

# ***Infrared frequency up-conversion in MEH-PPV***

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- Motivation
- MEH-PPV and its features
- Linear spectrum
- Multi-photon absorption
- Z-scan technique
- Three- and four-photon absorption measurements
- Infrared frequency up-conversion
- Conclusions

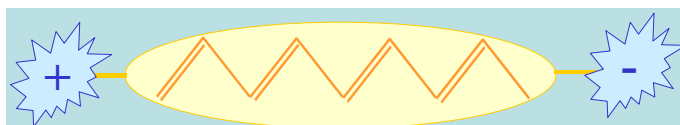
Materials exhibiting interesting electrical properties combined to high optical nonlinearities are desirable for photonics applications. Multi-photon absorption processes exhibits transition probabilities proportional to  $I^n$ , where  $I$  is the intensity of the laser pulse and  $n$  is the number of photons.

Such phenomenon provides chromophore excitation with high degree of spatial selectivity. In addition, the ability to create excited states with less energetic photons provides improved penetration in absorbing or scattering materials. Such features can be used to a variety of applications such as three-dimensional optical data storage, optical limiting, lithographic micro-fabrication, fluorescence excitation microscopy and imaging, photodynamic therapy, and infrared frequency up conversion lasing.

Here the three-photon and four-photon absorption cross-section (3PA and 4PA) spectra of MEH-PPV were determined from 1200 to 1900 nm. 3PA and 4PA excited emission were also observed, which open new windows for applications, such as up-conversion fluorescence devices.

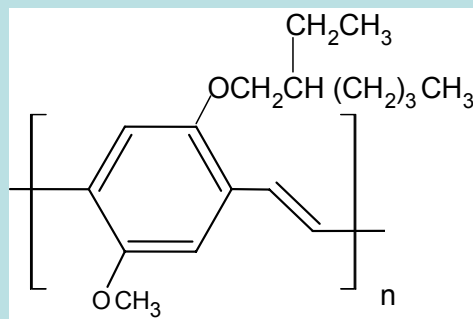
## Why conjugated materials, such as MEH-PPV, present high nonlinear optical processes?

→  $\pi$ -conjugation along the polymer backbone

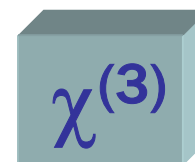


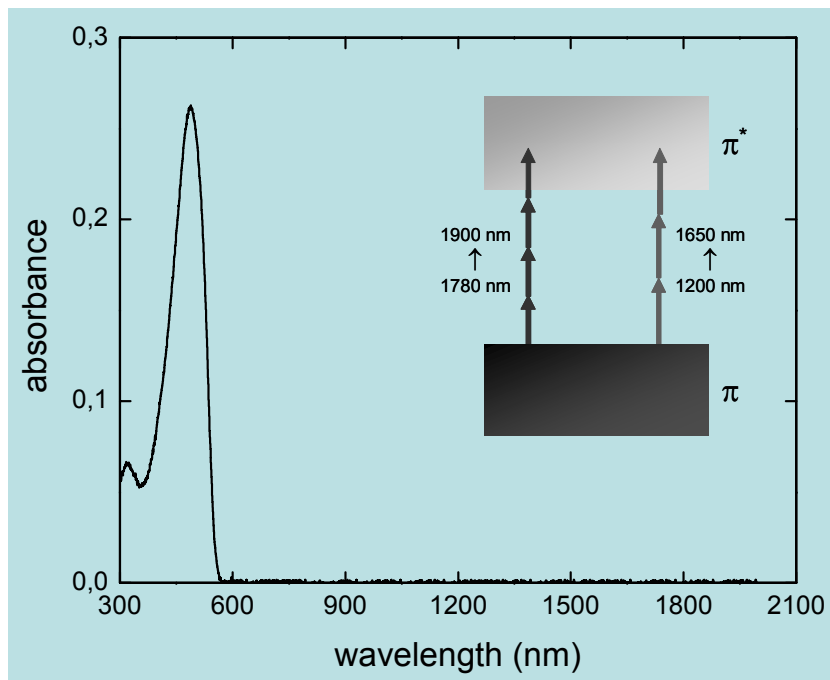
### MEH-PPV

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene)



High optical nonlinearities





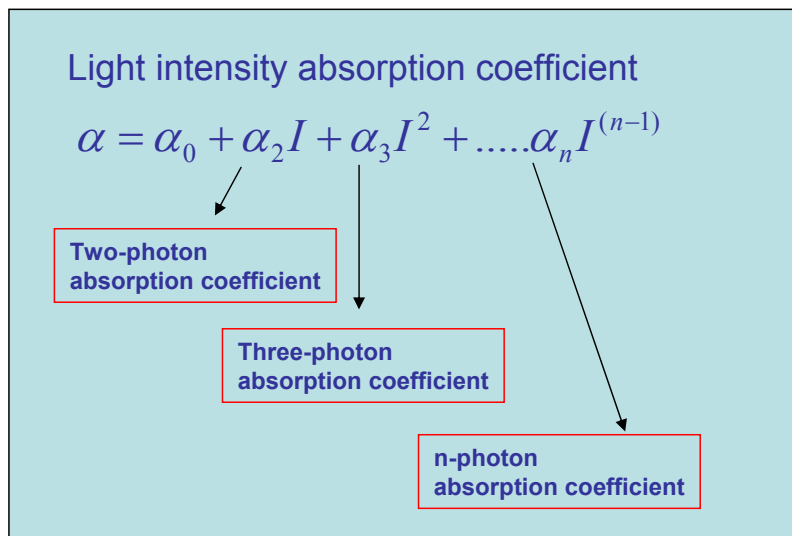
- MEH-PPV presents a  $\pi$ - $\pi^*$  absorption band around 490 nm.

- Completely transparent in the near infrared region

- Its asymmetry (highest symmetry C<sub>2h</sub>), makes selection rule restrictions to be relaxed allowing transitions to occur between equal or different parity states independently of the number of photons required.

A number of transitions using three and four photons can be attained by proper selection of the excitation wavelength.

In the presence of intense laser pulses, molecules can instantaneously absorb two or more photons, being promoted to an excited state. These multi-photon absorption processes exhibit transition probabilities proportional to  $I^n$ , where  $I$  is the intensity of the laser pulse and  $n$  is the number of photons absorbed in the event, which implies in chromophore excitation with high degree of spatial selectivity

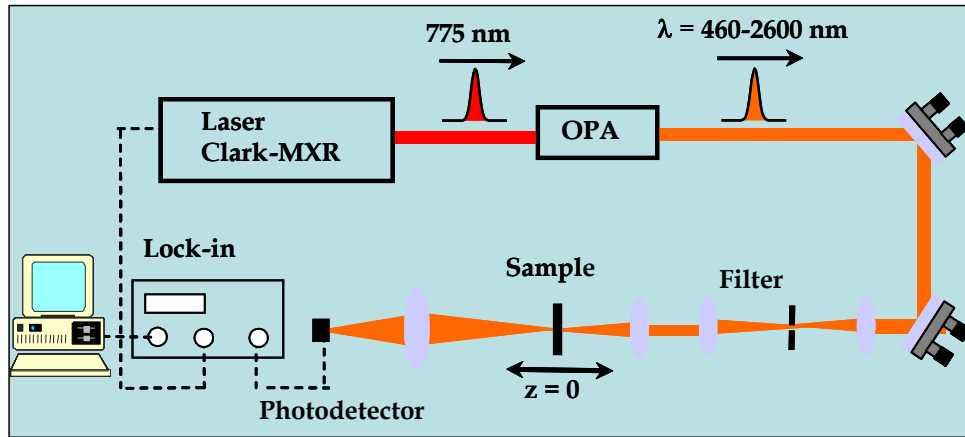


n-photon absorption cross-section

$$\sigma_{nPA} = \frac{\alpha_n (h\nu)^{n-1}}{N_0}$$

# Z-scan technique

## Experimental setup



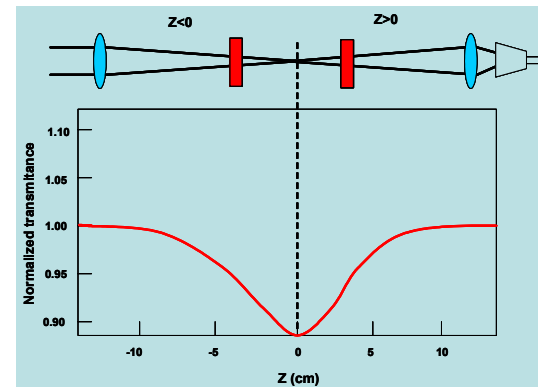
### Laser system

$\lambda = 1400 \text{ nm m};$   
 $\tau = 150 \text{ f};$   
 $F = 1 \text{ KHz}$

### OPA

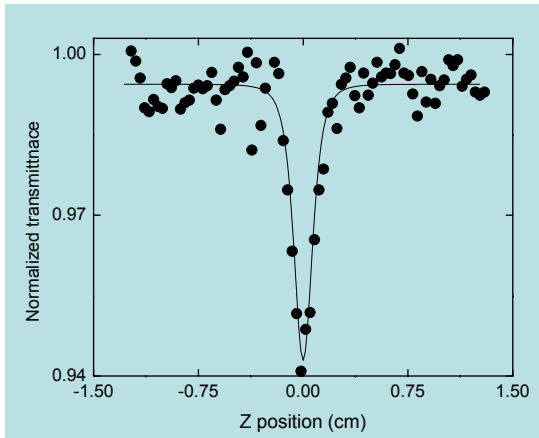
Tunable  $\lambda$  -460 - 2600 nm  
 $\approx 120 \text{ fs}$   
20-60  $\mu\text{J}$

Typical signature obtained by the absorptive open aperture Z-scan technique

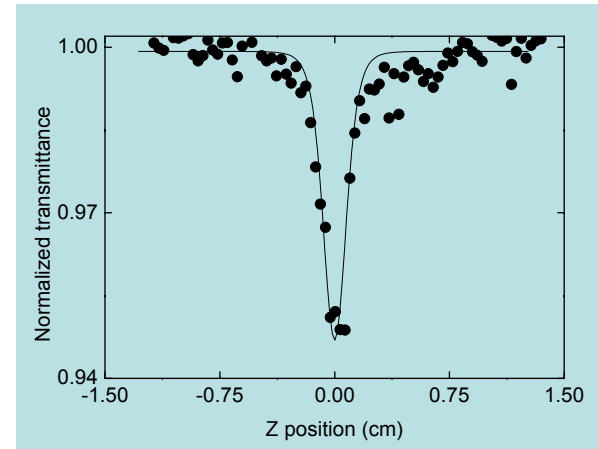


# Z-scan measurements

3PA → λ = 1400 nm



4PA → λ = 1820 nm



$$T(z) = \frac{1}{\sqrt{\pi} \sqrt{2\alpha_3 L(I_0 w_0^2/w^2(z))^2}} \int_0^1 \frac{R(x)}{x\sqrt{-\ln x}} dx$$

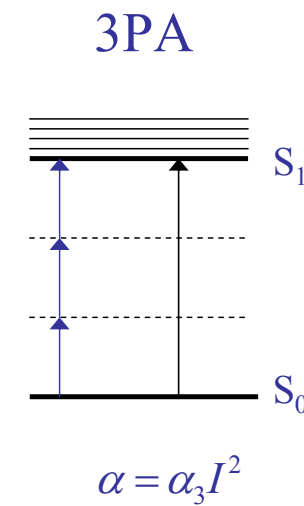
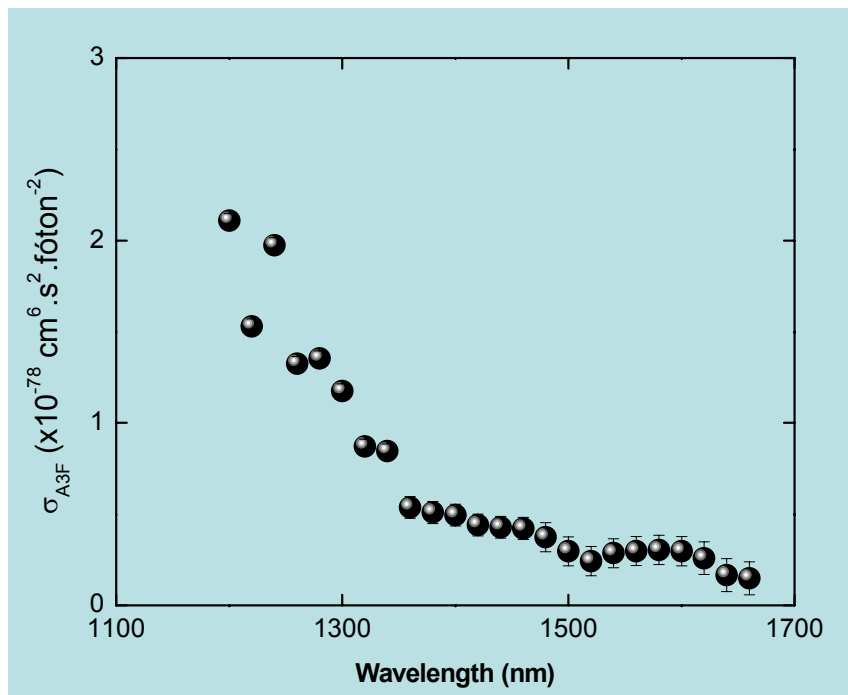
$$R(x) = \ln\left(\sqrt{1 + 2\alpha_3 L(I_0 w_0^2/w^2(z))^2 x^2} + \sqrt{2\alpha_3 L(I_0 w_0^2/w^2(z))^2 x^2}\right)$$

$$T(z) = \frac{1}{3\sqrt{\pi} \sqrt[3]{3\alpha_4 L(I_0 w_0^2/w^2(z))^3}} \int_0^1 \frac{R(\Delta)}{x\sqrt{-\ln x}} dx$$

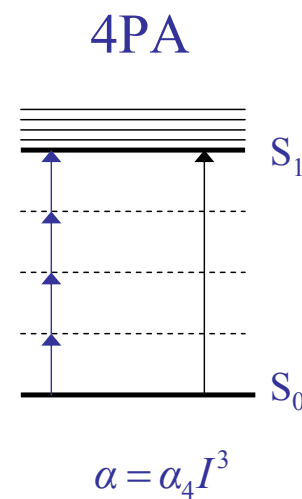
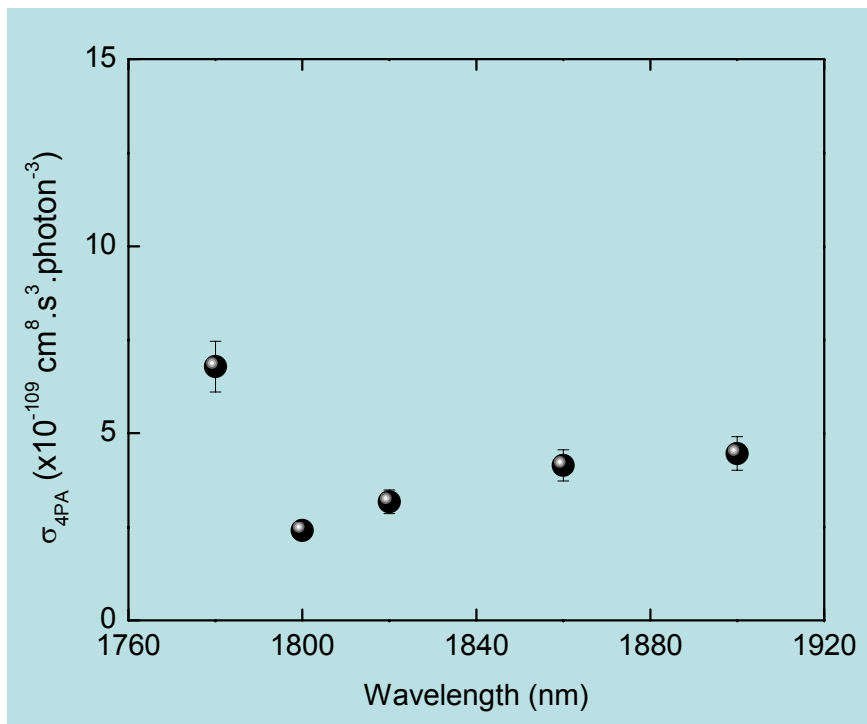
$$R(\Delta) = \ln\left(\frac{\sqrt{\Delta^2(x) + \Delta(x) + 1}}{\Delta(x) - 1}\right) - \sqrt{3} \arctan\left[\frac{2\Delta(x) + 1}{\sqrt{3}}\right] + \frac{\sqrt{3}\pi}{2}$$

$$\Delta(x) = \sqrt[3]{1 + \left(3\alpha_4 L(I_0 w_0^2/w^2(z))^3 x^3\right)^{-1}}$$





$\sigma_{3PA}$  increases by one order of magnitude when  $\lambda$  moves from 1650 towards 1200 nm, owing to the resonance enhancement of the 3PA, as the excitation wavelengths approaches 1/3 of the energy of the one photon state and due to the strong two-photon state at  $\sim 600$  nm, which is close to 2/3 of the one-photon energy level



$\sigma_{4PA}$  values are of the same order of magnitude of other organic materials

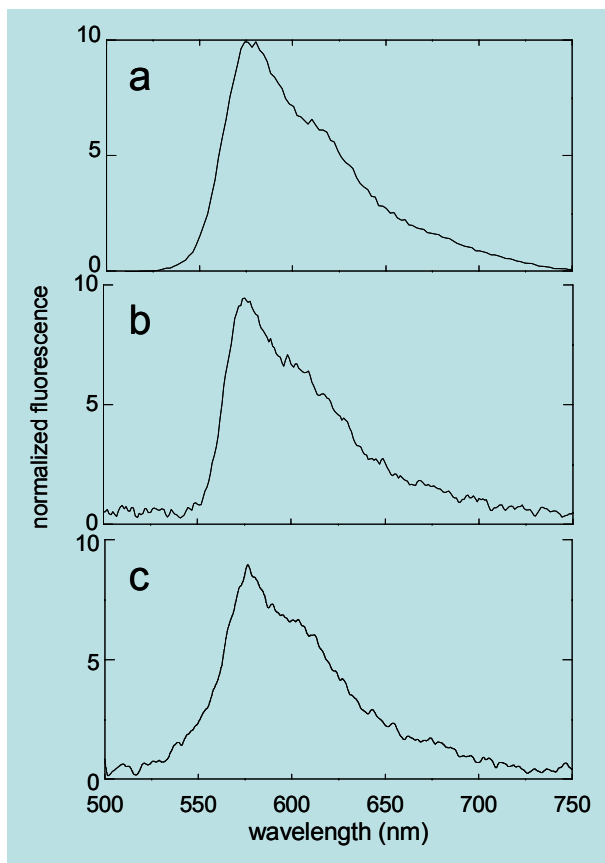


Figure 3a-c show the fluorescent emission for MEH-PPV induced via pure 3PA (1260 nm), a mixture of 3PA and 4PA (1700 nm) and pure 4PA (1800 nm), respectively.

All curves present identical profile, revealing that the relaxation process occurs from the bottom of the same excited state, independently of the excitation wavelength.

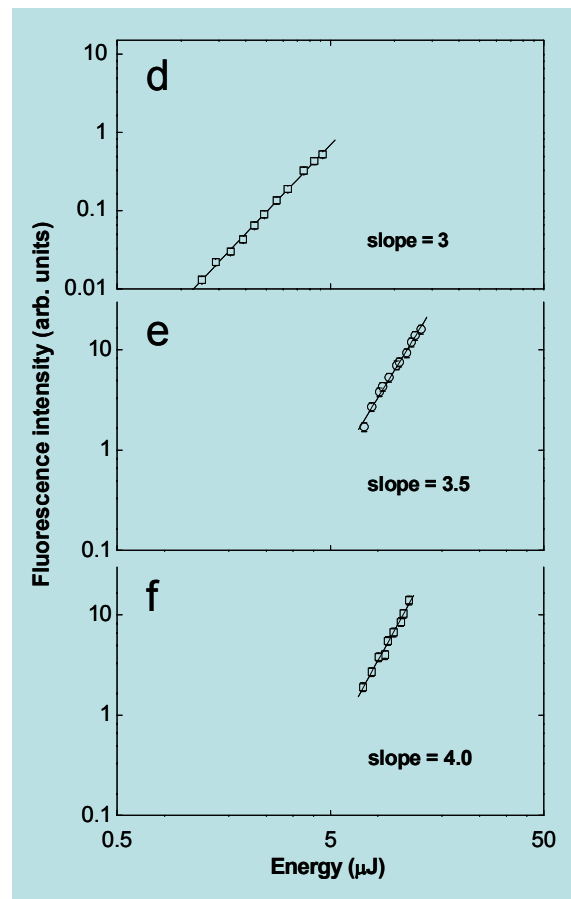
This polymer presents an emission peak around 575 nm, enabling its use for infrared frequency up-conversion devices.

Nonlinear process involving the simultaneous absorption of  $n$  photons, are expected to provide a slope of  $n$  for curves of fluorescence intensity versus input energy.

A slope of 3 (Fig. d) was obtained using excitation at 1260 nm (Pure 3PA). The same slope (not shown) was observed for excitations at 1400 and 1500 nm.

A slope of 3.5 (Fig. e) was obtained using excitation at 1700 nm, indicating a mixture of 3PA and 4PA (competition of processes).

A slope of 4 (Fig. f) was obtained using excitation 1800 nm, revealing a a pure 4PA process, predicted by the linear absorption spectrum of MEH-PPV.



Our results demonstrate for the first time multi-photon absorption (3PA and 4PA) processes in MEH-PPV. The 3PA and 4PA cross-sections, determined from 1220 to 1900 nm, are comparable to other organic molecules reported in the literature. The strong three and four photon-induced emission, combined with its well-established physical and chemical properties and commercial availability prompts MEH-PPV as a new material for photonics applications such as, for instance, up-conversion lasers. According to the excitation wavelength, it is possible to select a specific nonlinear process (3PA or 4PA), which enables MEH-PPV to be pumped by several commercial lasers in the near infra-red, giving a wide flexibility for applications with this material.

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