Excited State Absorption Study in Sulfonated-Halogenated Porphyrins

L. De Boni[1], P.J. Gonçalves[2], C.J.P. Monteiro[3], M. M. Pereira[3], S.C. Zilio[1], C. R. Mendonca[1]

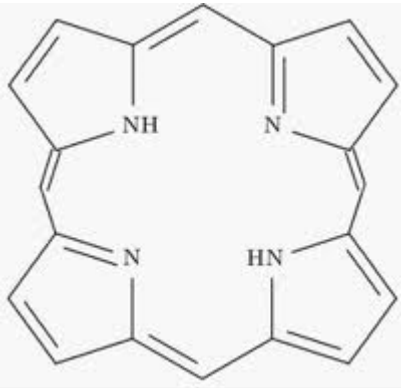
1- Instituto de Física de São Carlos,Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos, SP, Brazil,

2- Instituto de Física, Universidade Federal do Goias, Goiânia, GO, Brasil

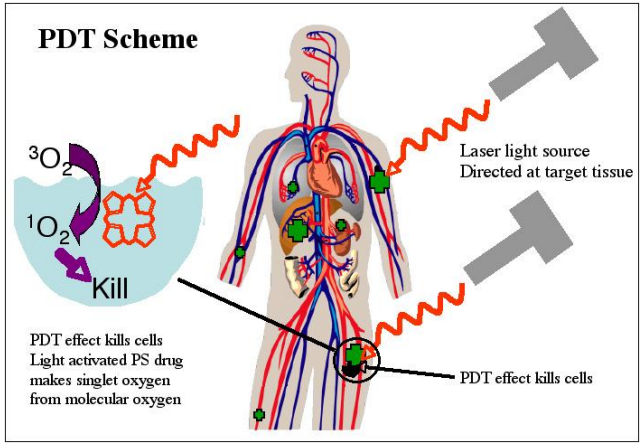
3- Departamento de Química, Universidade de Coimbra, Coimbra, Portugal

Motivation

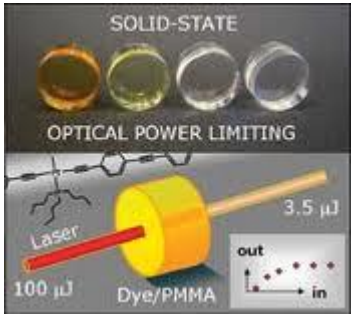
Porphyrins



Photodynamics therapy



Optical Limiter



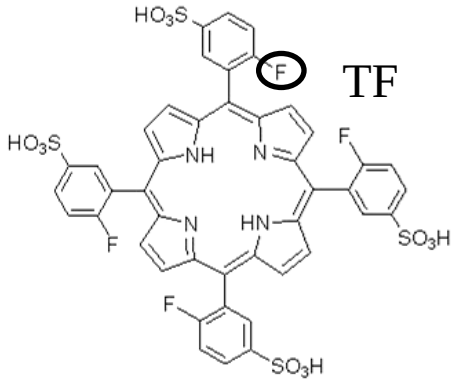
To obtain wide nonlinear spectra with proper resolution as function of the pH state of the porphyrins.

- Acid
- Basic

- Excited state absorption
- Excited state life time
- Population and structural dynamics
- Triplet state formation

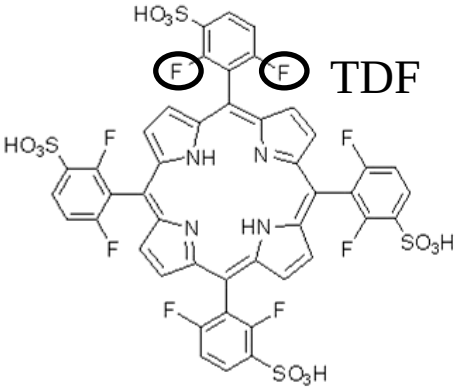
Samples

5,10,15,20-*meso*-tetraquis(2-fluor-5-sulfofenil)



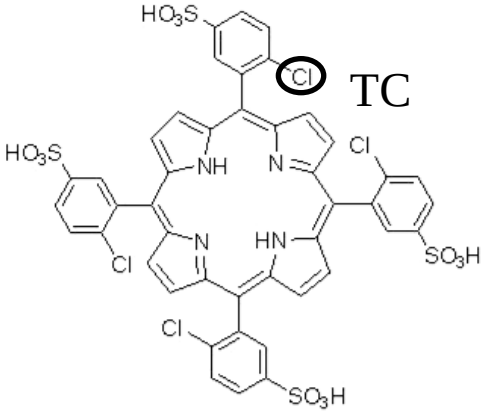
TFPPSO$_3$H

5,10,15,20-*meso*-tetraquis(2,6-fluor-3-sulfofenil)



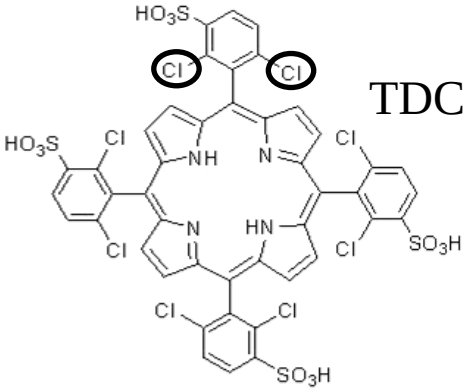
TDFPPSO$_3$H

5,10,15,20-*meso*-tetraquis(2-cloro-5-sulfofenil)



TCPPSO$_3$H

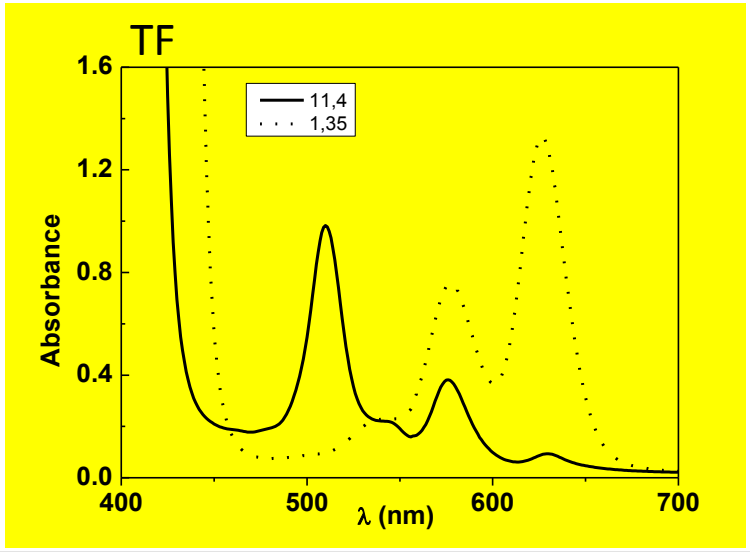
5,10,15,20-*meso*-tetraquis(2,6-dicloro-3-sulfofenil)

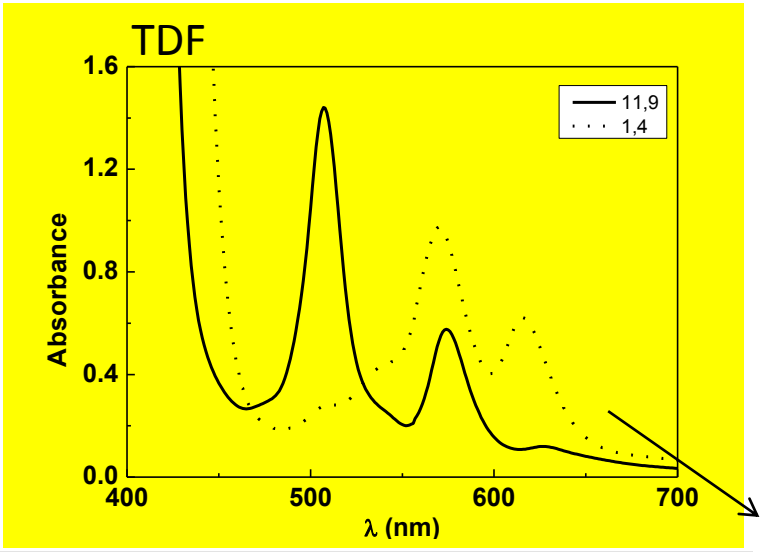


TDCPPSO$_3$H

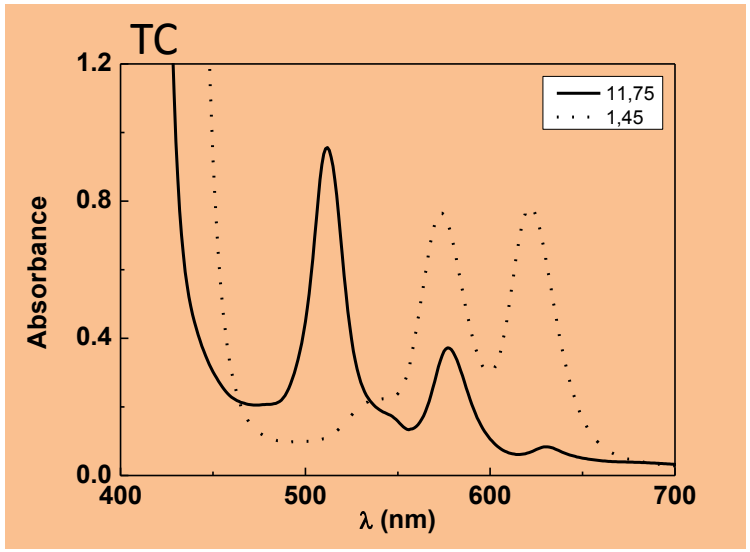
Changes in pH: basic and acid

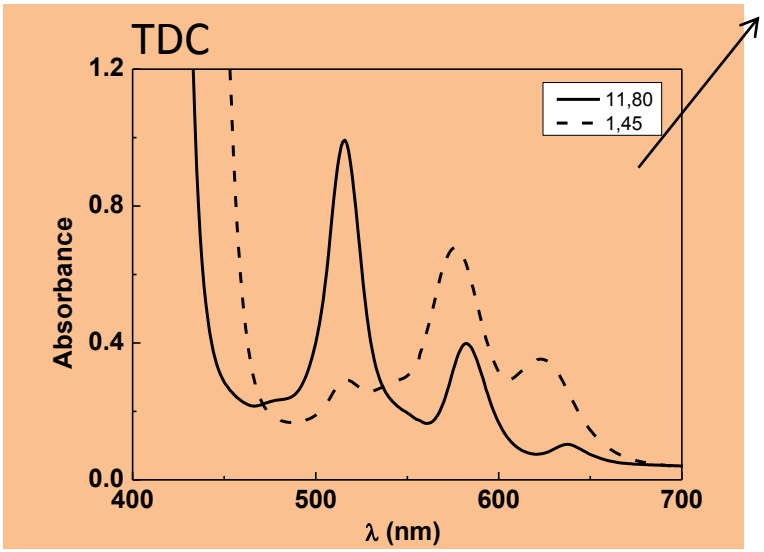
Linear absorption





More than one species

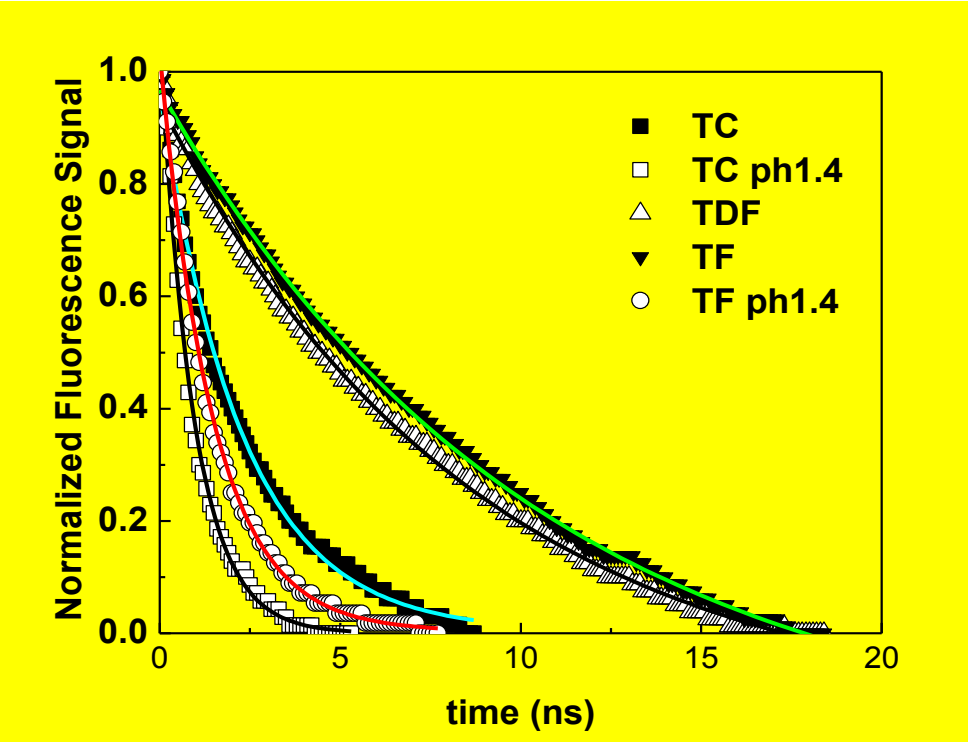




Fluorescence Lifetime

Excitation is done by using a 532nm 70ps laser pulse

Fluorescence signal is collected by using a optical fiber and the time was measured with fast Silicon detector (500ps rise time)



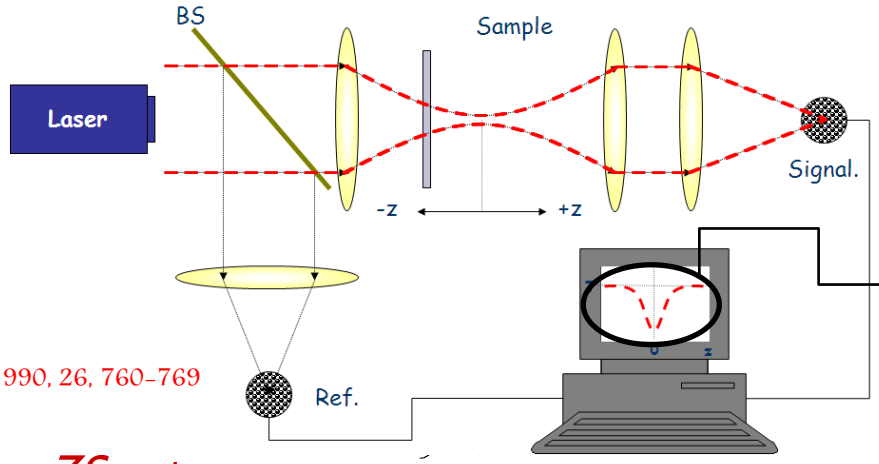
Mono-exponential

	pH	τ_{fl} (ns)
TF	1.4	1.5
TF	11	11.4
TDF	11,9	8.7
TC	1.45	0.9
TC	11,75	2.3
TDC	11,8	0,41*

*Value obtained by ours Collaborators

The Technique

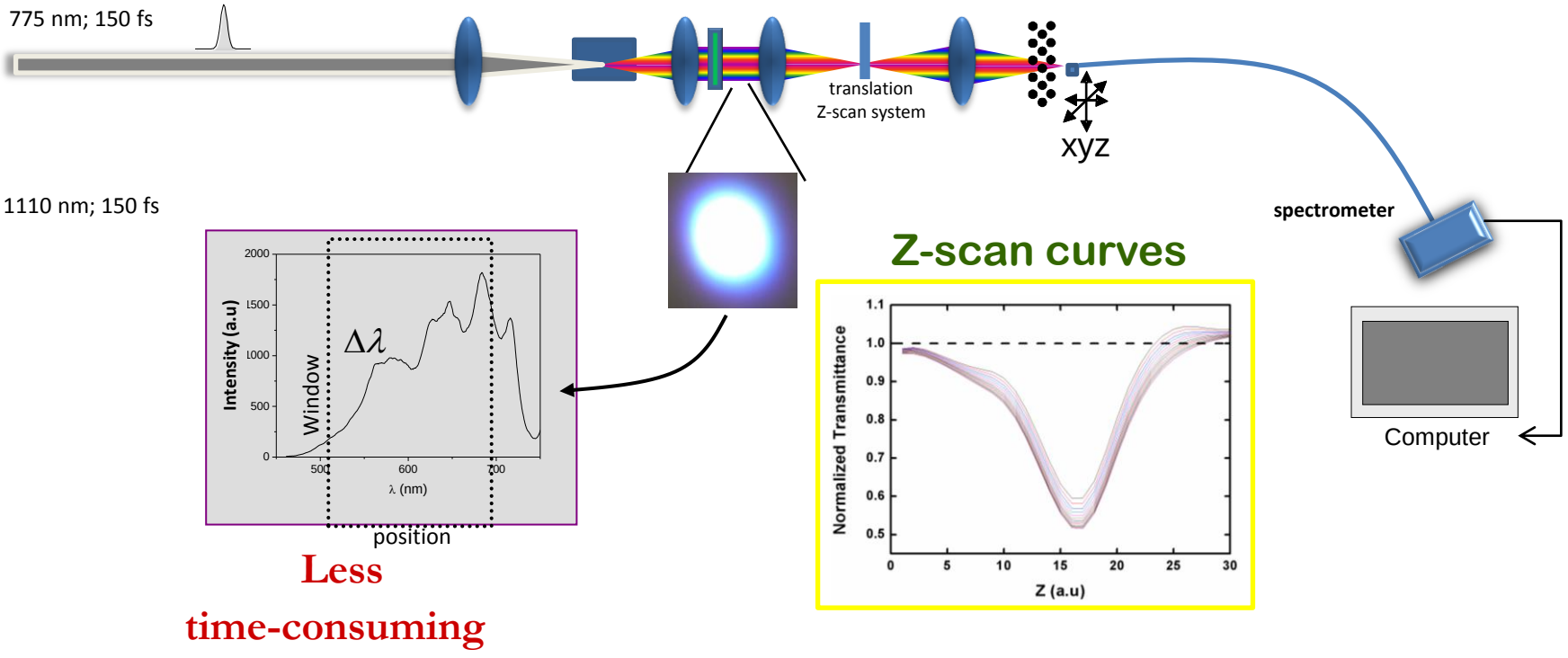
Z-scan technique



Decreasing in the Transmittance at the focal point

Sheik-Bahae, M. et al.., IEEE J. Quantum Elect. 1990, 26, 760-769

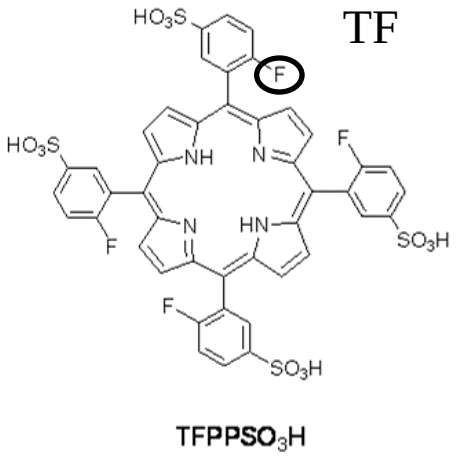
✓ *White light continuum ZS setup*

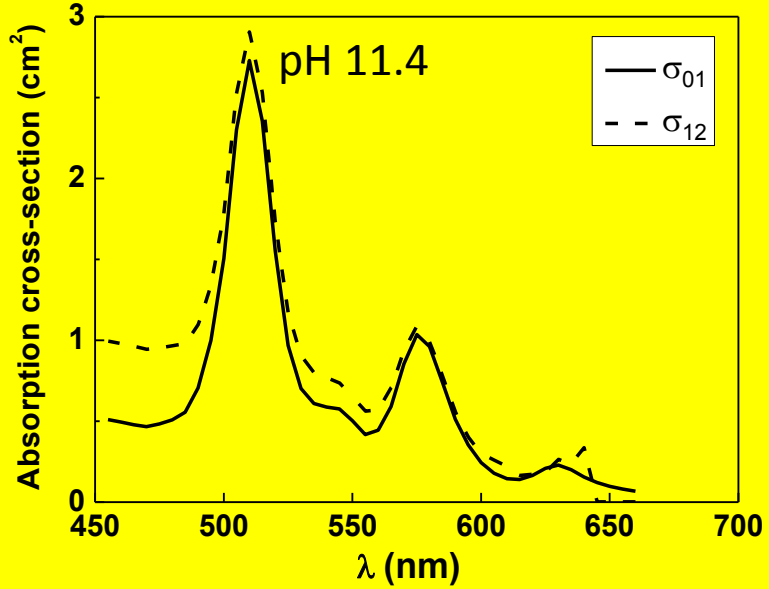


Less time-consuming

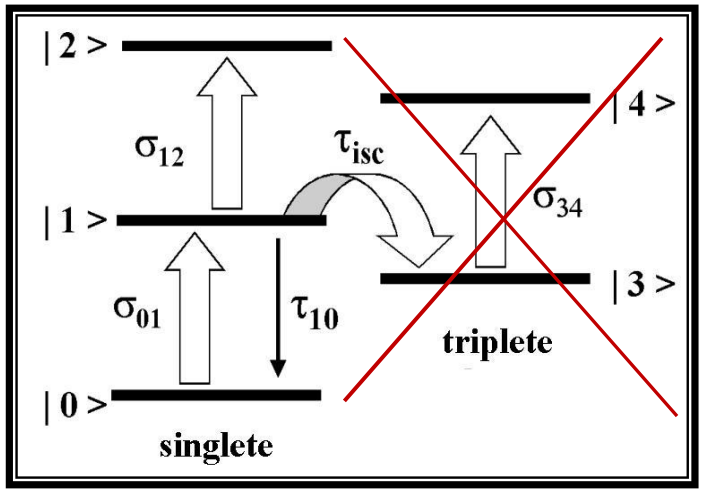
Results

Excited state absorption spectra

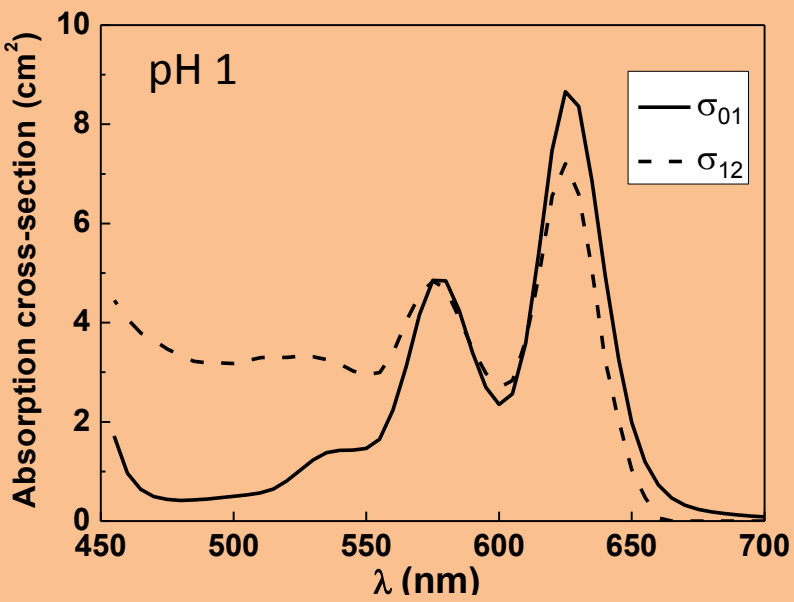




Rate equations only for singlet states

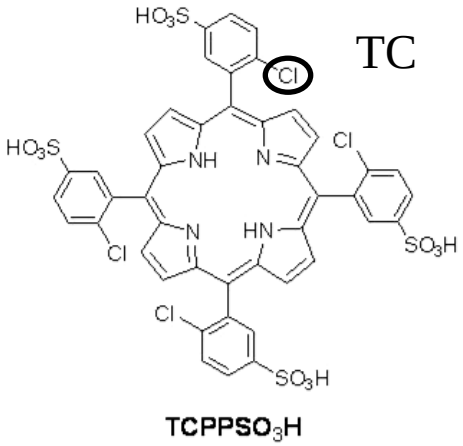


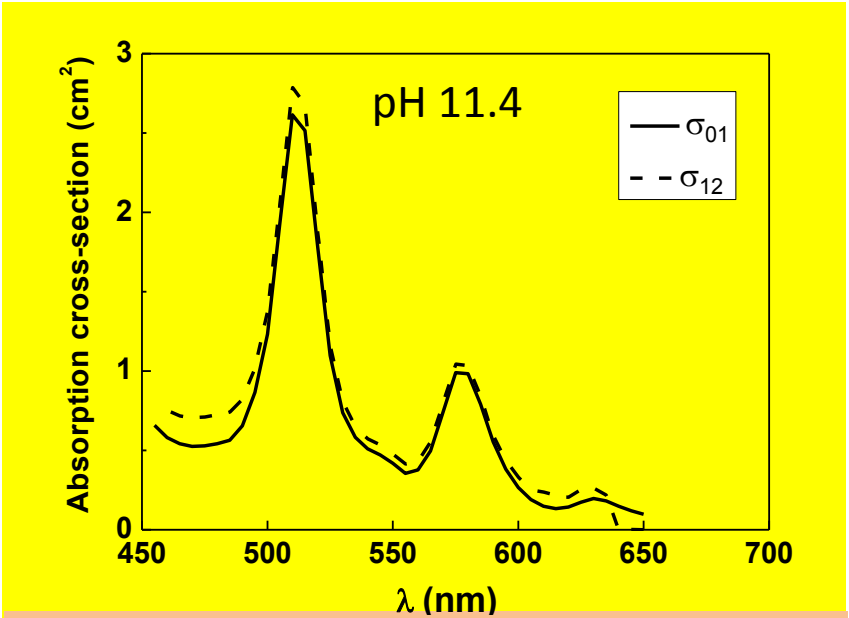
σ_{01} and τ_{10} are known



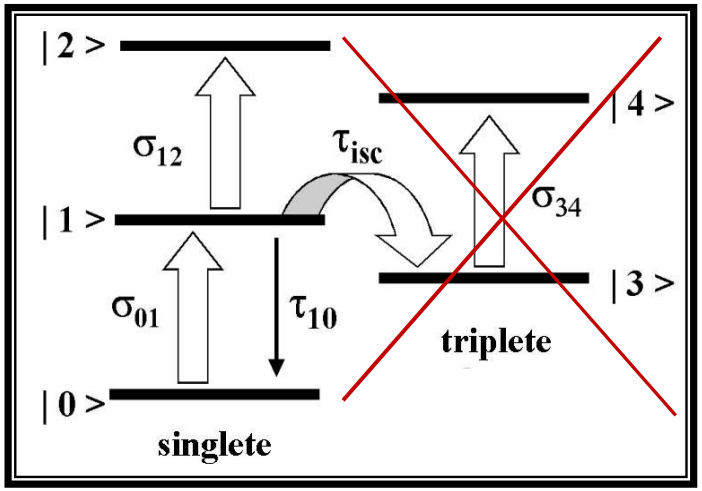
Results

Excited state absorption spectra

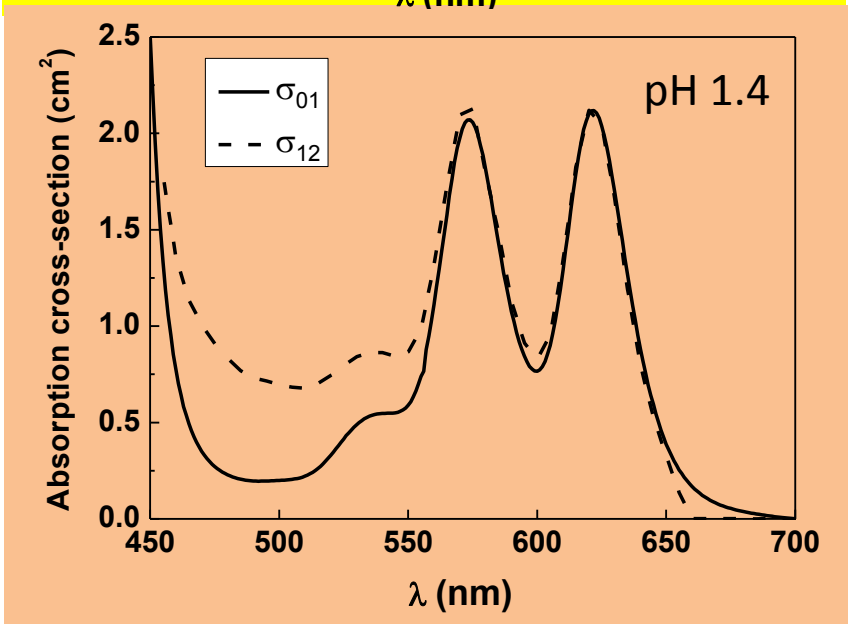




Rate equations only for singlet states

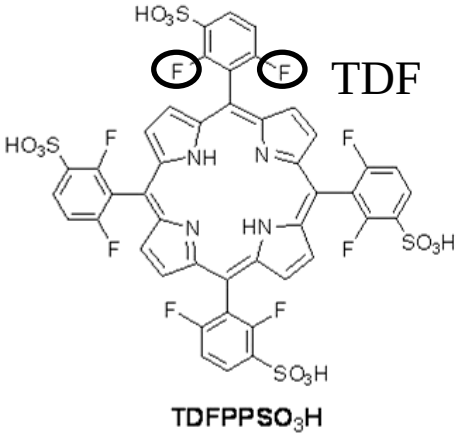


σ_{01} and τ_{10} are known



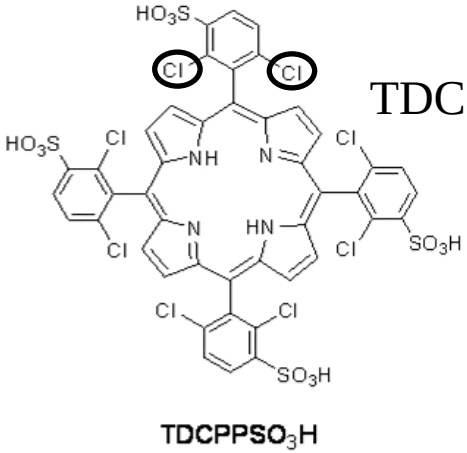
Results

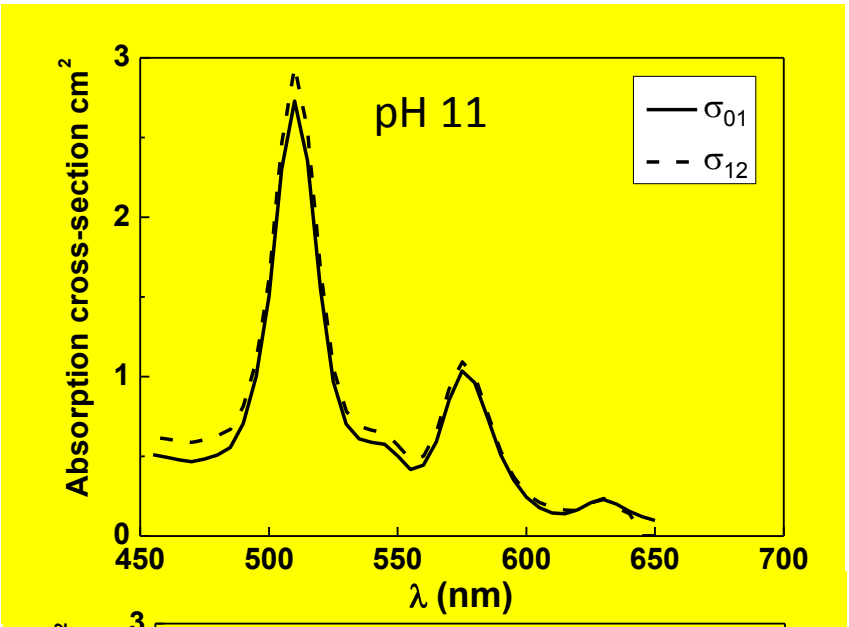
Excited state absorption spectra

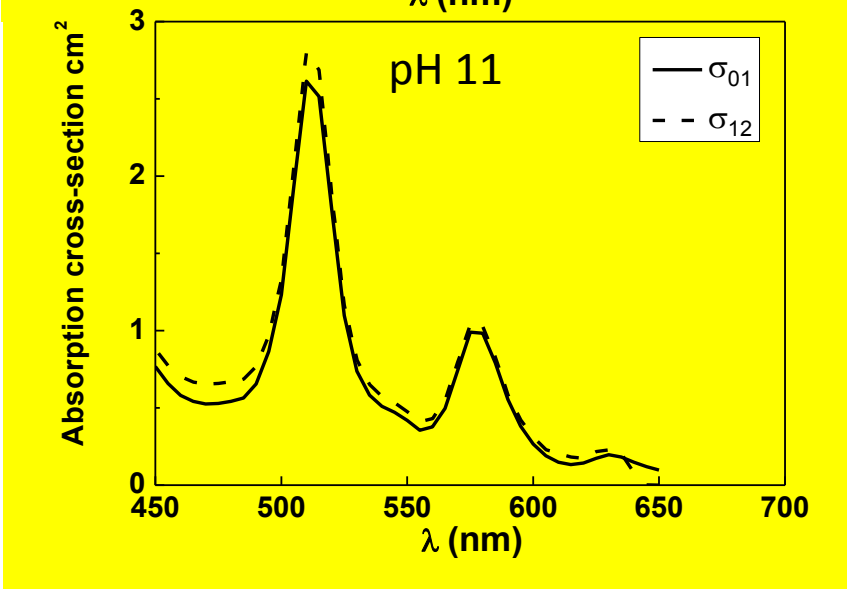


Rate equations only for singlet states

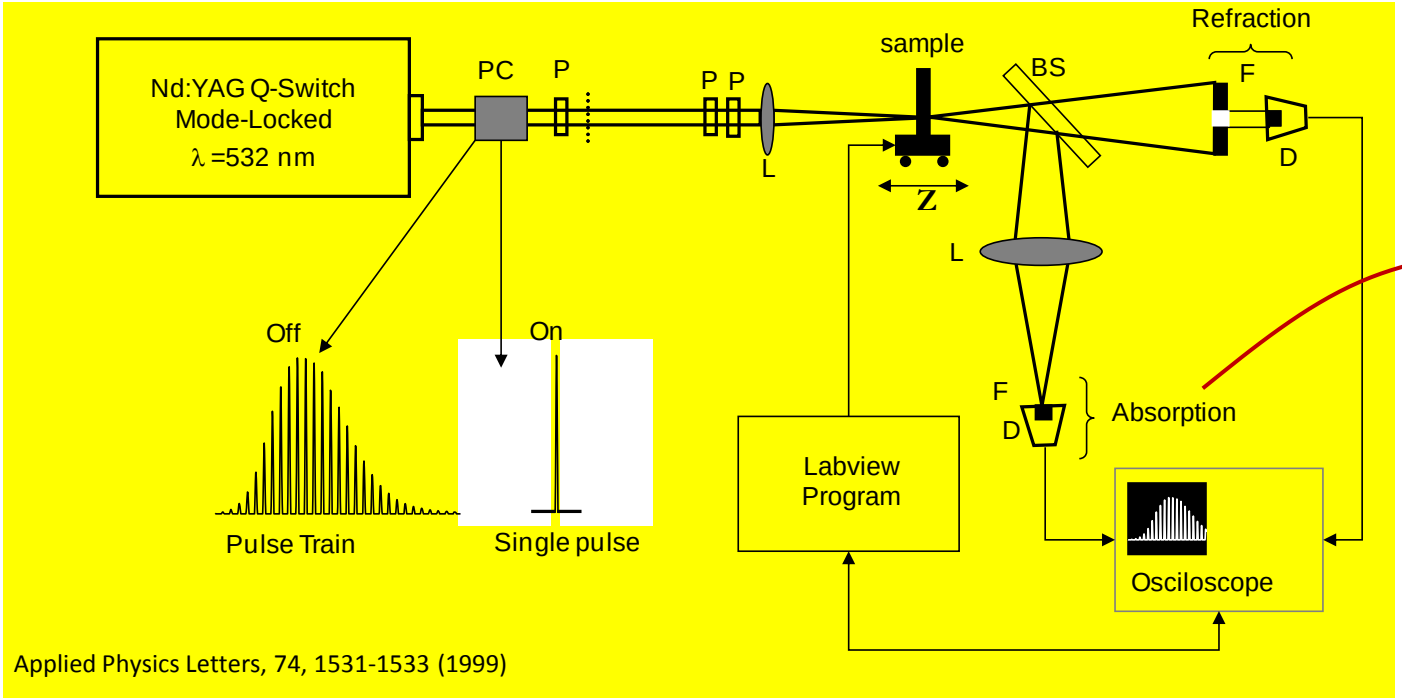
σ_{01} and τ_{10} are known





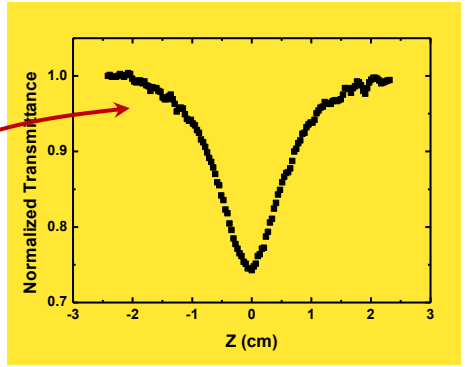


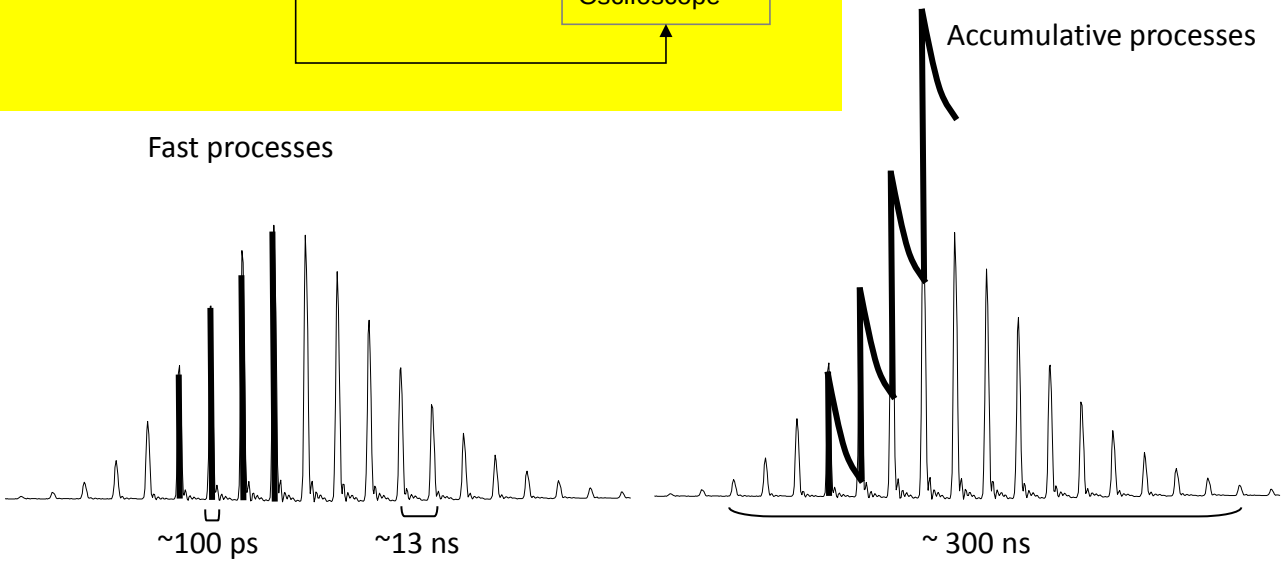
The Pulse Train Z-scan Technique



Applied Physics Letters, 74, 1531-1533 (1999)

Typical Z-scan curve

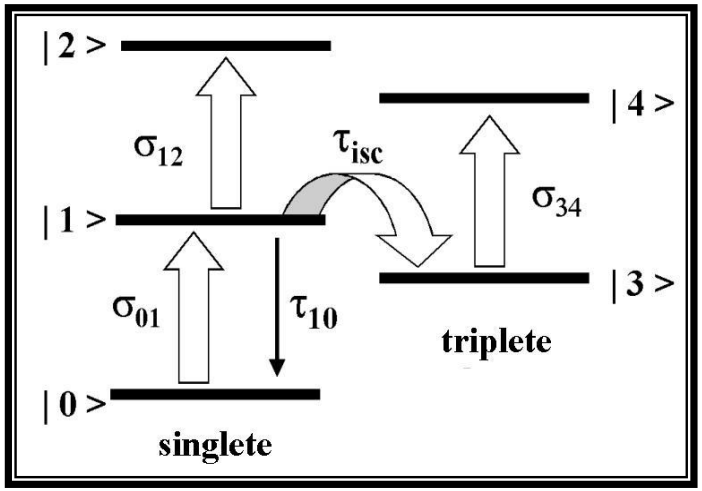




Sheik-Bahae, M. et al., IEEE J. Quantum Elect. 1990, 26, 760-769

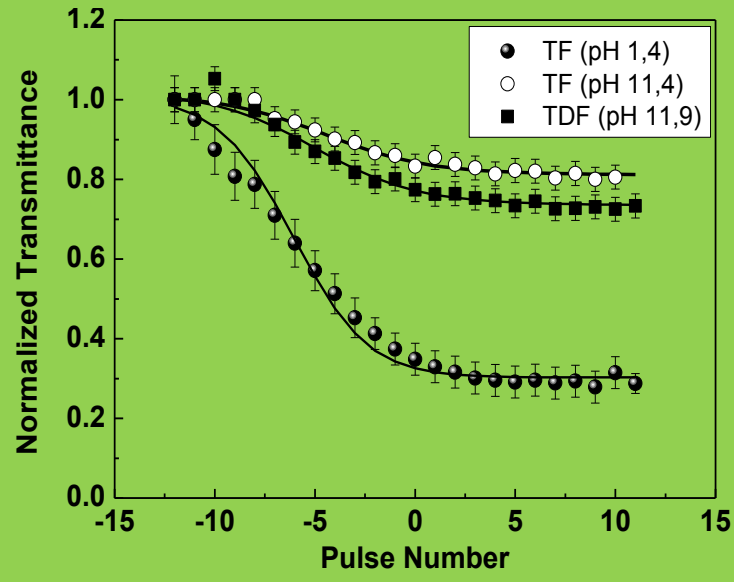
Results

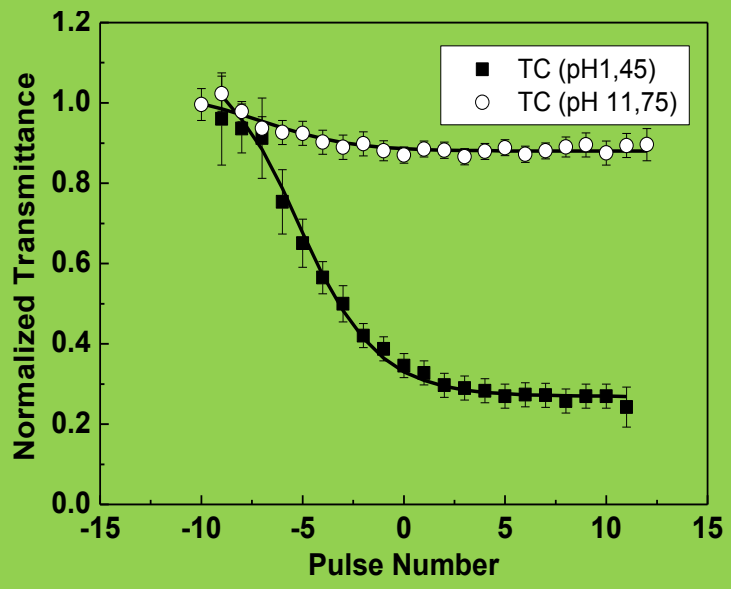
Rate equations considering the triplet states



NOW, σ_{01}, σ_{12} and τ_{10} are known

	pH	σ_{34}	σ_{34}/σ_{01}	τ_{isc} (ns)	φisc
TF	1.4	6,2	4,5	2,2	0,68
TF	11	1,28	2,0	13	0,88
TDF	11,9	0,73	1,4	10	0,87
TC	1.45	2,60	4,4	1,0	0,90
TC	11,75	0,82	1,2	2,5	0,92
TDC	11,8	0,69	1,0	-	-





Conclusion

- Halogenated atoms increases the intersystem crossing yield: important to PDT;
  - a weak RSA effect was observed in the singlet transition
  - a considerable enhancement of the RSA effect in the triplet state
- The vibronic structure of the porphyrins (D_{2h} molecular symmetry) is preserved upon electronic excitation;

pH effect

- it is possible to protonate TC and TF;
- Protonation:
  - increases σ_{12}/σ_{01} between 450 to 550 nm;
  - reduces τ_{S1}, τ_{isc} and φ_{isc};
  - increases σ_{01} , σ_{12} and σ_{34} at 532 nm; pulse train

- Protonation: conformational changes

- The protonation shows a high RSA: potential candidates for applications in optical devices, such as optical limiters.

Acknowledgements

FAPESP

CNPq

CAPES

Thank you