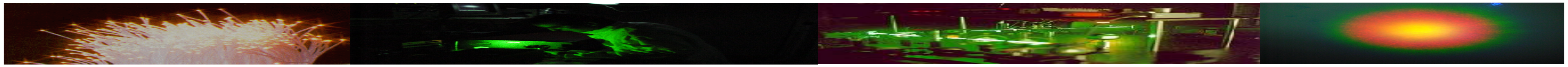

Controlling Two-Photon Excited Fluorescence in Perylene Derivatives via Femtosecond Pulses

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Abstract

In the present work we investigate the two-photon excited fluorescence (2PEF) in perylene tetracarboxylic derivatives (PTCDs). These compounds present extremely high two-photon absorption cross-section, which makes them attractive for applications in photonics devices. We used femtosecond pulses generated by a Kerr-lens modelocked Ti:Sapphire oscillator (15 fs, 60nm, 5nJ, 790 nm and 80 MHz).

Through distinct initial conditions of the excitation pulse (chirp) we have investigated changes in the 2PEF intensity and spectrum. By manipulation of pulse spectral components (pulse shaping) we have performed optimization of the 2PEF intensity of the PTCDs.

For the optimization of the 2PEF we used a spectral pulse shaping technique via micromachined deformable mirror (MMDM). In this case, the 2PEF intensity was used as feedback in a closed-loop learning algorithm (Genetic algorithm - GA) in order to control the deformation of the MMDM.

Perylene Tetracarboxylic Derivatives (PTCDs)

The perylene tetracarboxylic derivatives (PTCD) samples were provided by Dr. Ricardo F. Aroca from the *Materials and Surface Science Group* of Windsor University (Canada). Their concentrations are in the order of 10^{-5} mole L^{-1}. The absorption spectra in the UV-Vis region, obtained with a Cary 50 spectrophotometer, are presented in Fig. 2. These compounds present strong 2PEF, when excited at nonresonant conditions with strong laser pulse.

The compounds investigated are: bis (n-butylimido) perylene (BuPTCD), bis (benzimidazo) perylene (AzoPTCD), bis (benzimidazo) thioperylene (Monothio BZP) and n-pentylimido-benzimidazo perylene (PazoPTCD).

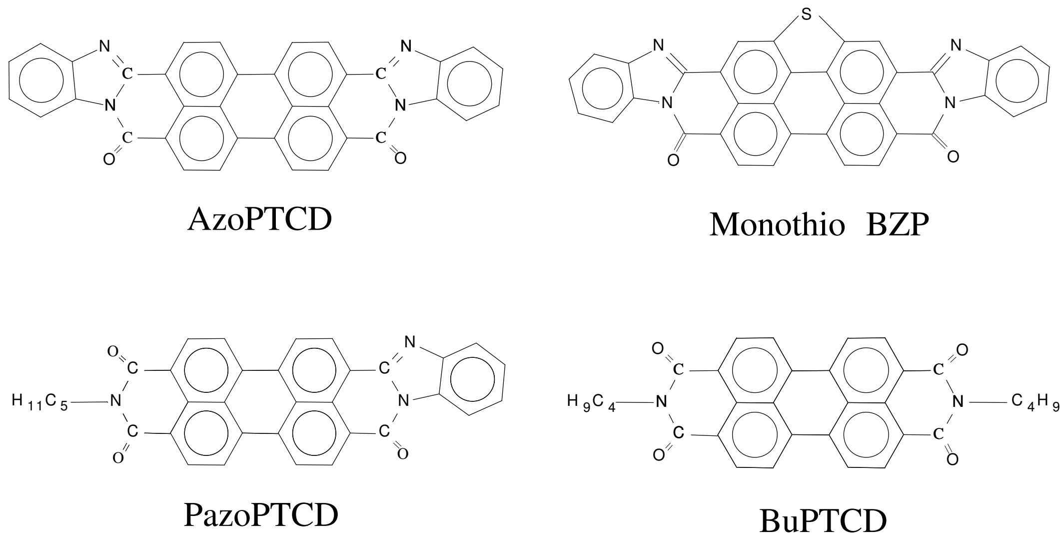

Figure 1: Molecular structures of the compounds investigated.

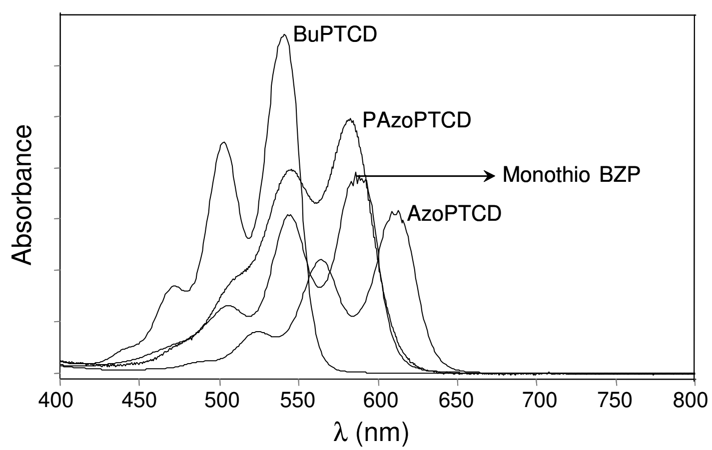

Figure 2: Absorbance spectra for the perylene samples dissolved with 10% trifluoroacetic acid (TFA) in dichloromethane.

Experimental Setup (Laser and Compression systems)

In this work were used laser pulses at about 790 nm with up to 15 fs, delivered by a commercial Ti:sapphire Kerr-lens modelocked (KLM) laser oscillator, to induce the 2PEF in our samples. The typical average power of the laser was 400 mW (~5 nJ per pulse).

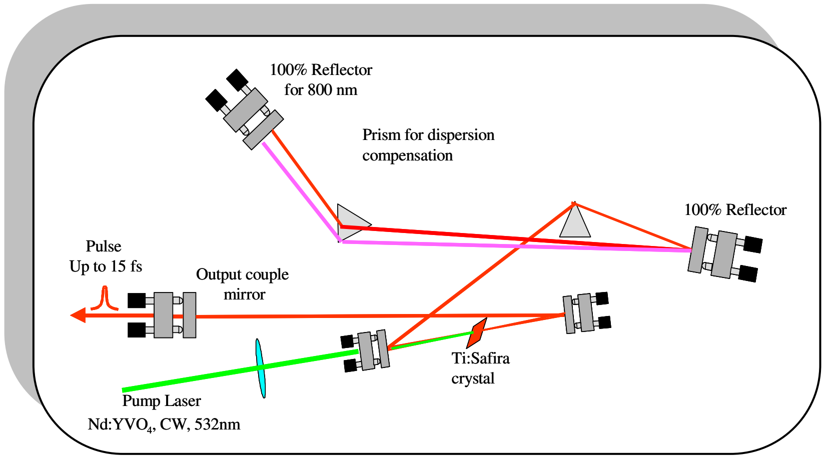

Figure 3: KLM Ti:sapphire femtosecond laser oscillator.

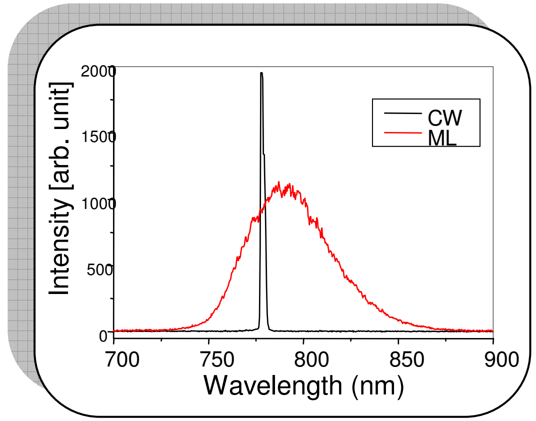

Figure 4: Emission spectrum of the laser.

We used a compression system consisting of a 600 grove/mm ruled grating and a 25 cm focal-length mirror. The output pulse passes through the compression system where, by changing the positions of curved mirror, we can adjust the linear chirp over a wide range.

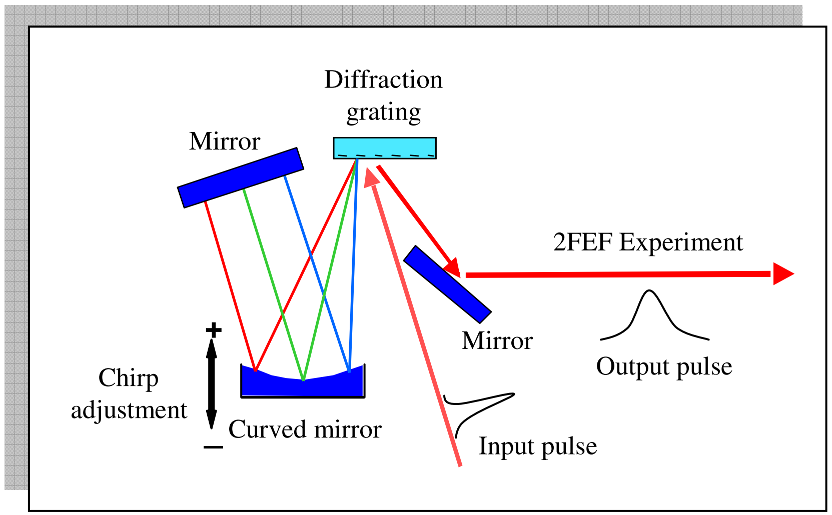

Figure 5: Layout of the experimental setup of compression system.

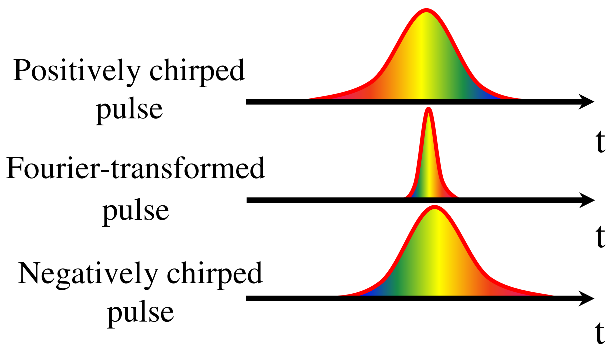

Figure 6: Pulses delivered for the compression system.

Experimental setup (Investigation of 2PEF)

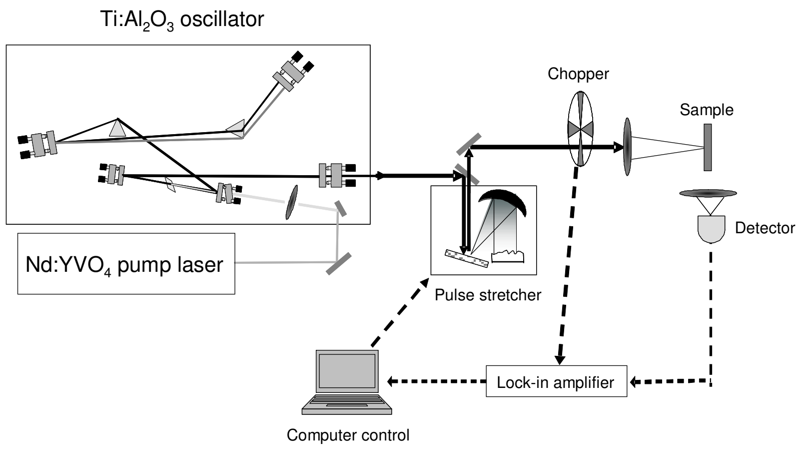

Figure 7: Experimental setup for 2PEF intensity measurement.

The two-photon excited fluorescence of PTCDs was collected perpendicularly to the incident beam direction, Fig. 7. The 2PEF intensity was acquired for distinct pulse chirps. The fluorescence was collected using a silicon PIN photo-detector coupled to a lock-in amplifier.

The two-photon excited fluorescence spectrum of PTCDs were measured using an Acton spectrometer (Spectra Pro 150), Fig. 8. Each spectrum was acquired for distinct chirps of the excitation pulse, in order to investigate changes in the spectrum that could imply fluorescence from not fully relaxed state.

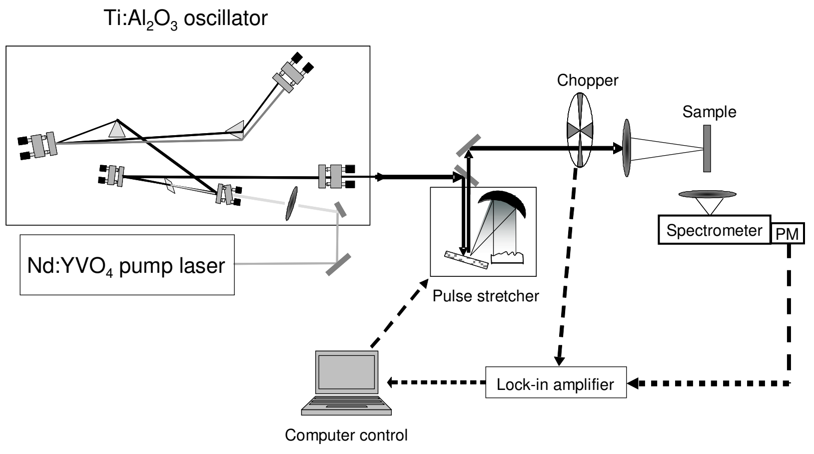

Figure 8: Experimental setup for 2PEF spectrum measurement.

Investigation of 2PEF intensity using chirped pulses

Two-photon absorption

$$\vec{P} \approx \chi^{(1)} \cdot \vec{E} + \chi^{(3)} \vdots \vec{E}\vec{E}\vec{E}$$

Total absorption $\alpha = \alpha_0 + \beta \cdot I$

2PA coefficient

$$\beta = \frac{\omega}{n_0^2 \varepsilon_0 c^2} \mathrm{Im}\left[\chi^{(3)}\right]$$

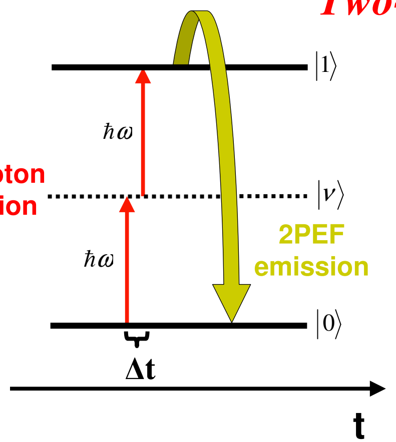

Figure 9: Two-photon excited fluorescence (2PEF) process.

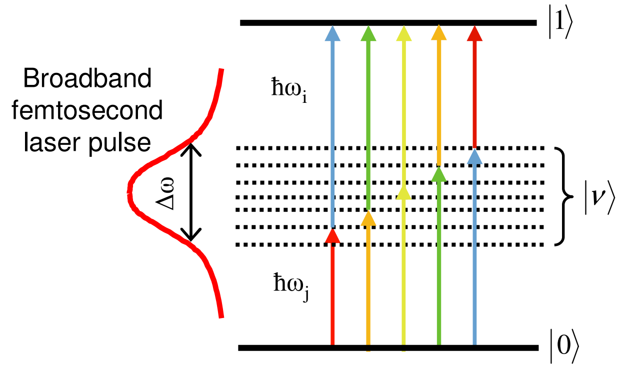

Figure 10: Different possible ways (Distinct pairs of photons can satisfy the transition).

2PEF Intensity vs Pulse Chirp

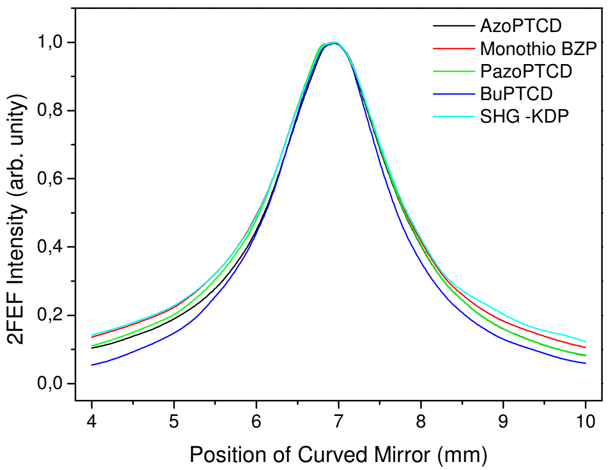

Figure 11: 2PEF intensity in the perylene tetracarboxylic derivatives.

Pulse Chirp vs Curved Mirror Position

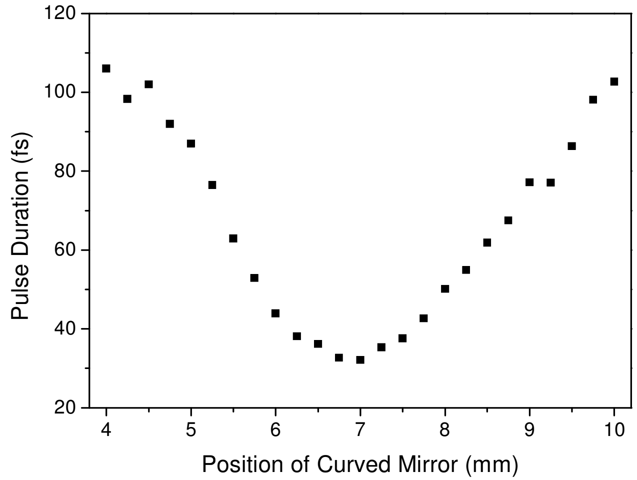

Figure 12: Measurements of pulse duration as function of position of curved mirror using FROG-SHG technique.

Investigation of 2PEF spectrum using chirped pulses

AzoPTCD

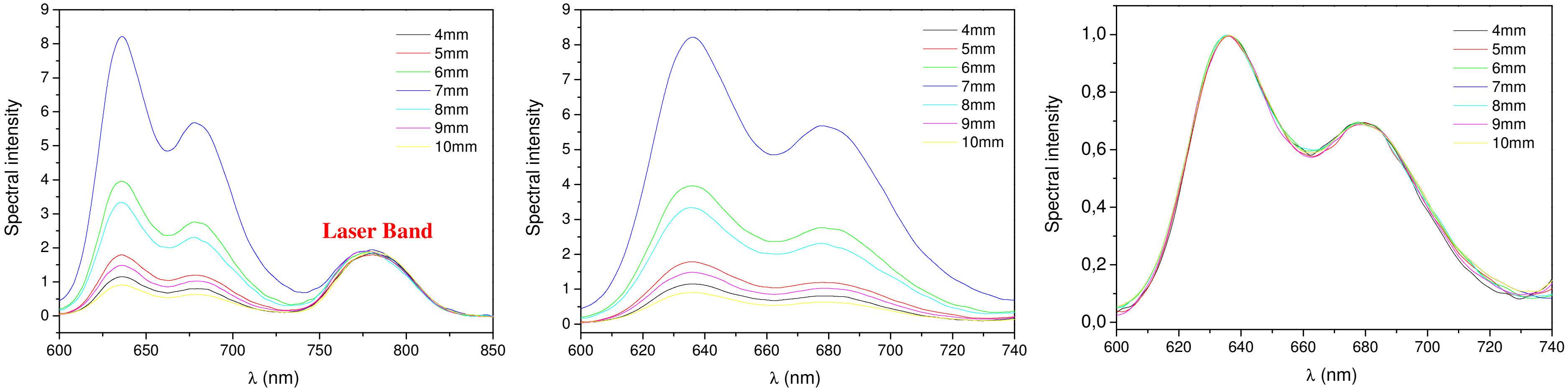

Figure 13: 2PEF spectra of bis (benzimidazo) perylene (AzoPTCD) for pulses with different chirps.

Monothio BZP

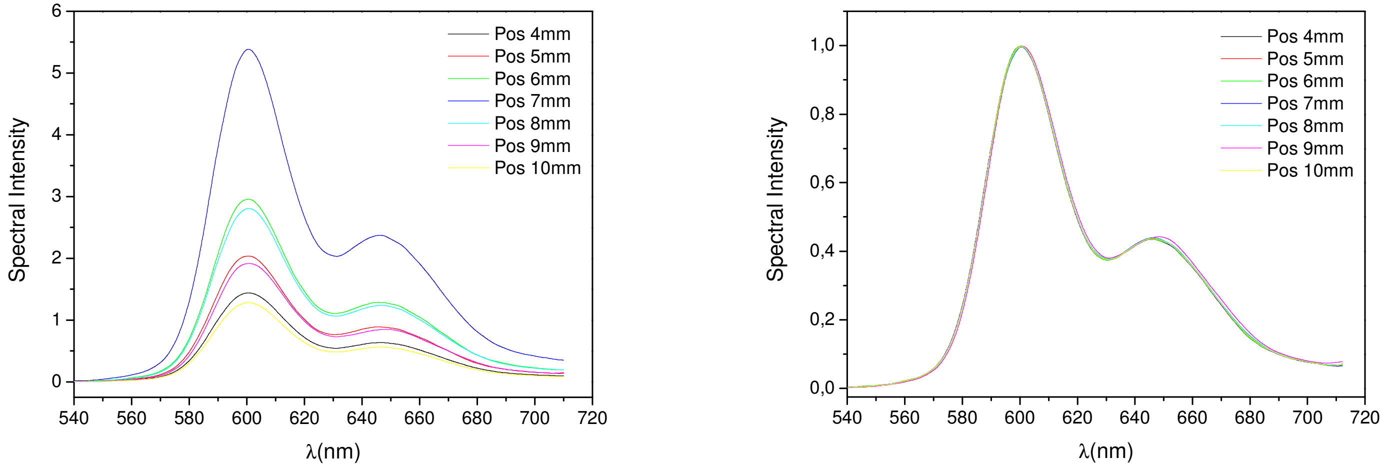

Figure 14: 2PEF spectra of bis (benzimidazo) thioperylene (Monothio BZP) for pulses with different chirps.

Investigation of 2PEF spectrum using chirped pulses

PazoPTCD

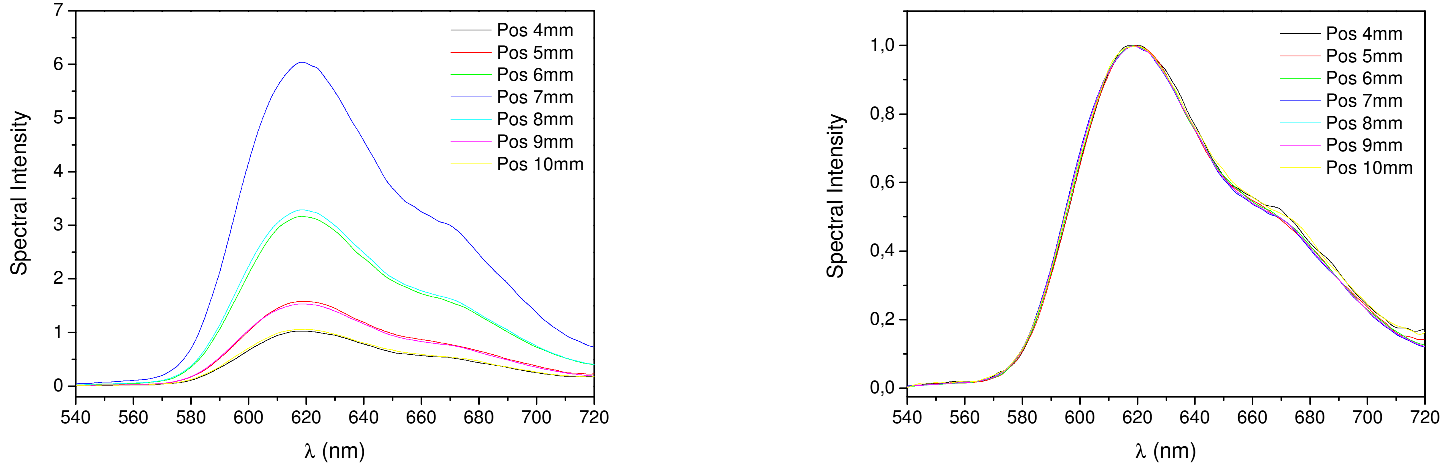

Figure 15: 2PEF spectra of n-pentylimido-benzimidazo perylene (PazoPTCD), for pulses with different chirps.

BuPTCD

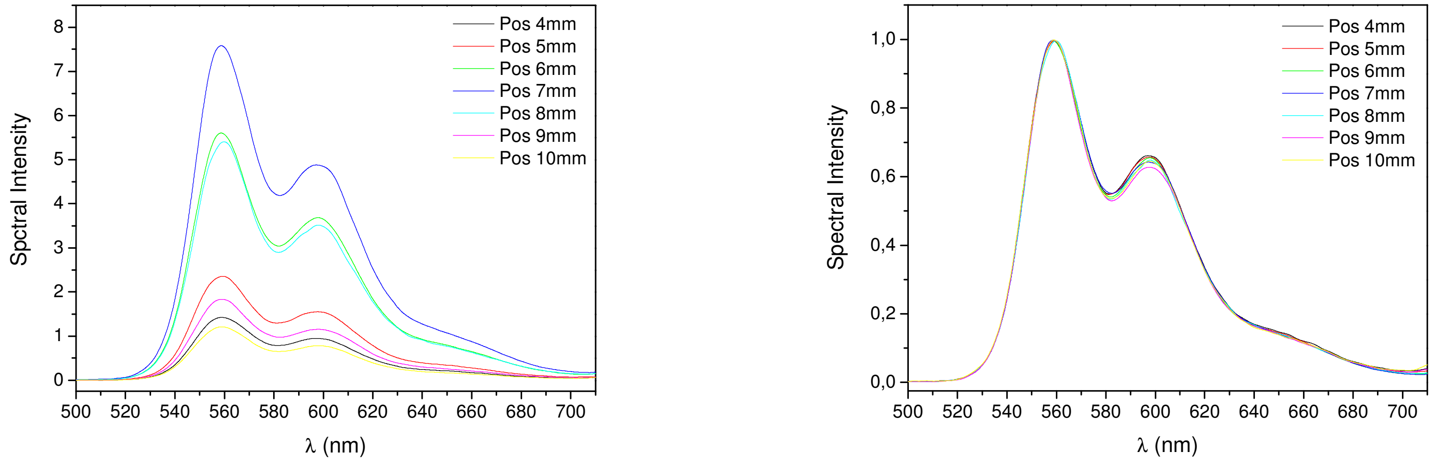

Figure 16: 2PEF spectra of bis (n-butylimido) perylene (BuPTCD), for pulses with different chirps.

Optimization of 2PEF using shaped pulses

We used a micromachined deformable mirror (MMDM) to shape the pulse in the phase domain. The mirror in the MMDM is a 600 nm gold-coated silicon nitride membrane (8 mm x 30 mm) suspended over an array of 19 actuator-electrodes. The maximum deflection is 4 µm with a response time of 1 ms. Potential applied to the actuator creates an electrostatic attraction between the membrane and the electrode, deforming the mirror surface. The total surface deflection of the mirror is a linear combination of the influence function for all actuators.

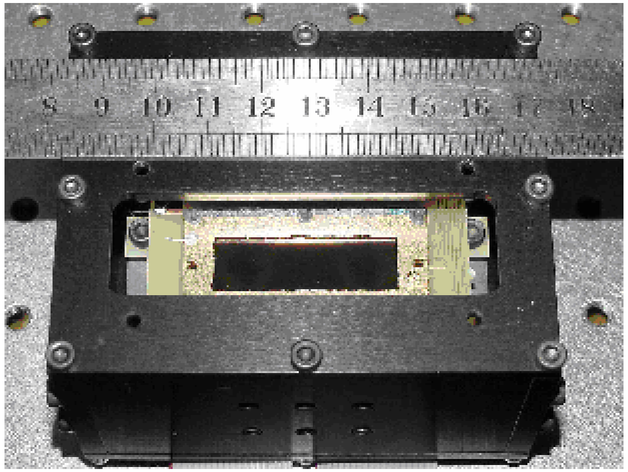

Figure 17: Micromachined deformable mirror (MMDM).

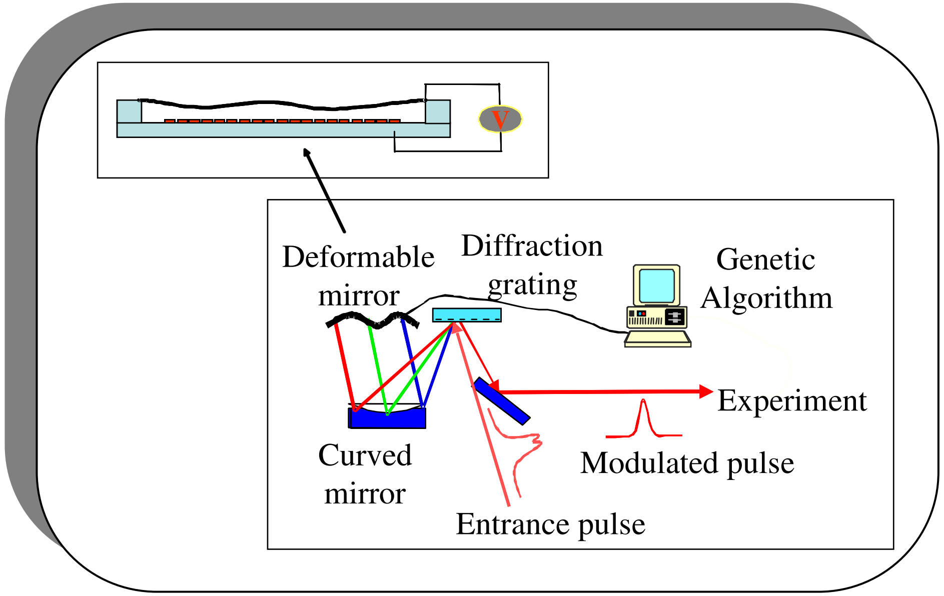

Figure 18: Experimental setup for pulse shaping.

Deviation of the mirror surface causes the light to travel a different path, changing the phase of the spectral component in one position with respect to other. The MMDM is placed at the Fourier plane of a zero dispersion stretcher consisting of a 600 grove/mm ruled grating and a 25 cm focal-length mirror. To control the deformation of the MMDM we have used a genetic algorithm (GA) program implemented in LabVIEW. Such algorithm is very powerful in the case of multiple variable problems.

Optimization of 2PEF using shaped pulses

The optimization of the 2PA is obtained using an evolutionary strategy (genetic algorithm - GA) which begins with a set of random pulse shapes whose associated fluorescence signal is measured. Those pulses that produce the most intense fluorescence are retained, duplicated, perturbed and reproduced, as the GA requires. This process is repeated until a desired number of interactions (generations). Basically, the GA is a search and optimization methodology inspired in the biological evolution, consequently, the biology concepts such as chromosome (father and children), reproduction, crossover, mutation, etc are applied in the computational GA code.

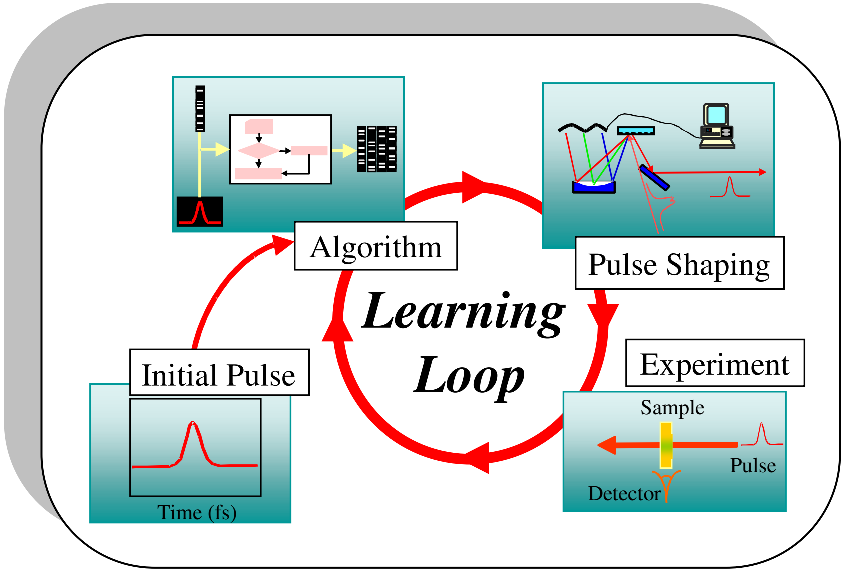

Figure 19: Experimental setup for pulse shaping optimization using GA.

2PEF Optimization Process Evolution

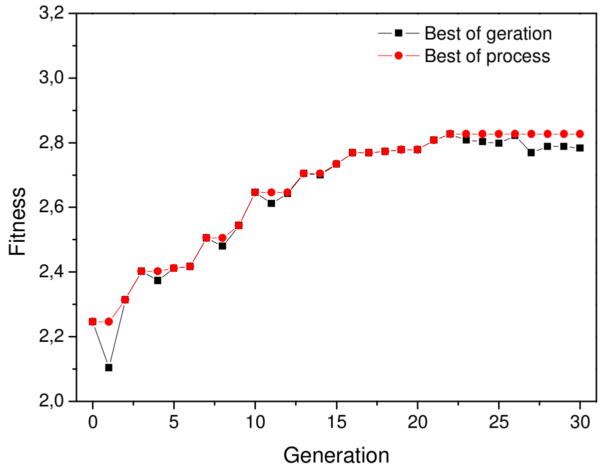

Figure 20: Fitness parameter evolution obtained through the GA during the optimization process.

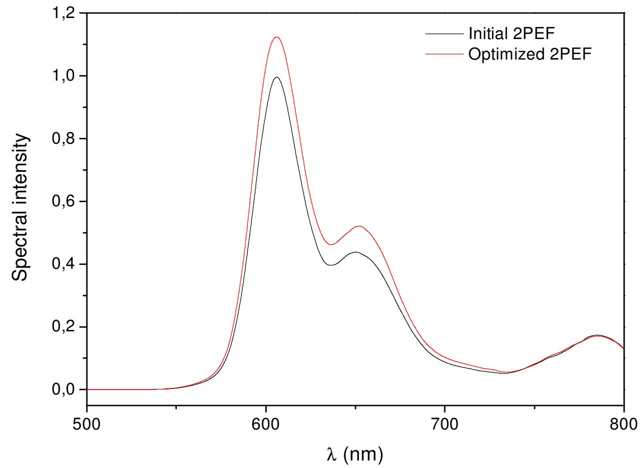

Figure 21: 2PEF spectra of Monothio BZP before and after 2PEF optimization process.

Optimization of 2PEF using shaped pulses

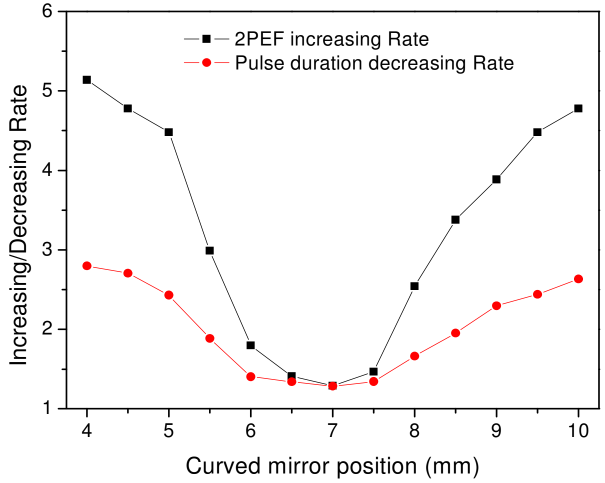

Figure 22: 2PEF increasing rate and pulse temporal duration decreasing parameters for different optimization processes realized.

Through the optimization processes we observed that the optimized 2PEF is achieved for transform-limited pulses, obtained in the end of the optimization process (30 generations), for distinct initial pulse chirps, as revealed by the FROG trace (flat phase distribution). The results pointed out that for low energy regime, the 2PEF presented for PTCDs is sensitive only to the pulse intensity, being their spectrum insensitive to the pulse phase configuration.

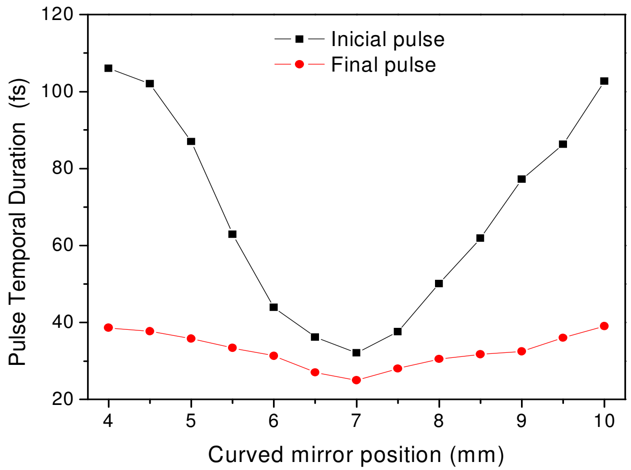

Figure 23: Pulse temporal duration as function of the curved mirror position before and after the optimization processes.

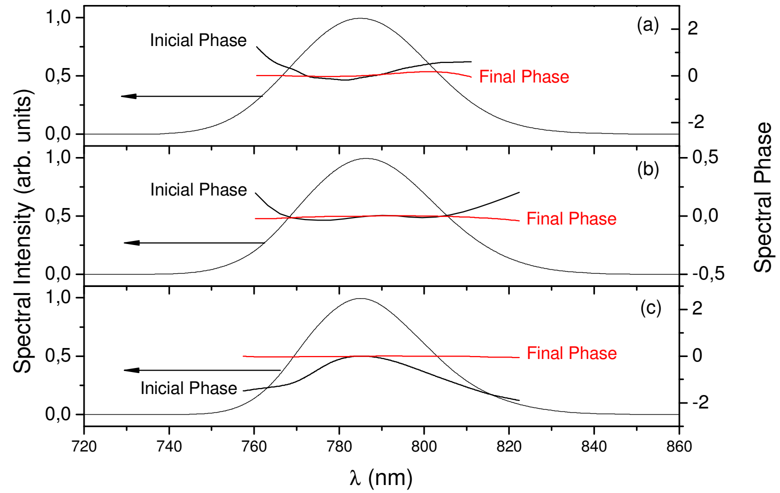

Figure 24: Pulse phase configuration before and after the 2PA optimization process for three different initial conditions: (a) Position 6 mm, (b) Position 7 mm e (c) Position 8 mm of the curved mirror. The pulse spectrum (left axes) and the pulse spectral phase (right axes).

Conclusion

➲ We found that two-photon excited fluorescence intensity (which is directly proportional to the excited state population) depends on, for low energies pulses, only of the pulse chirp quantities, positive or negative, being more intense for transform-limited pulses.

➲ The 2PEF spectrum of the perylene tetracarboxylic derivatives (PTCD) is independent of the pulse chirp. Further investigation must be carried out using high energies pulses (amplified system);

➲ The 2PEF optimization processes have converged to similar results (final pulse duration, 2PEF intensity and spectrum), independently of the initial conditions of the excitation pulse for every PTCDs.

References

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FAPESP

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