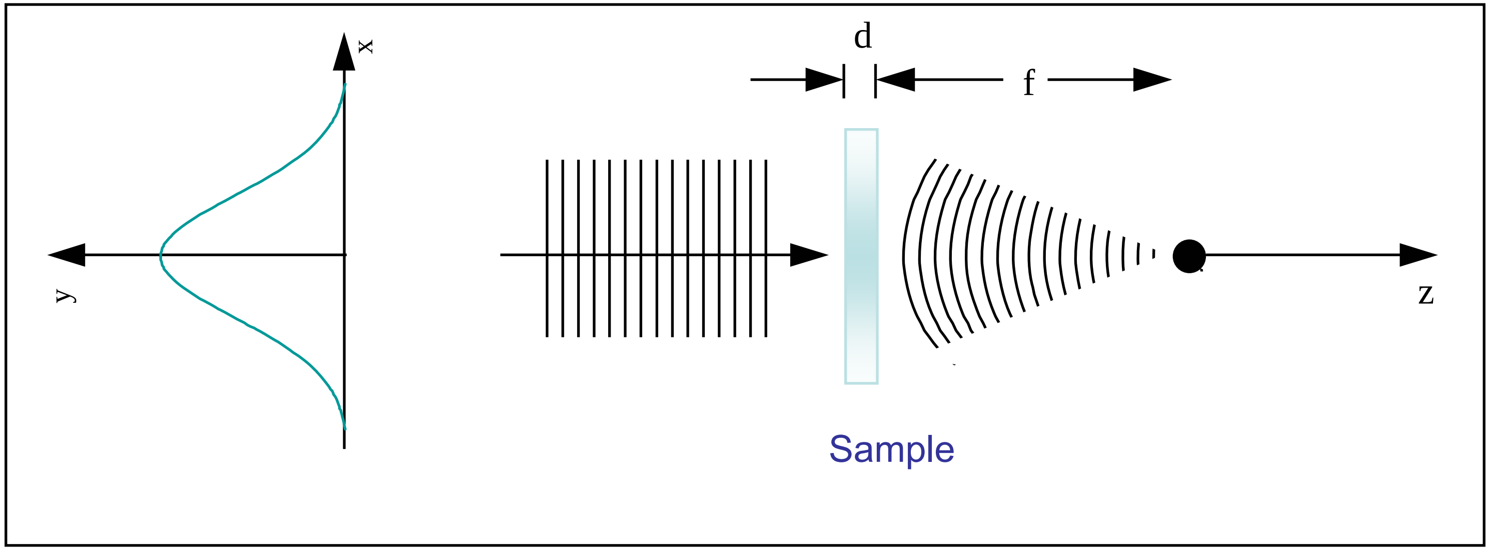
Kerr media:

$$n = n_0 + n_2 I$$

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

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

$n_2 > 0$ Material behaves as a convergent lens



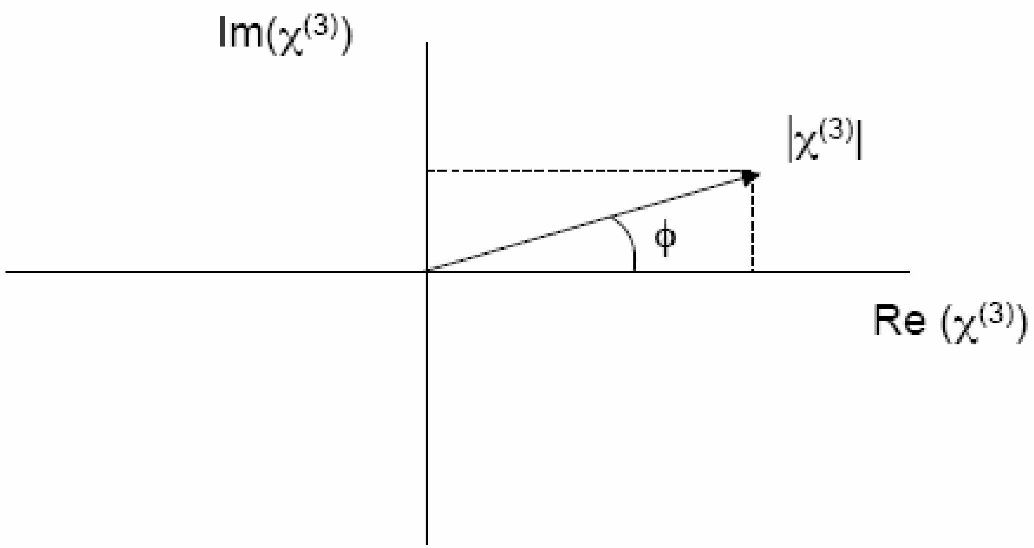
Nonlinear Optics

$\chi^{(3)}$ 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:

$$n = n_0 + n_2 I$$

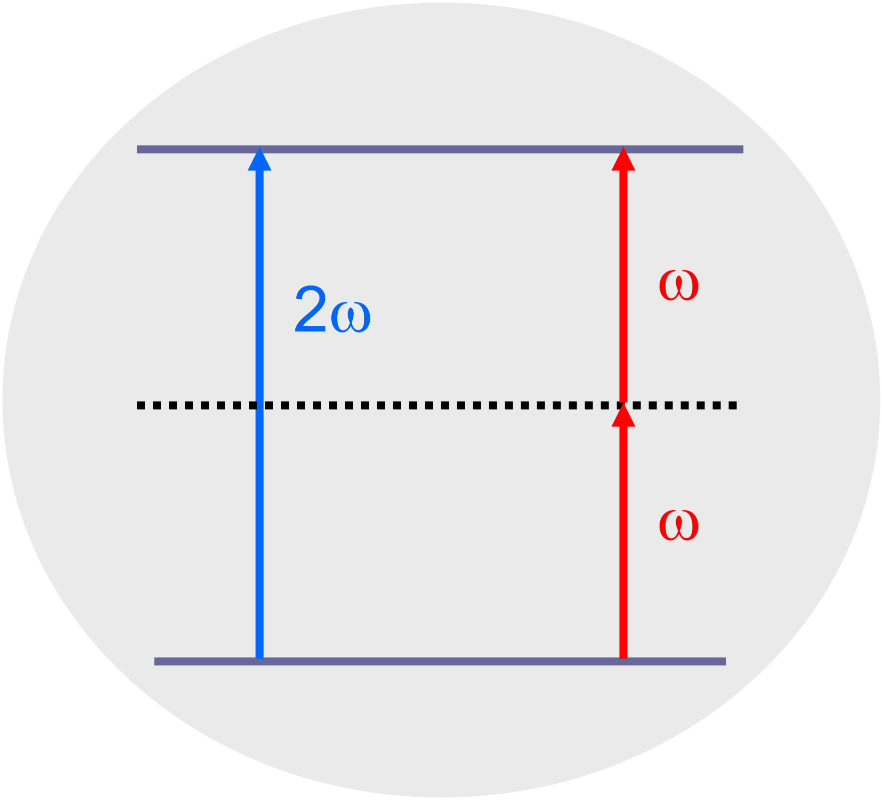
- self-phase modulation
- lens-like effect

Absorptive process:

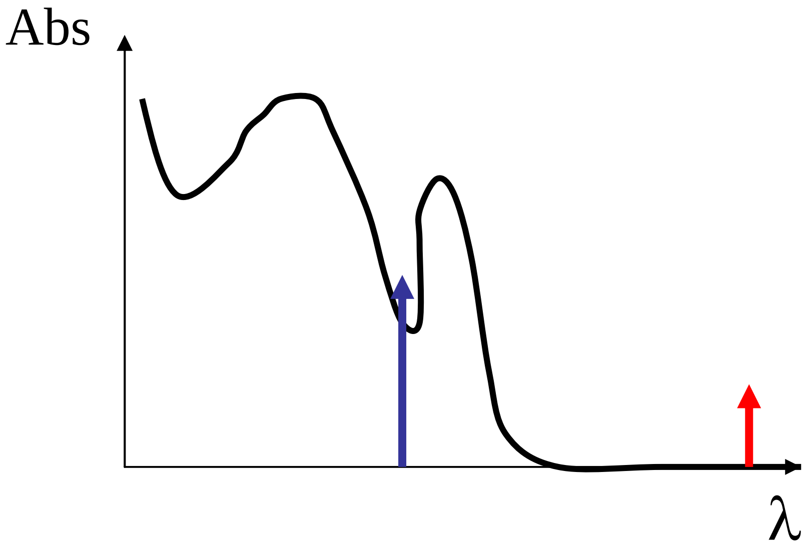
$$\alpha = \alpha_0 + \beta I$$

- nonlinear absorption
- two-photon absorption

two-photon absorption



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



Applications:

optical limiting

fluorescence microscopy

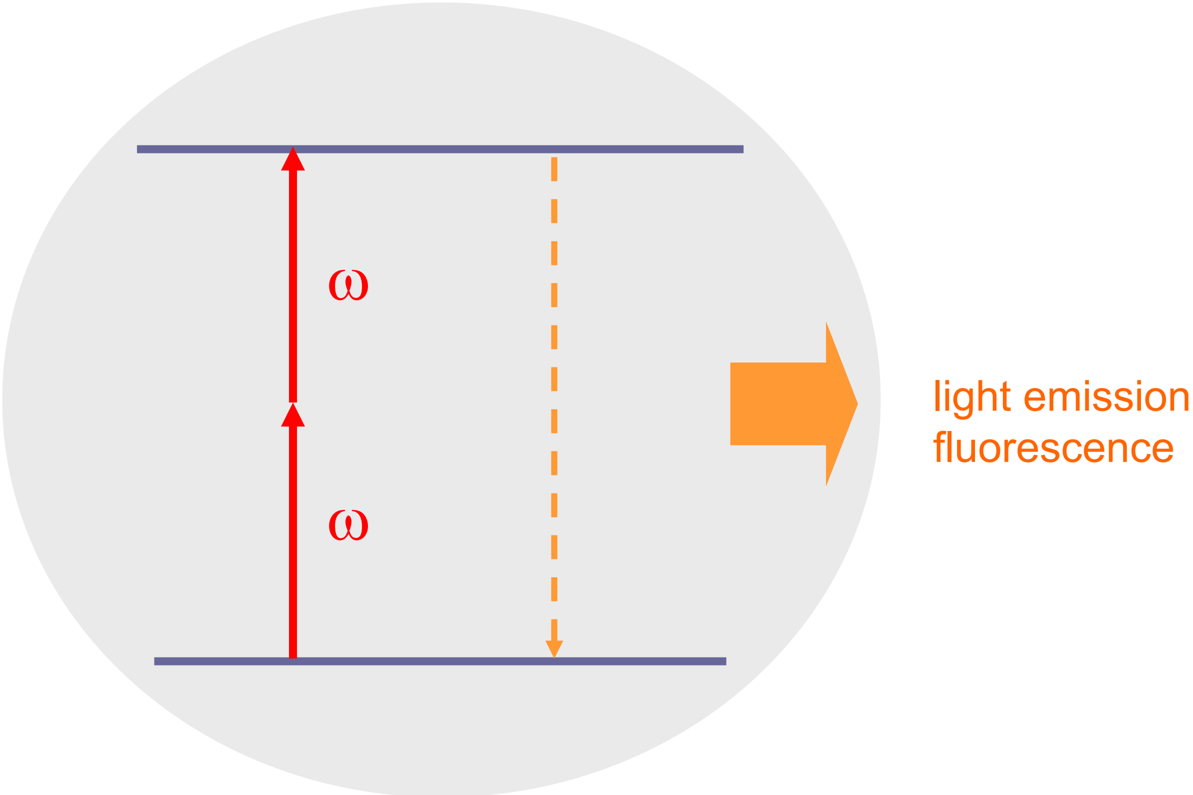
microfabrication

optical limiting

To protect eye and sensors from intense laser pulses

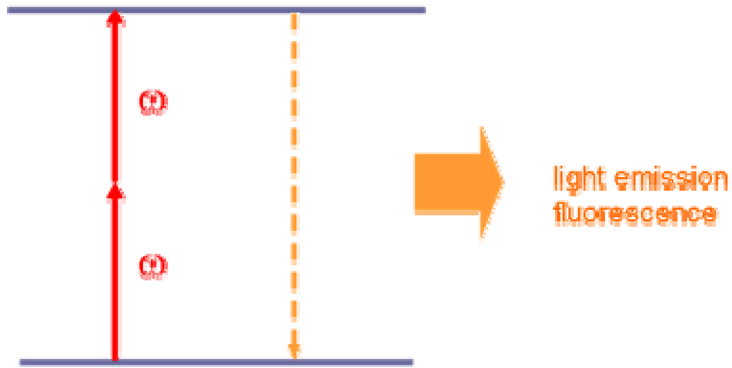
two-photon fluorescence

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

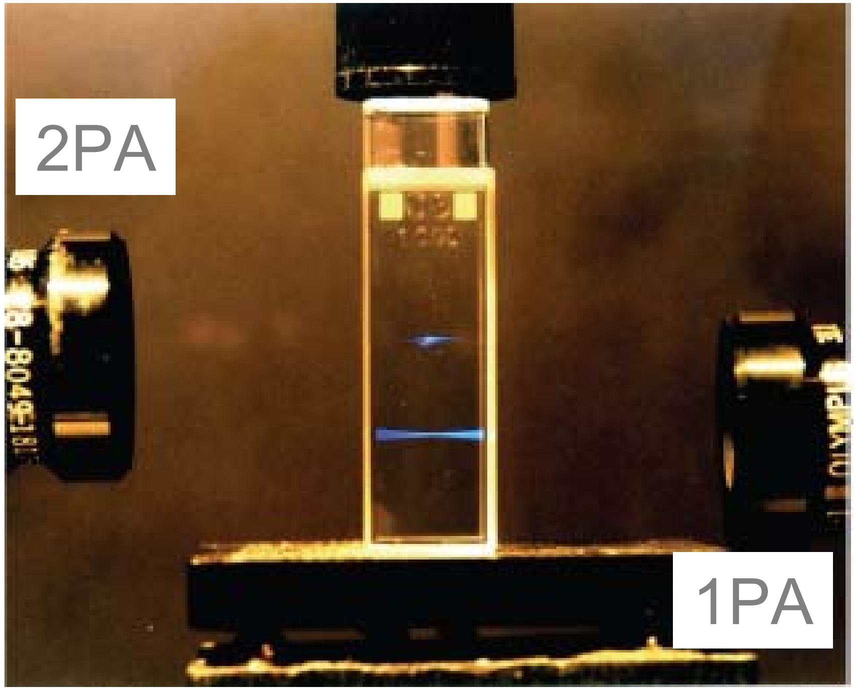


$$\boxed{\text{TPA rate constant} \propto \delta I^2}$$

localization of the excitation with 2PA



dilute solution of fluorescent dye



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

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

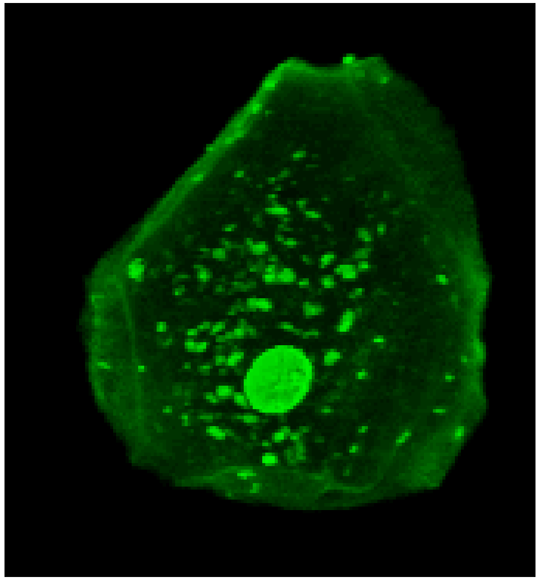
$$\Rightarrow TPA \sim \frac{1}{z^4}$$

spatial confinement of excitation

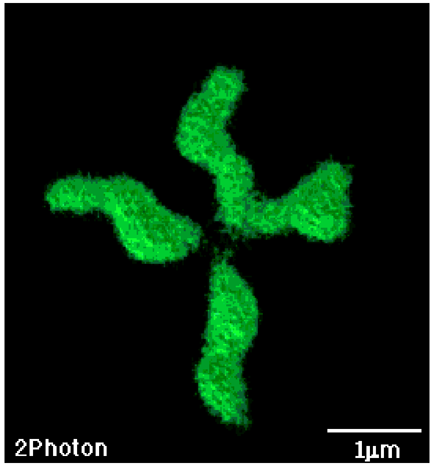
two-photon fluorescence microscopy

- Microscopy by two-photon fluorescence

3D image of a cell



Laboratory for Optics and Biosciences
Ecole polytechnique

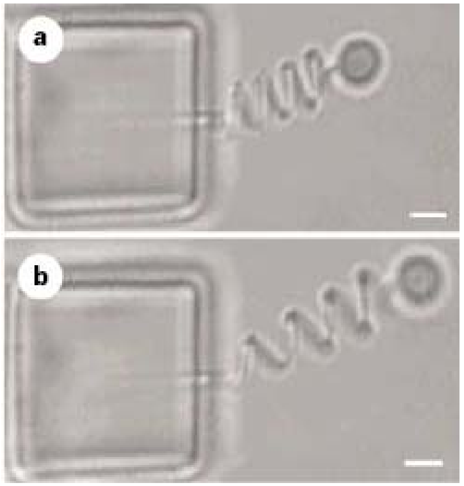


Human chromosome

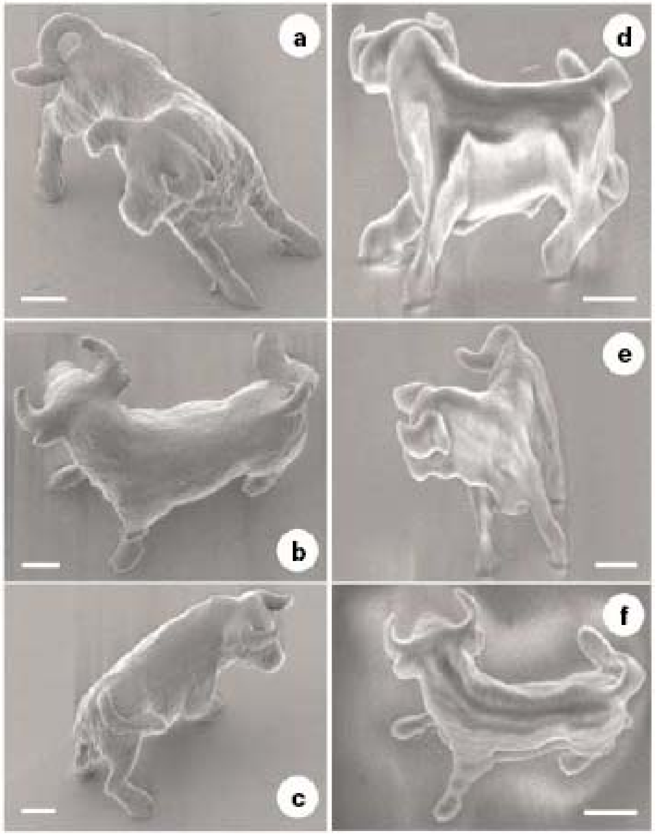
microfabrication

- **Two-photon polymerization**

Nature 412, 697-698 (2001)



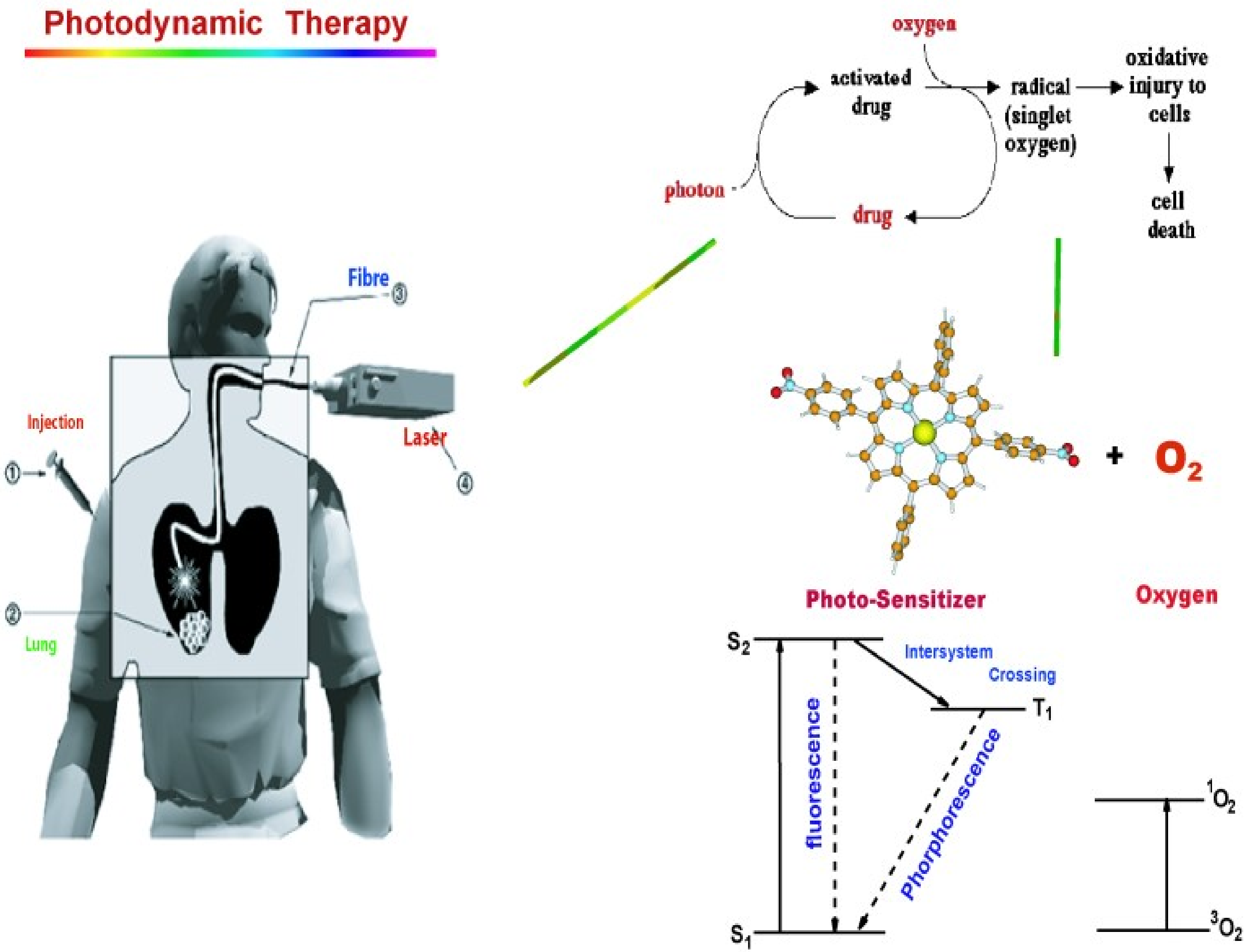
oscillator



Bull

two-photon photodynamic therapy

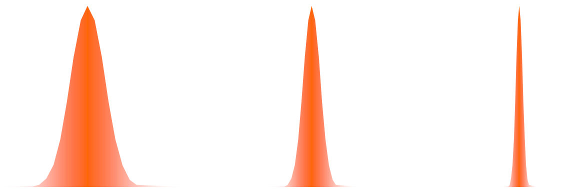
- PDT via dois fótons



Real applications in nonlinear optics

Very intense light: femtosecond pulses

Ti:Sapphire lasers



$\boxed{1\ \text{fs} = 10^{-15}\ \text{s}}$

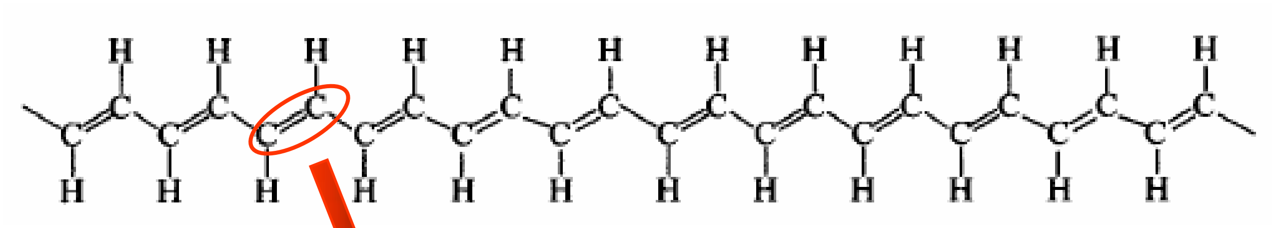
Laser intensities ~ *100 GW/cm²*

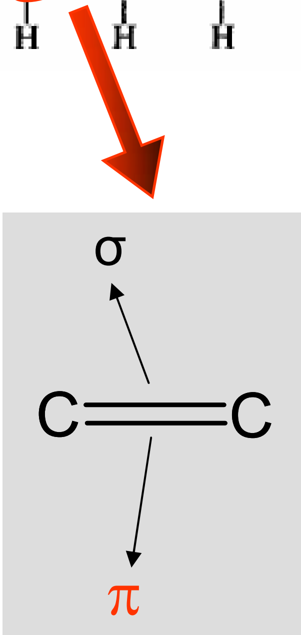
1×10^{11} W/cm^2

Organic materials

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

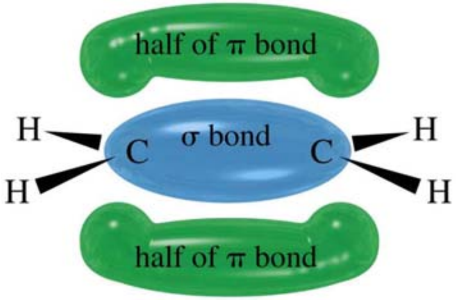
• π-conjugated structures





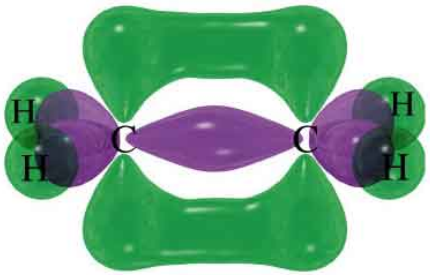
Conjugation: alternation of single and doubles bonds between carbon atoms

π-conjugation



σ bond: forms a strong chemical bond; localized

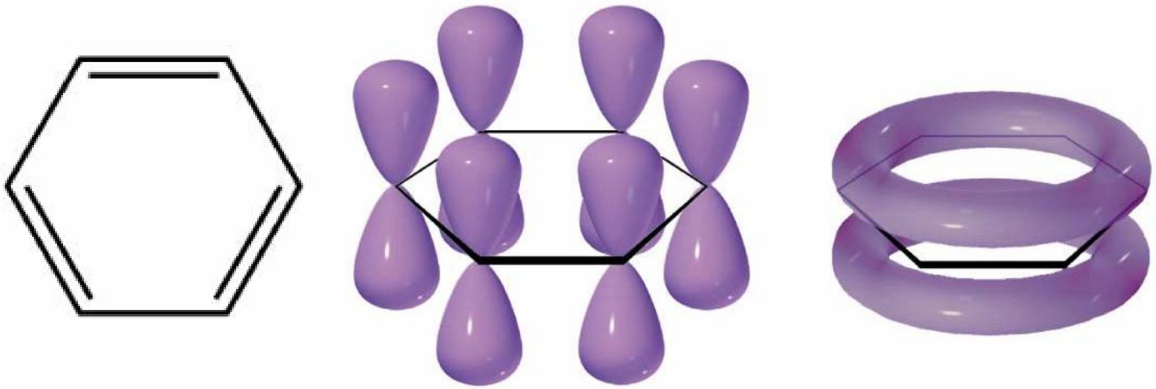
π bond: weaker bond; out of the C atoms axis



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

π-conjugation

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



π bond in conjugated system: delocalized electrons

high optical nonlinearities

$\chi^{(3)}$

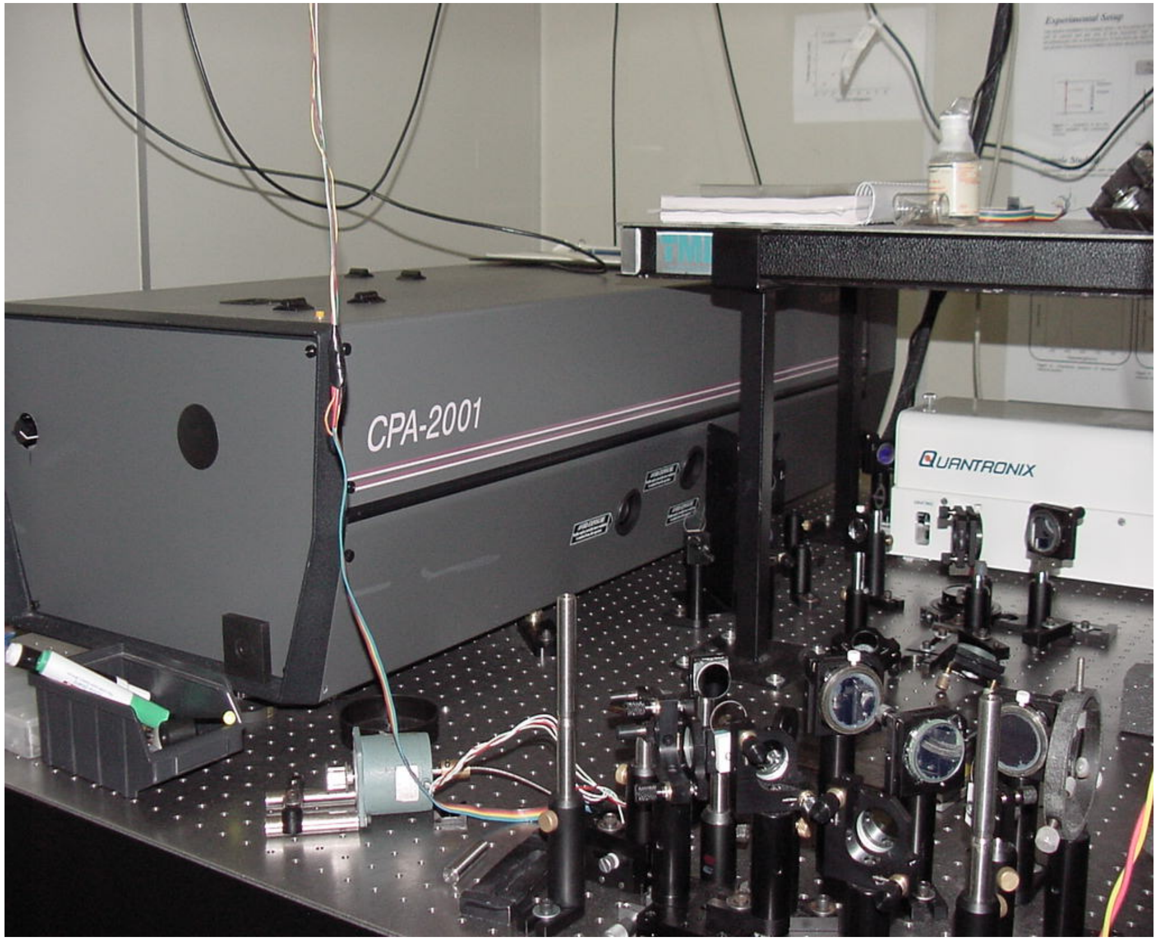
Research

- 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

150 fs laser system



Ti:Sapphire amplifier

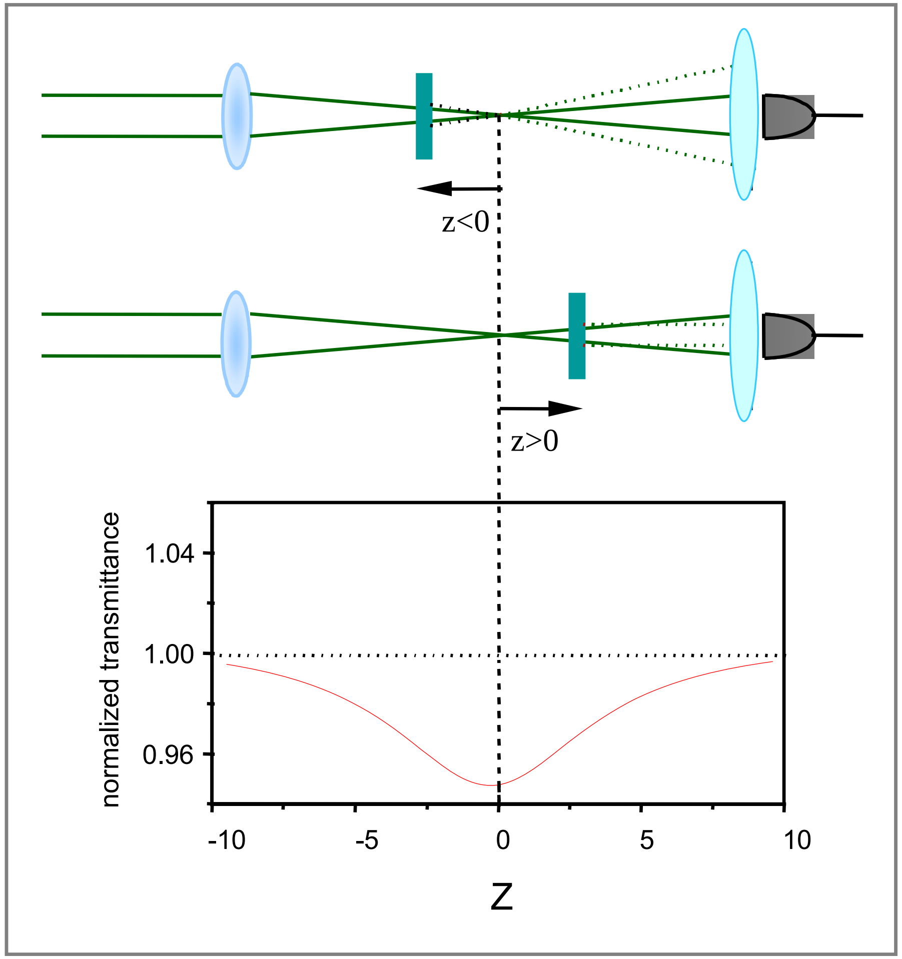
775 nm

150 fs

800 μJ

Z-scan (nonlinear absorption)

open aperture Z-scan



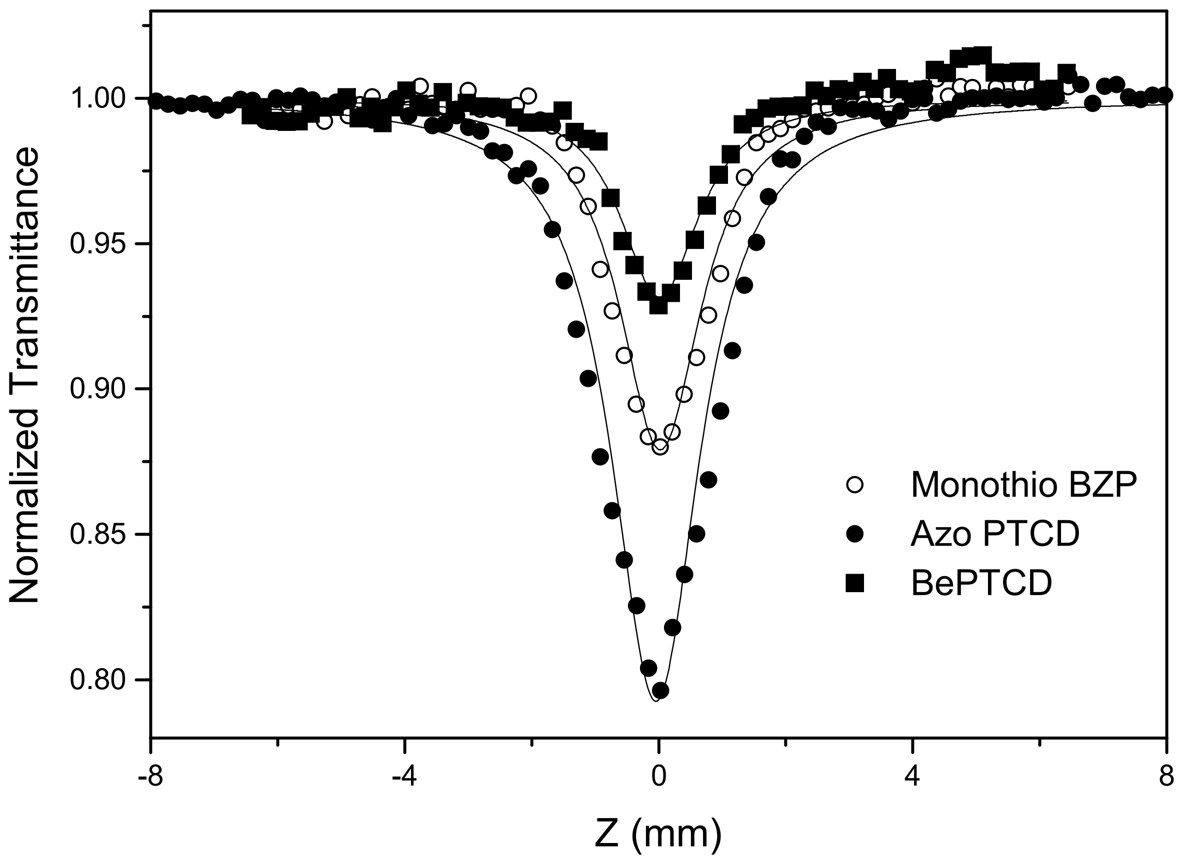
$$\alpha(I) = \alpha_0 + \beta I$$

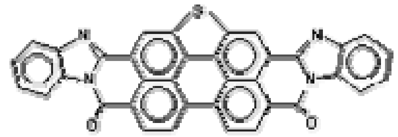
$$\Delta T \propto \beta I$$

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

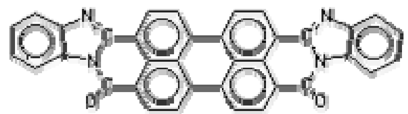
$$q_0(z,t) = \beta I_0 L / \left(1 + z^2 / z_0^2\right)$$

Nonlinear absorption

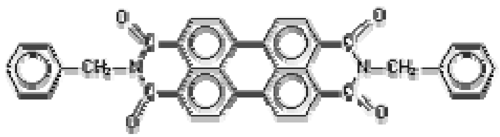




Monothio BZP



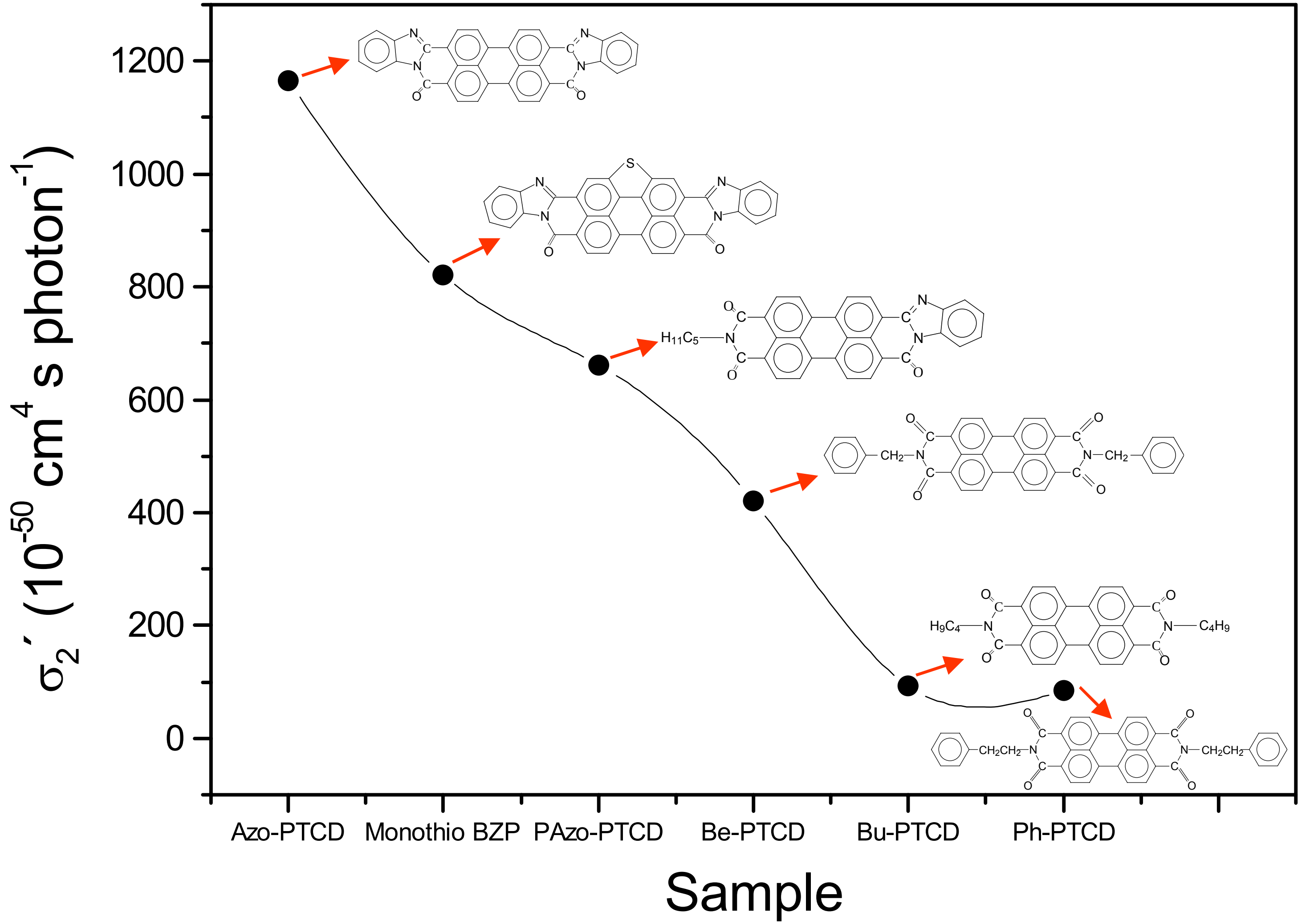
AzoPTCD



BePTCD

775 nm

Two-photon absorption of perylenes

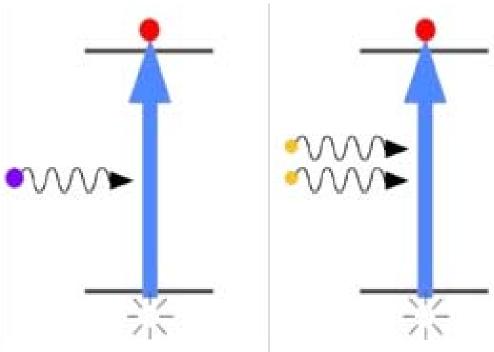


Correlation between molecular structure and the nonlinear response

Nonlinear spectrum

<u>nonlinear absorption</u>

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



<u>nonlinear refraction</u>

$$n = n_0 + n_2 I$$

intense laser (ultra short pulses)

discrete λ s

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

nonlinear spectrum ???

Nonlinear absorption spectrum

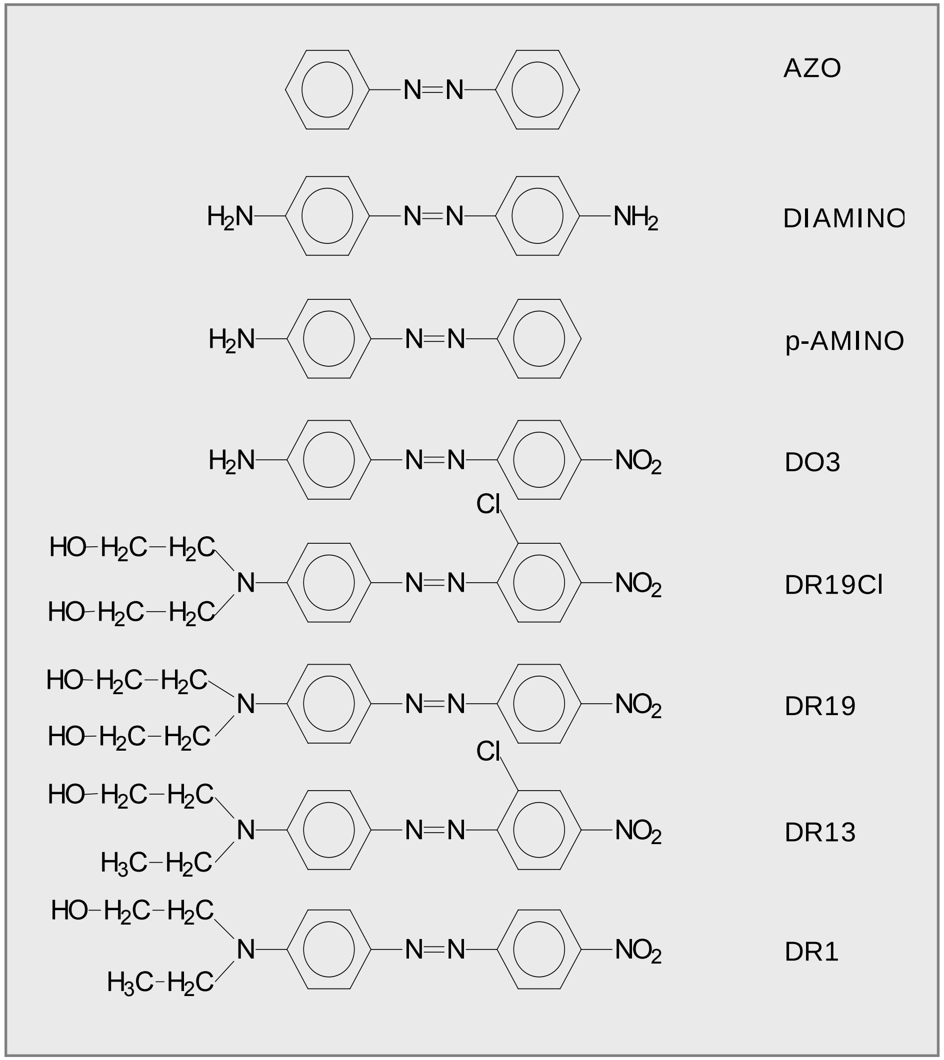
Optical parametric amplifier

460 - 2600 nm

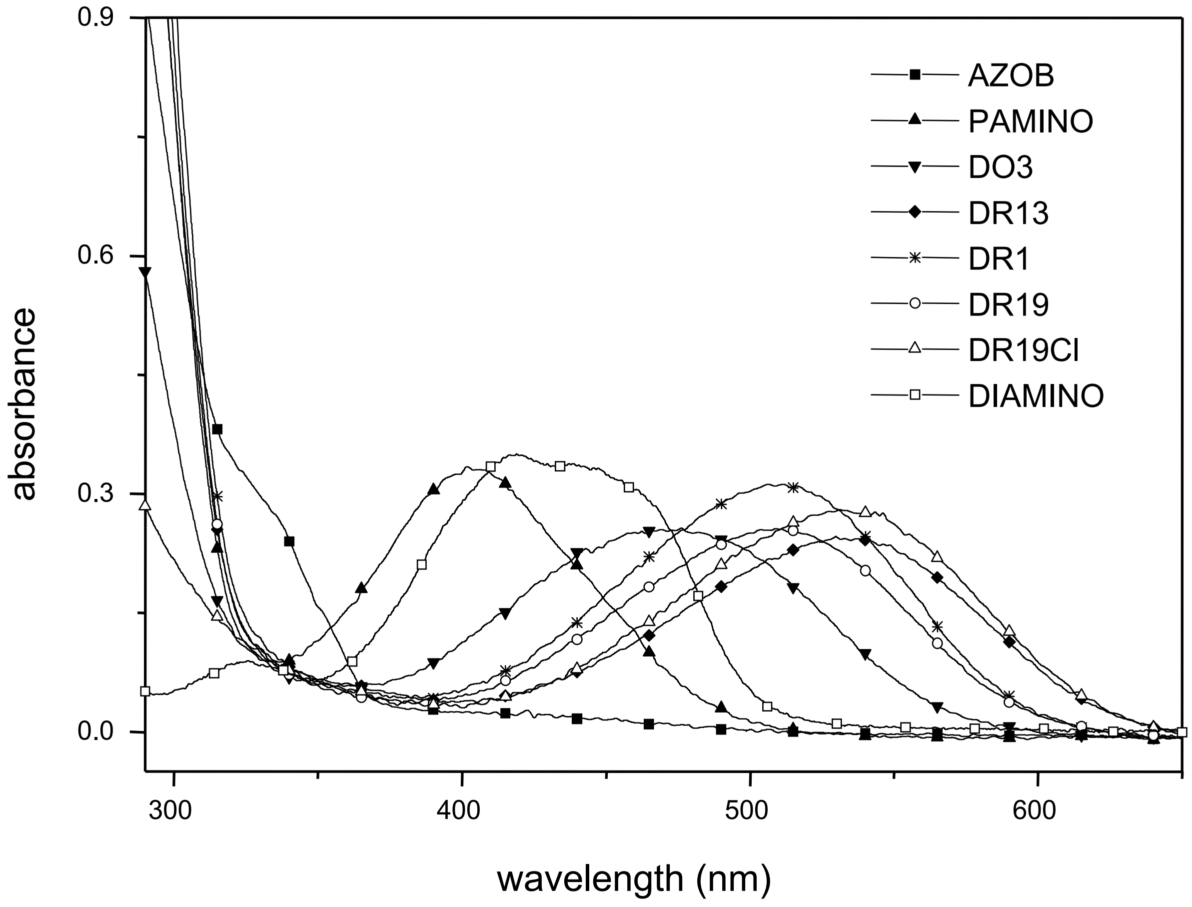
$\approx$ *120 fs*

20-60 μJ

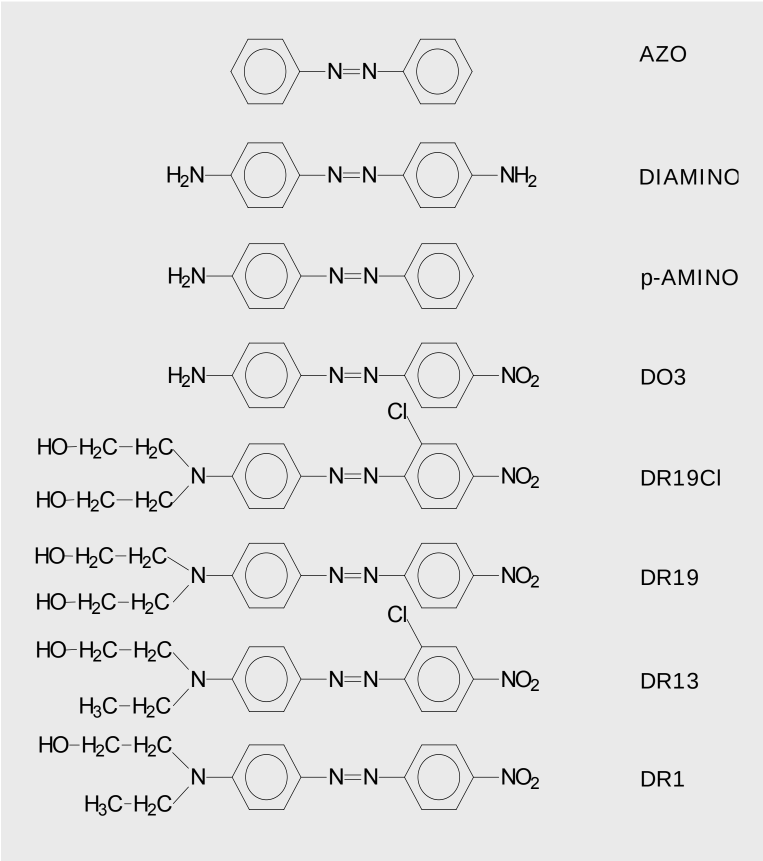
Azoaromatic samples

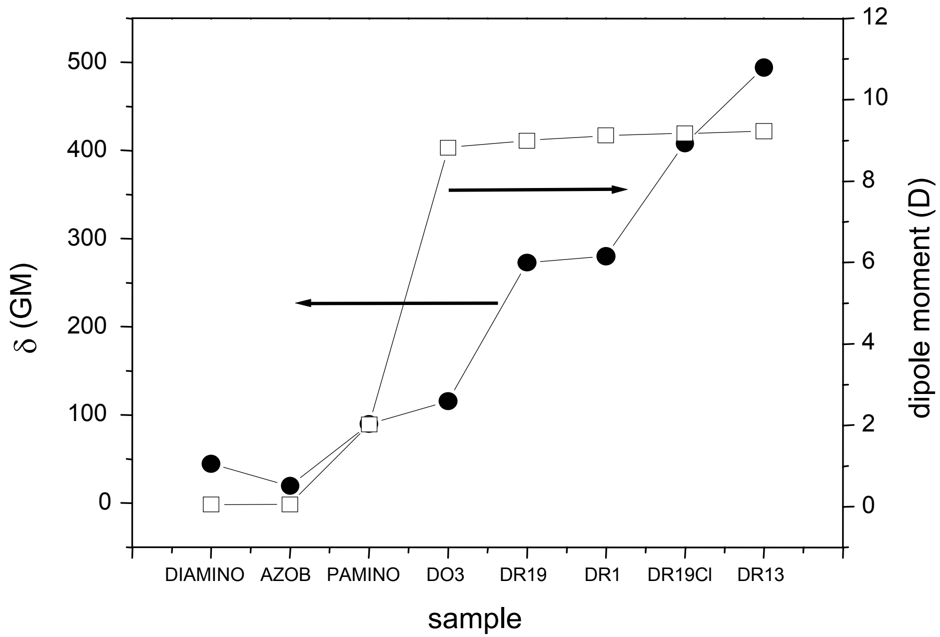


Linear absorption of azoaromatic compounds



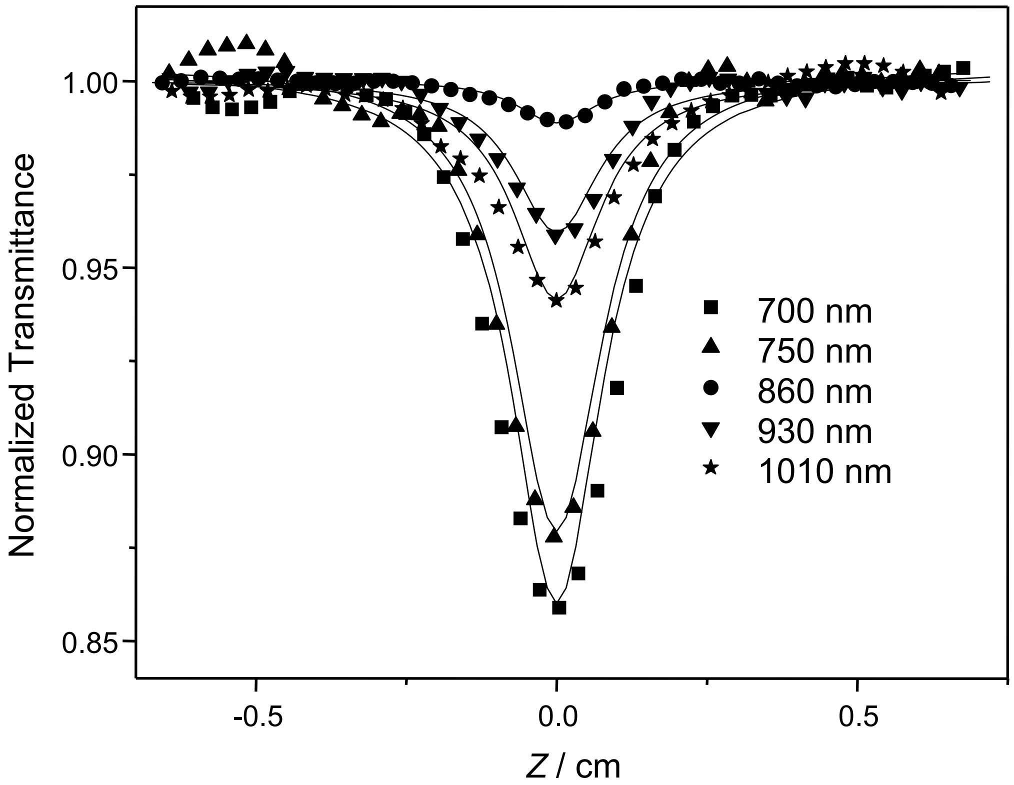
Two-photons absorption



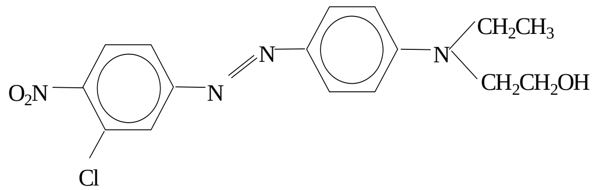


775 nm

Two-photon absorption



DR13

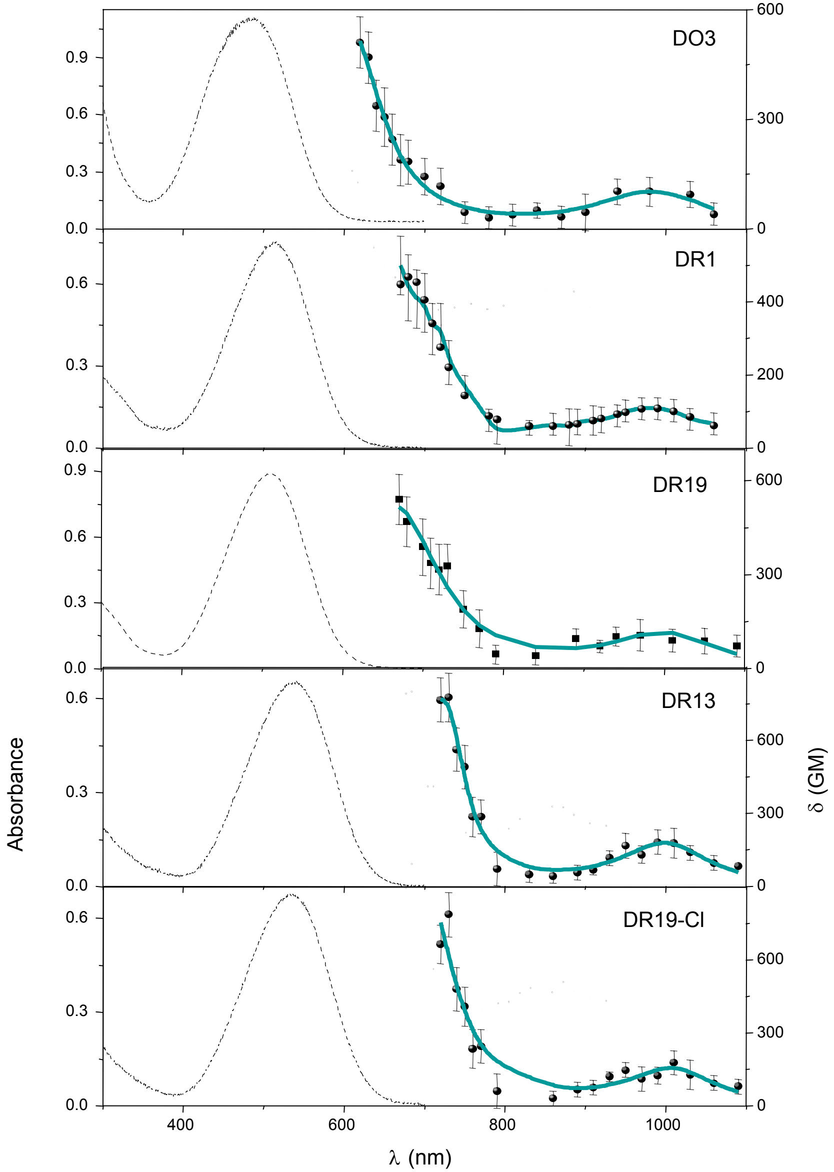


$$T(z) = \sum_{m=0}^{\infty} \frac{\left[-q_0(z,0)\right]^m}{(m+1)^{3/2}}$$

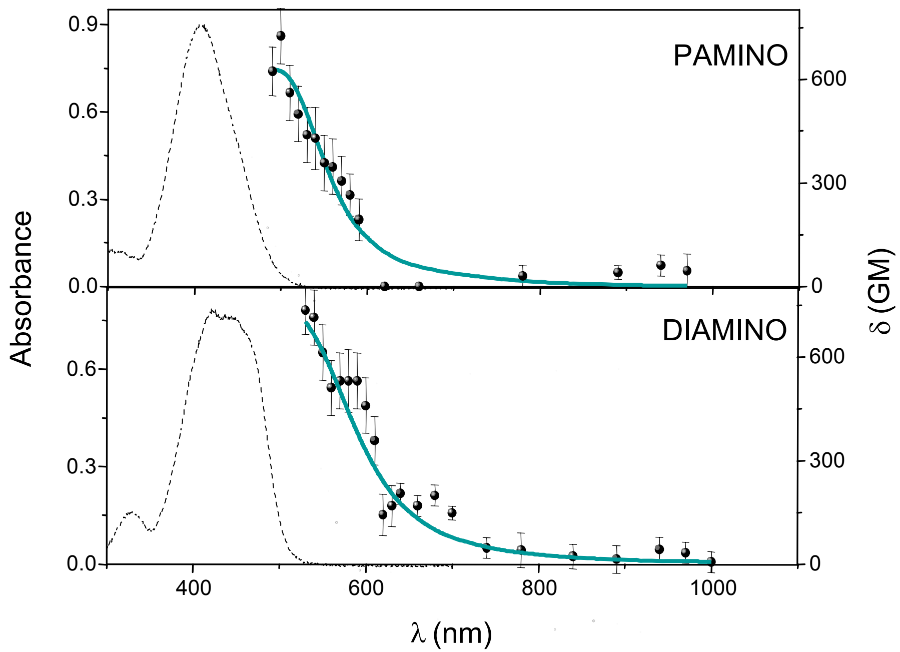
$$\alpha = \alpha_0 + \beta I$$

β: two-photon absorption coefficient

Psuedostilbenos

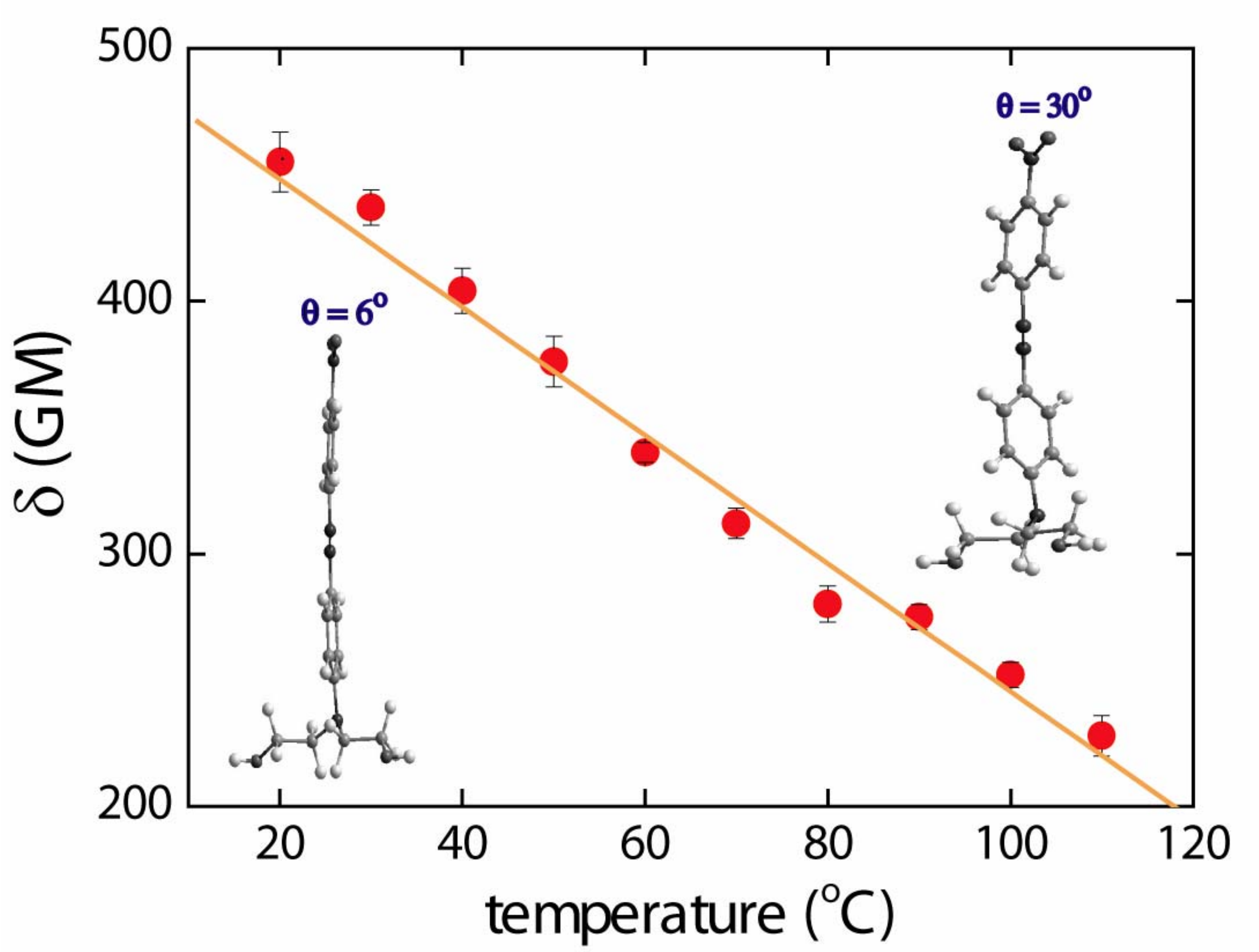


Aminoazobenzenos



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

Planarity of the π-bridge

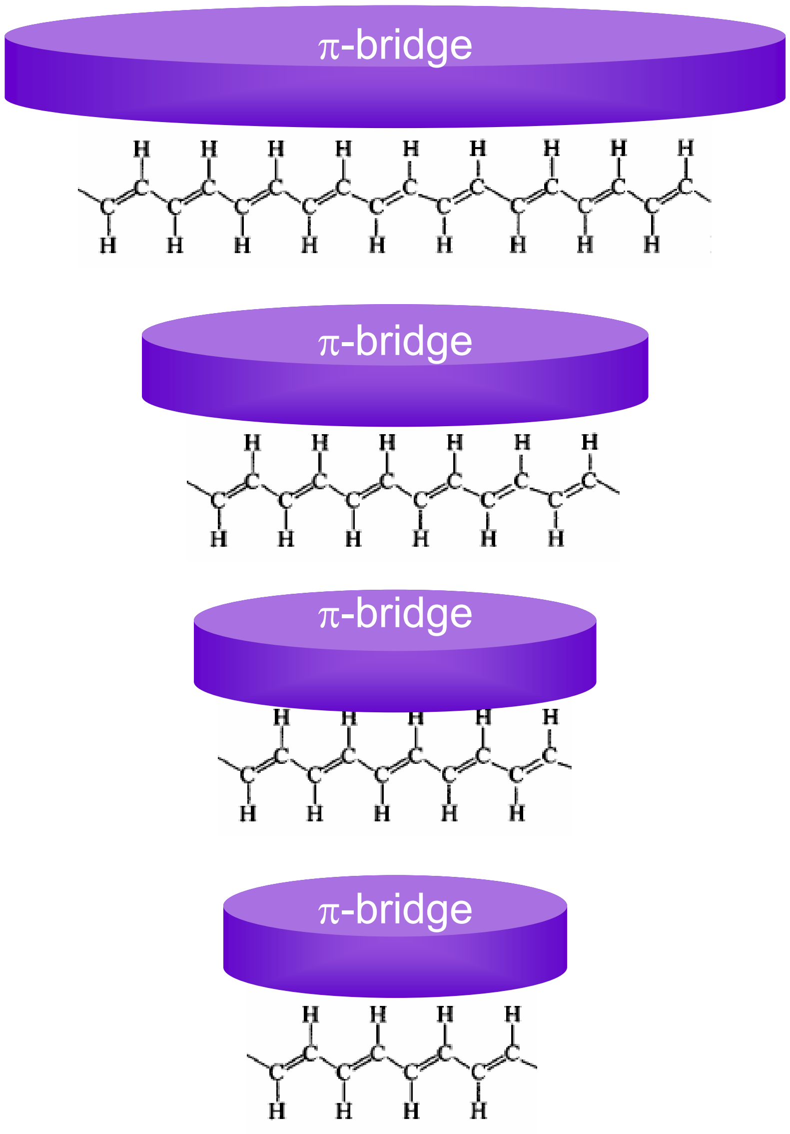


Thermally induced torsion in the molecular structure

Molecular design strategy

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

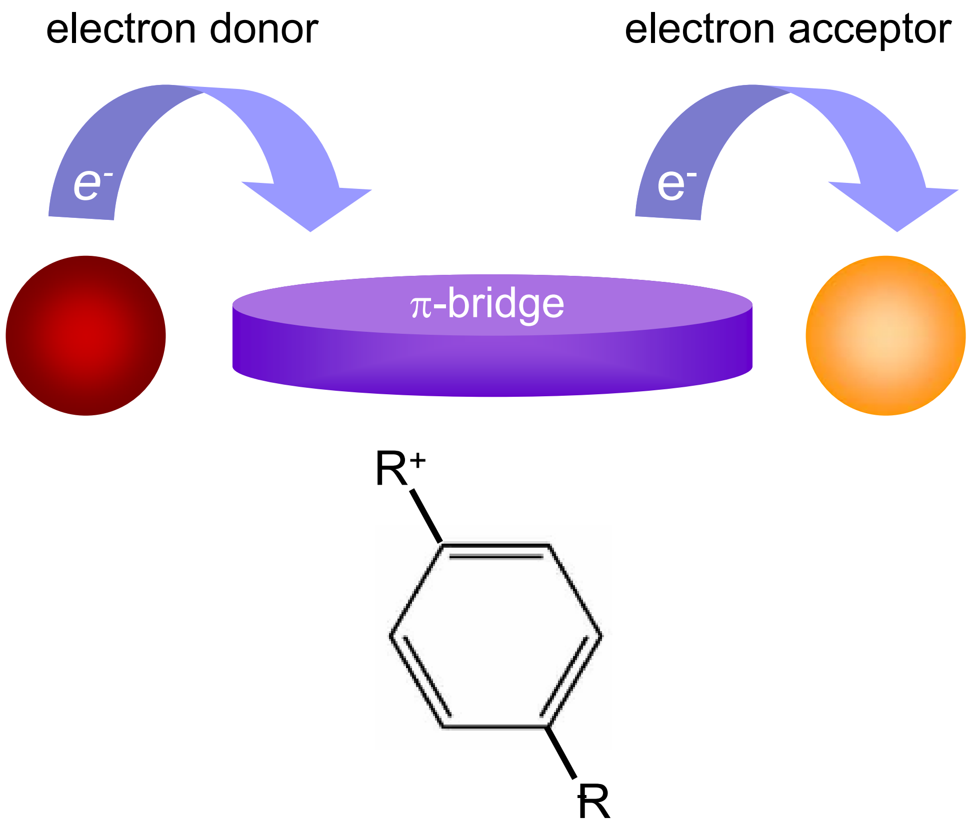
Increasing the conjugation



Increase in the optical nonlinearity

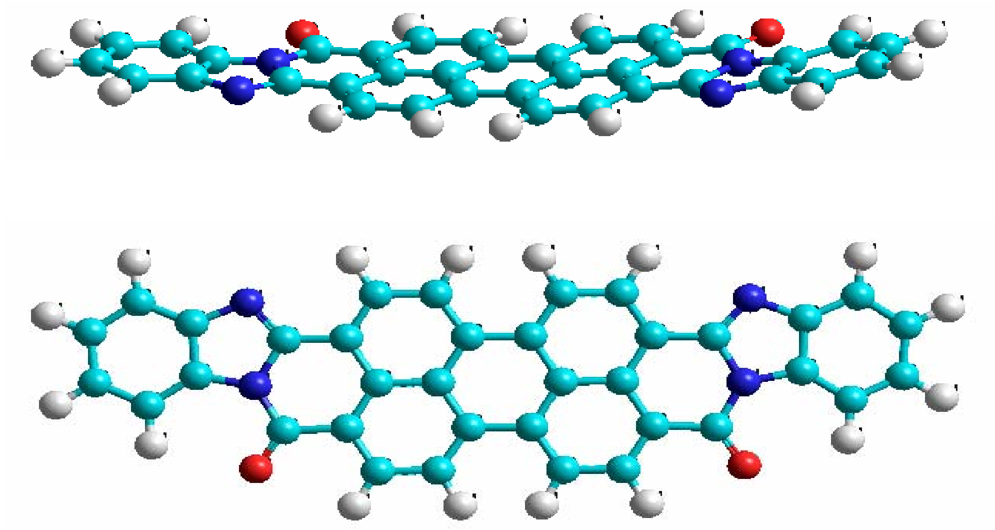
Increasing the π-conjugation

Donor and acceptor groups



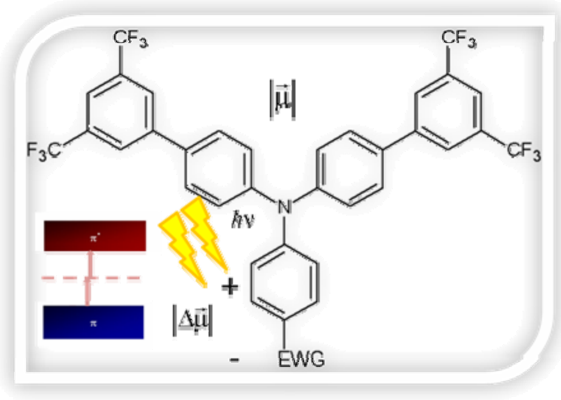
Incorporating electron donor and acceptor groups in a predictable way leads to an enhancement of the optical nonlinearity

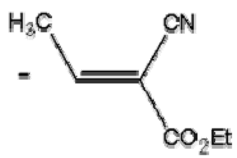
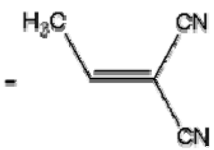
Planarity of the π-bridge

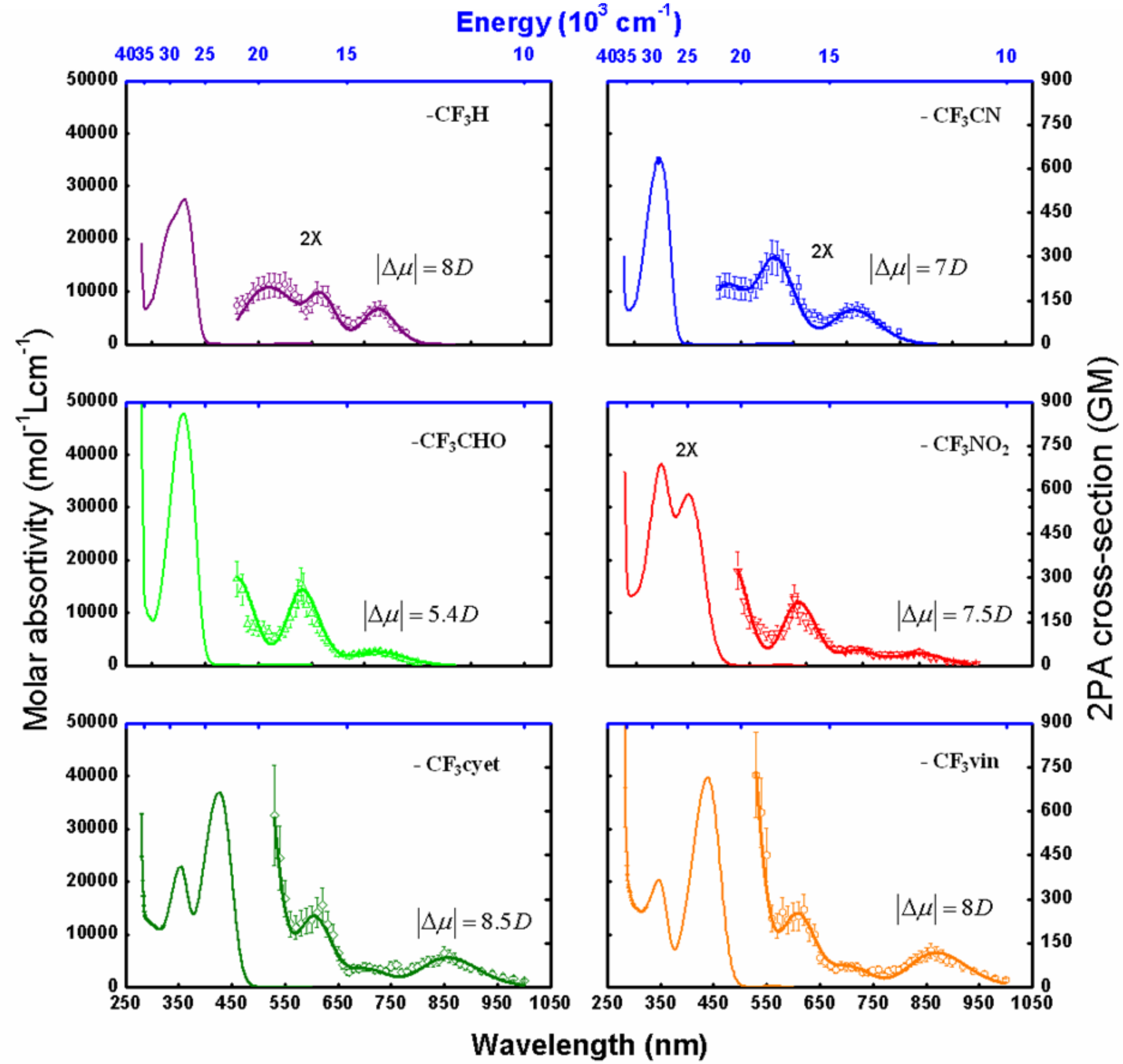


Perylene compounds are very planar molecules, which explains its high optical nonlinearities

2PA: triarylamine compounds with electron withdrawing substituints



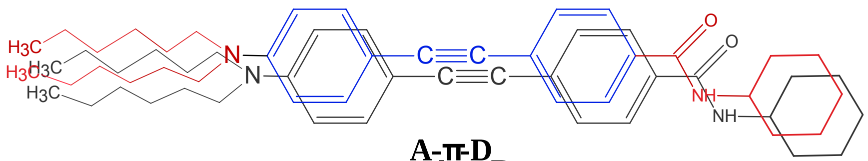
1. -H
2. -CN
3. -CHO
4. $-NO_2$
5. - 
6. - 



Prof. Elena Ishow

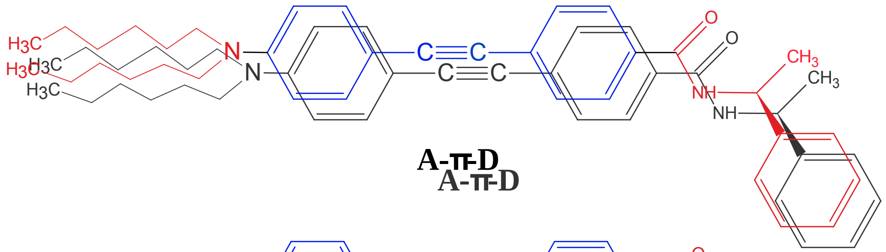
Chiral Compounds

JCM874



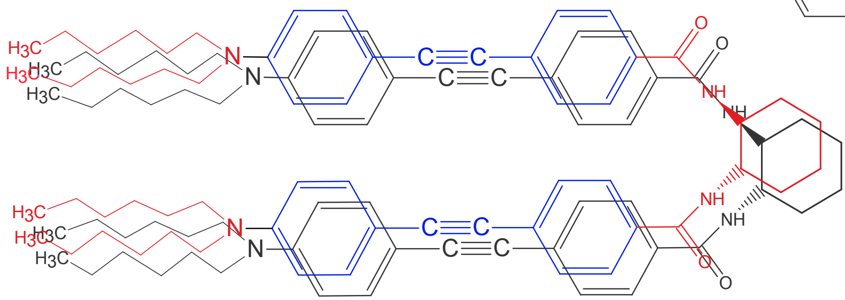
A-π-D

FD43



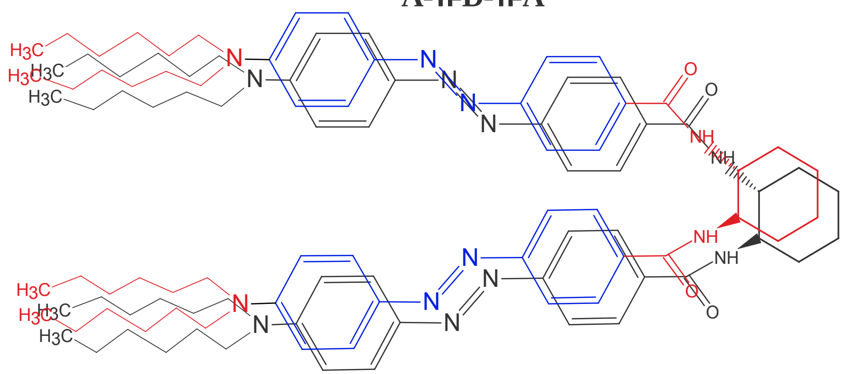
A-π-D

FD48



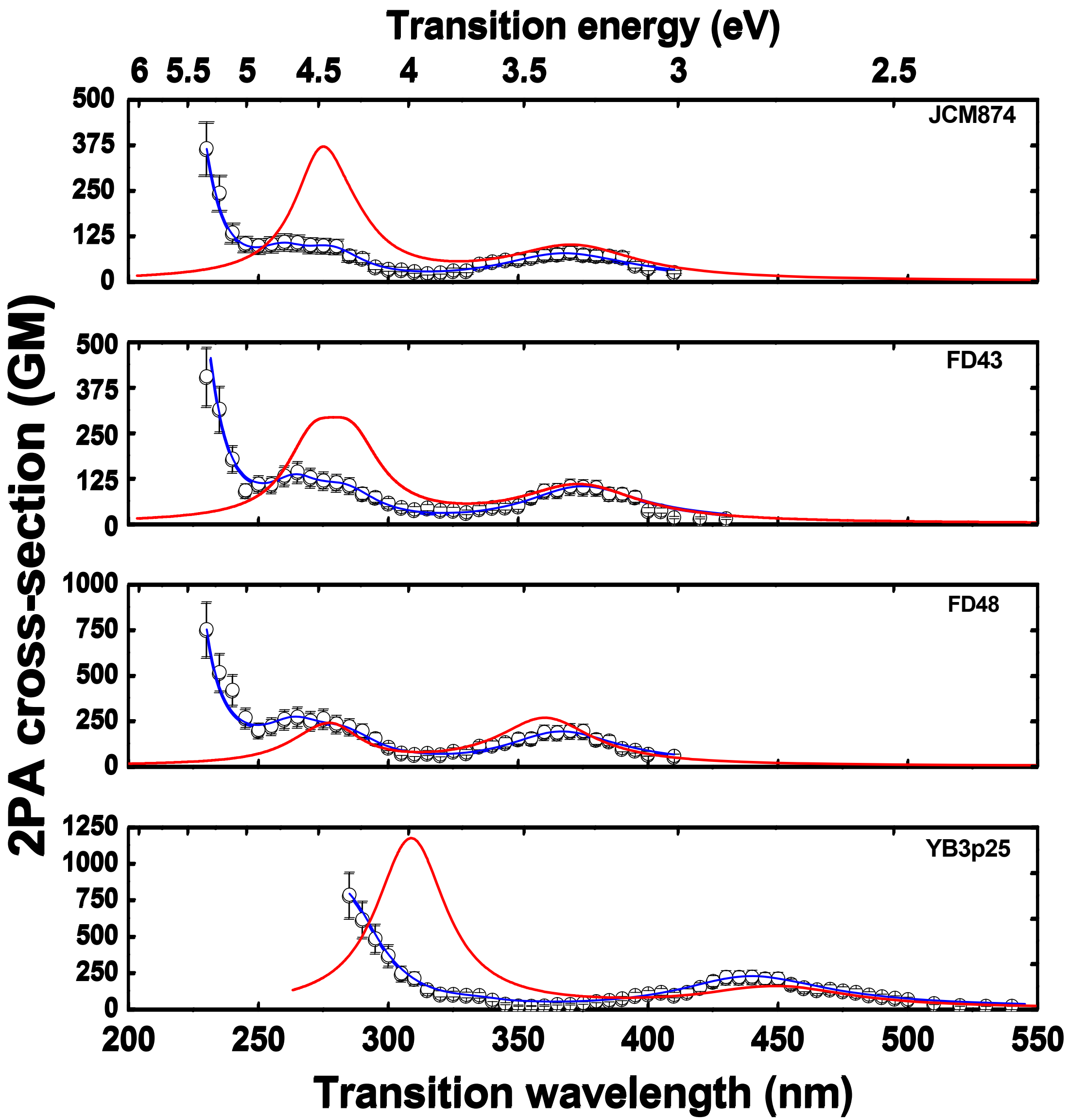
A-π-D-π-A

YB3p25

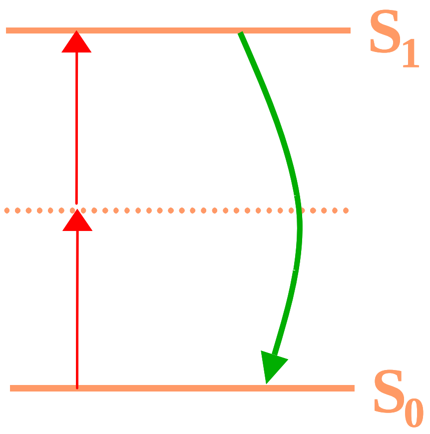


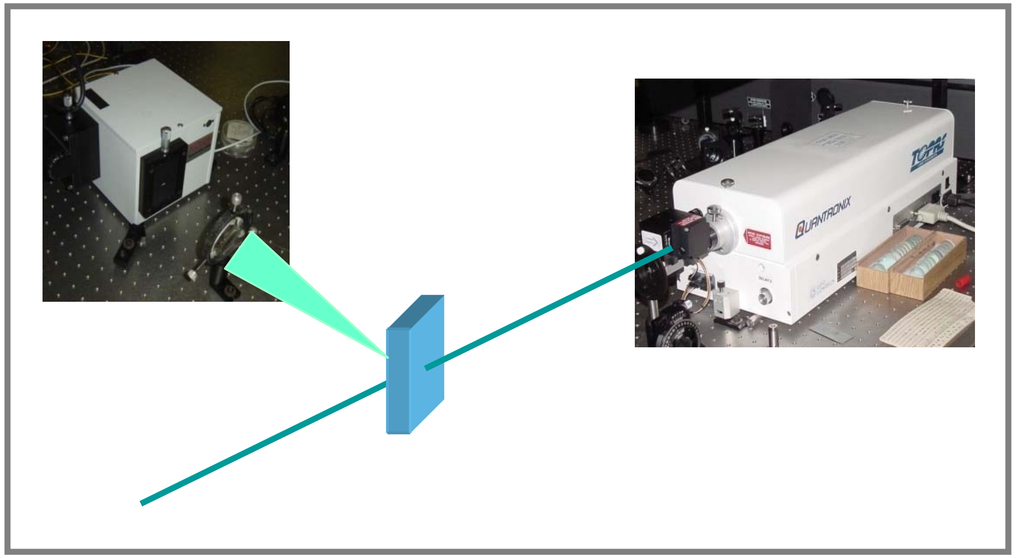
A-π-D-π-A

Comparison between experimental and theoretical results



Two-photon excited fluorescence

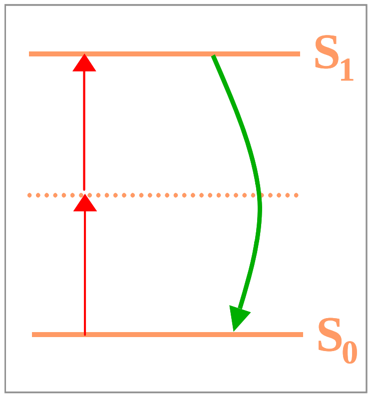




$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

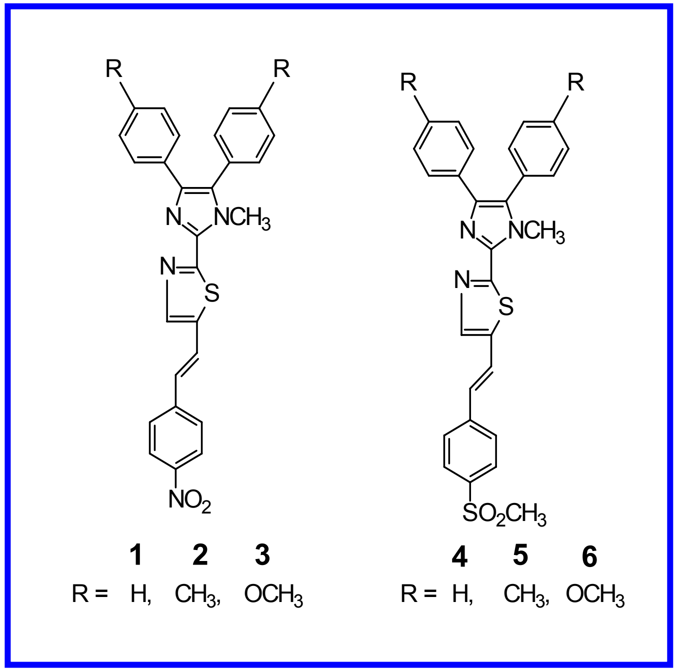
$$F \approx I^2$$

Multi-photon excited fluorescence



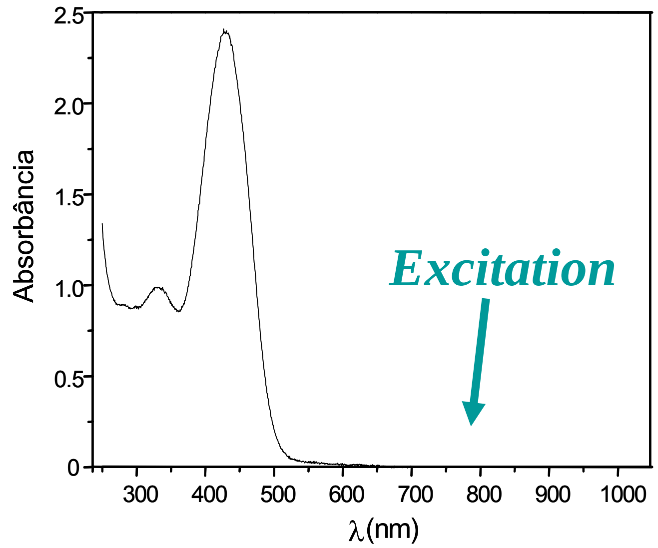
$$\frac{dN_2}{dt} \approx N_1 \delta I^2$$

$$F \approx I^2$$

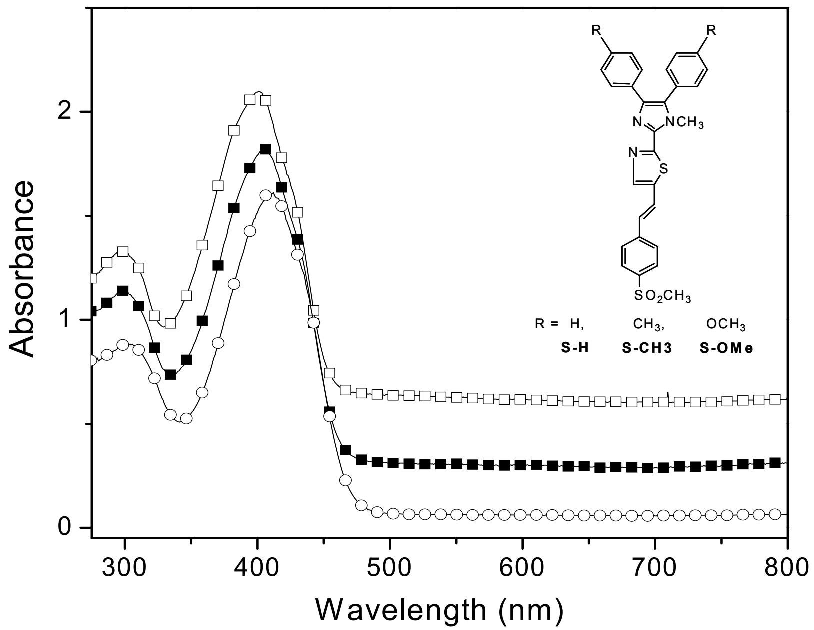


NITRO **SULFONIL**

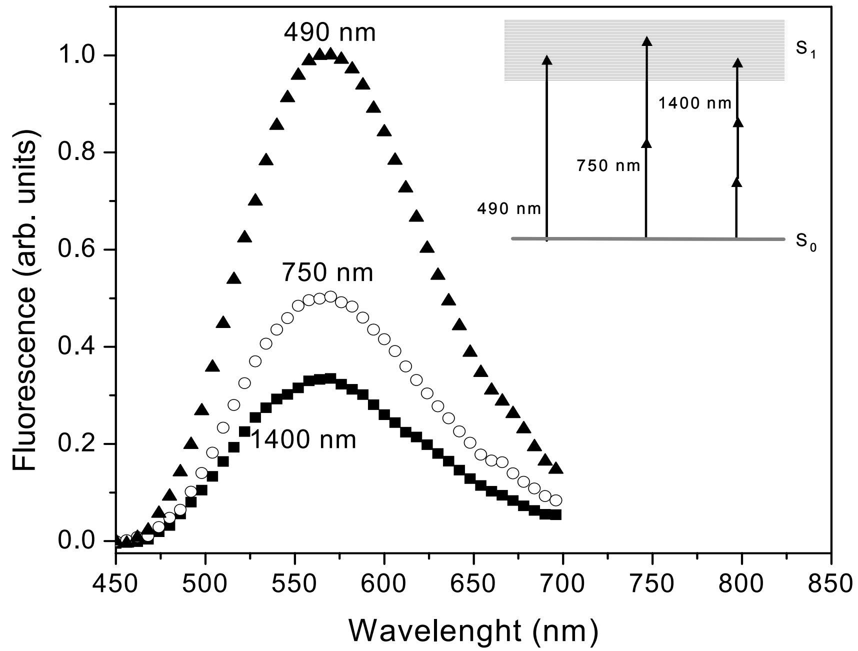
Y-shaped



Fluorescence excited by two and three photons

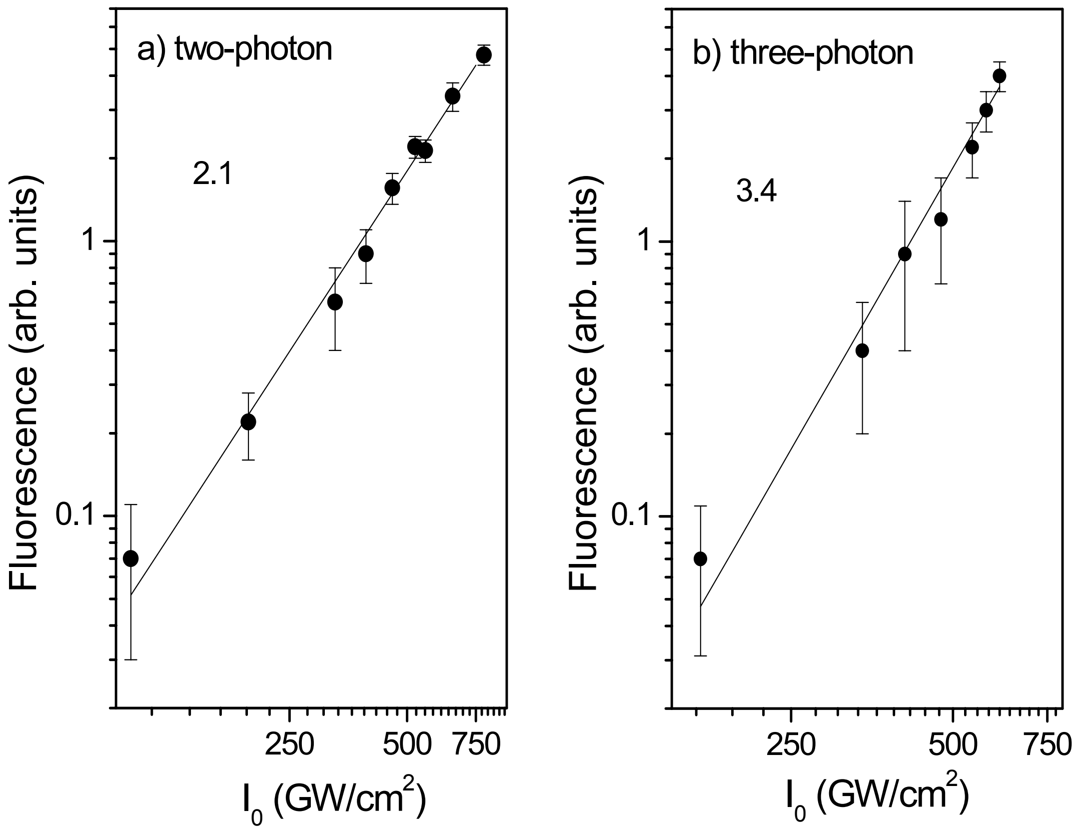


Absorption



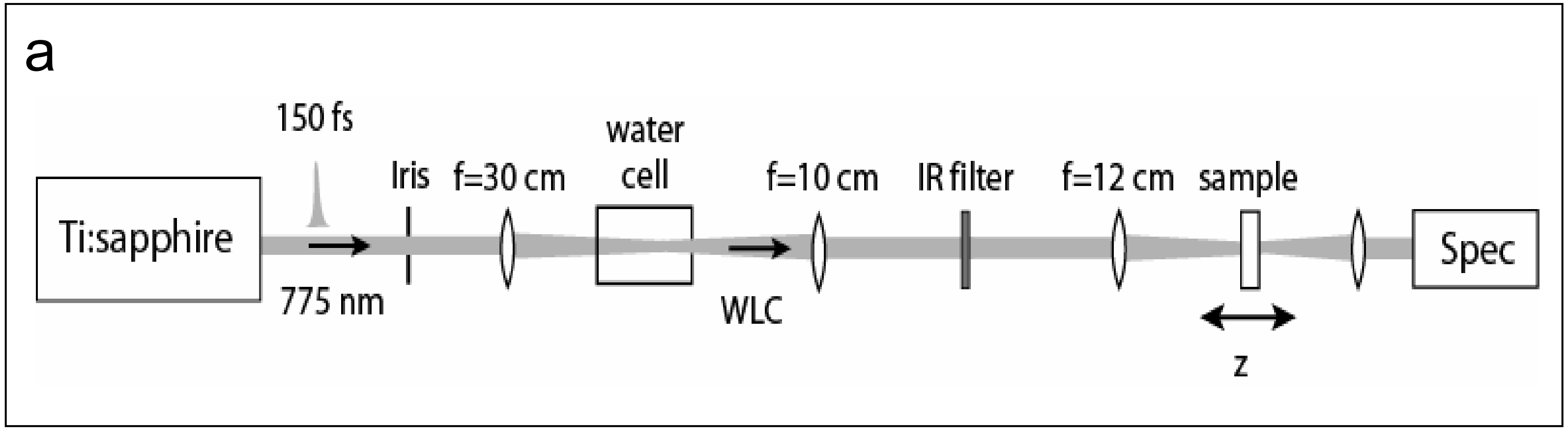
Fluorescence

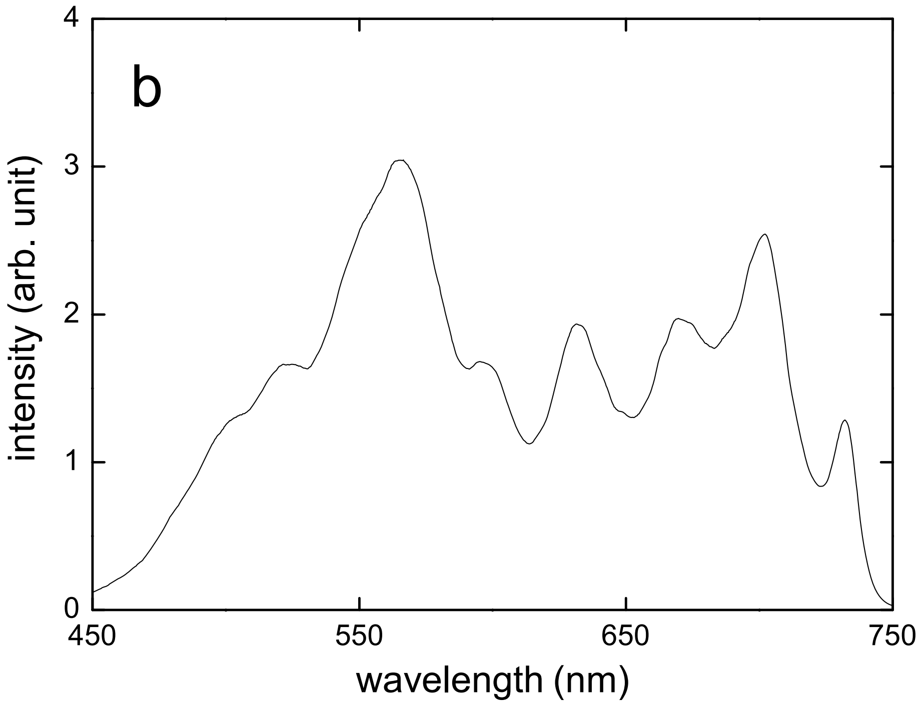
Two-photon excited fluorescence

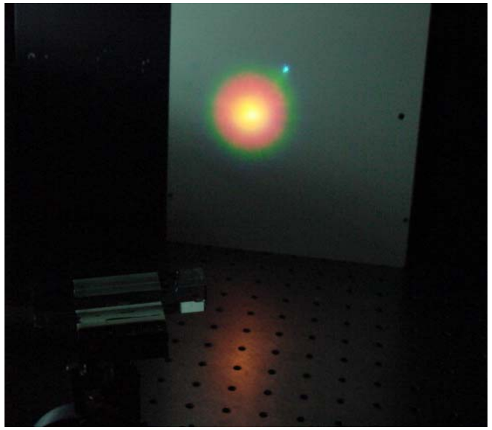


Sample	*N* (10^{18} molecules/cm^3)	σ_2 (10^{-50} cm^4 s) @ 750 nm	σ_3 (10^{-78} cm^6 s^2) @ 1400 nm
S-H	3.2	500	4.5
S-CH3	2.6	1450	5.6
S-Ome	2.4	1550	7.3

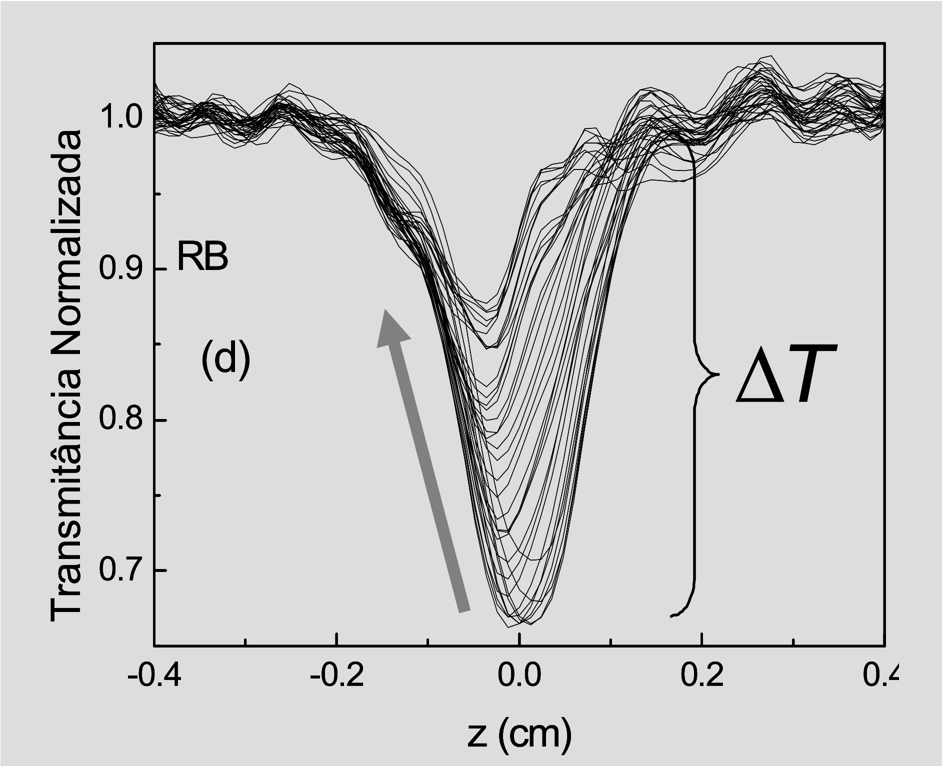
White light continuum Z-scan

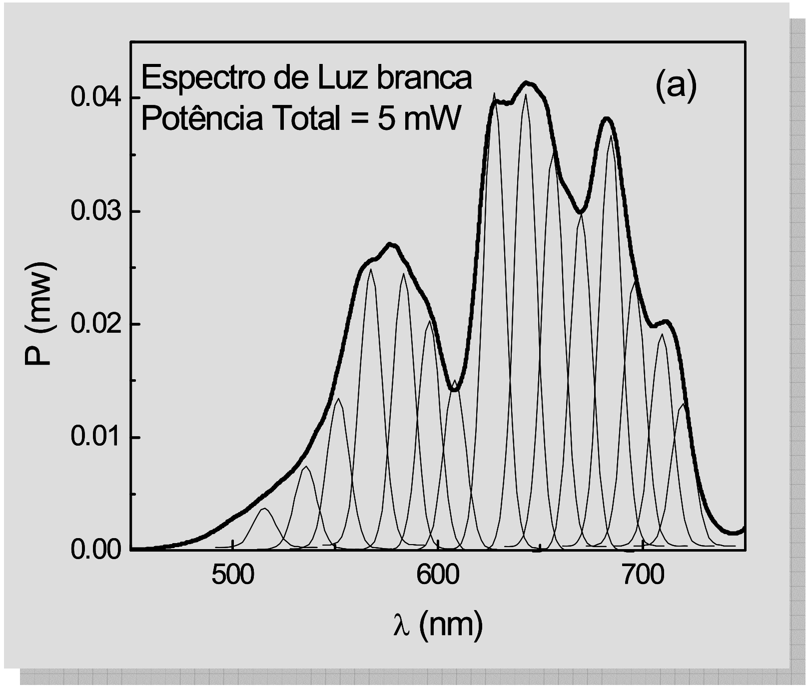




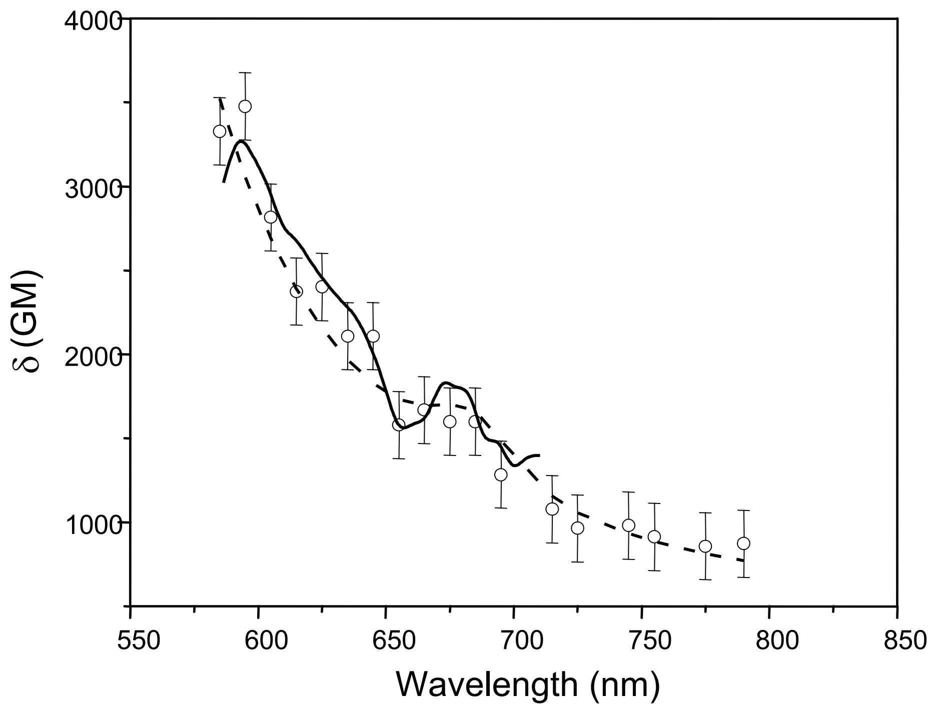


White light continuum Z-scan





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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Thank you !

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