Resonant Nonlinear Absorption in J-aggregates of meso-tetrakis(sulfonatophenyl) porphyrin

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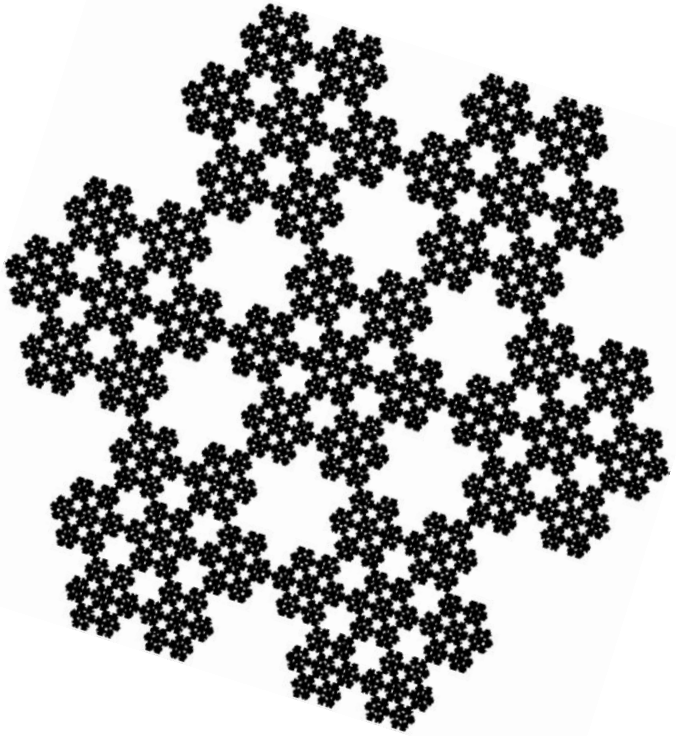
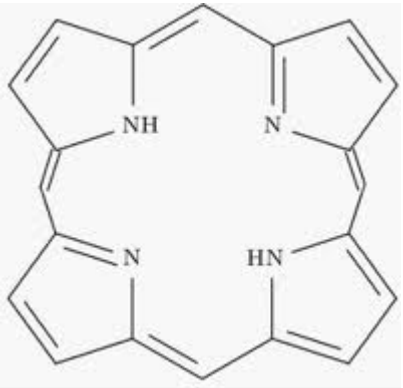
Outline

- Motivation
- Molecule background
- Experimental setup
- Results
- Conclusion

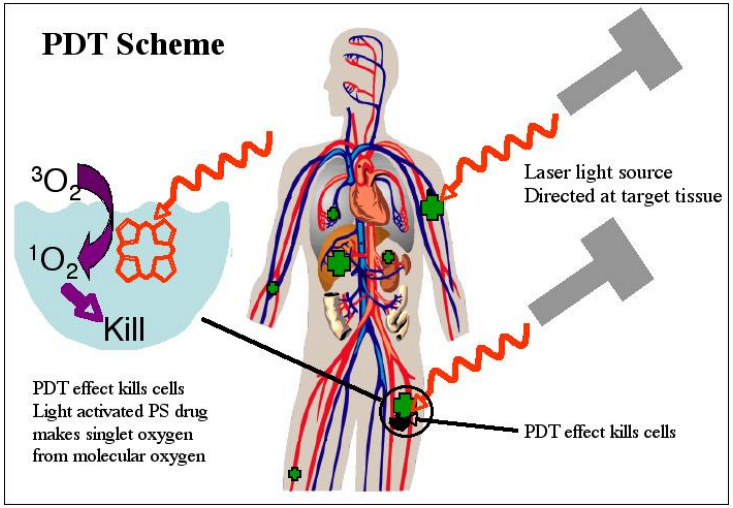


Motivation

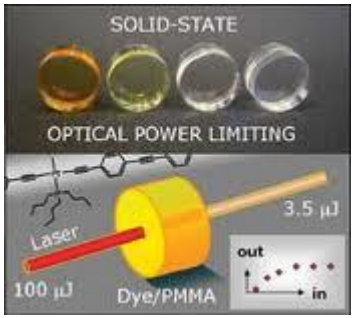
Porphyrins



Photodynamics therapy



Optical Limiter



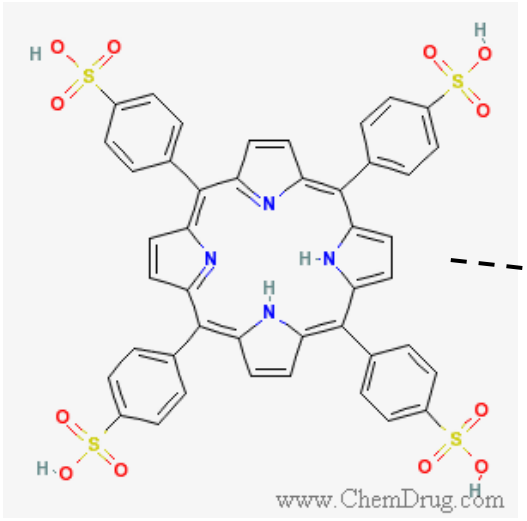
Study and understand the population dynamics in aggregated samples

How ?

- Excited state absorption
- Life time of the states

Sample

✓ **meso-tetrakis(sulfonatophenyl) porphyrin**

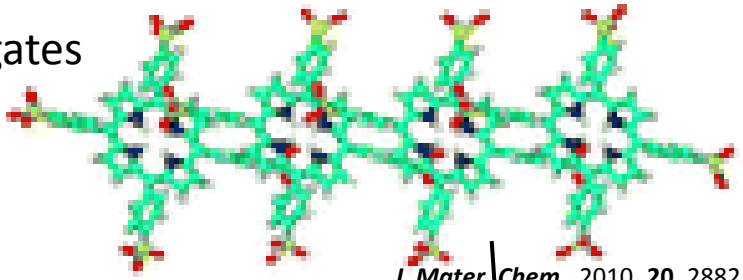


J-Aggregated x Monomers

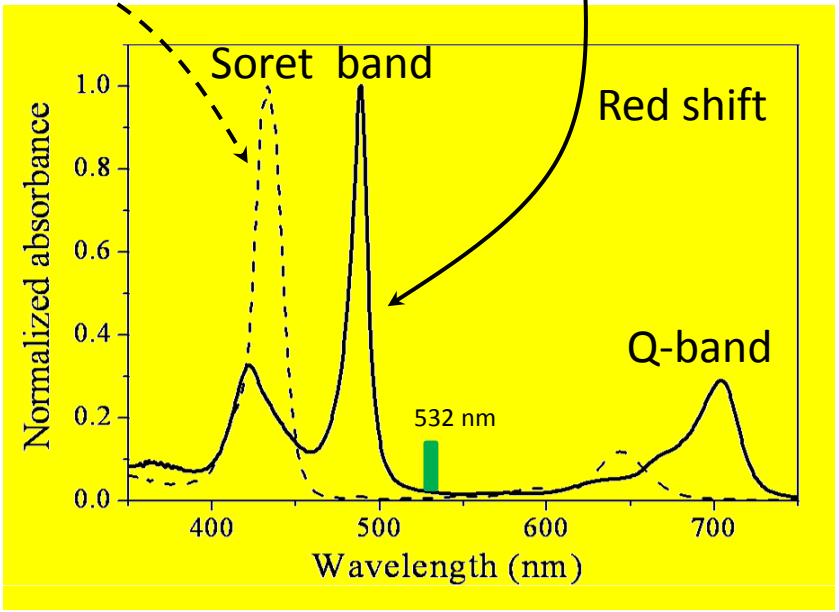
side-by-side H-bond

J- Aggregates

monomer



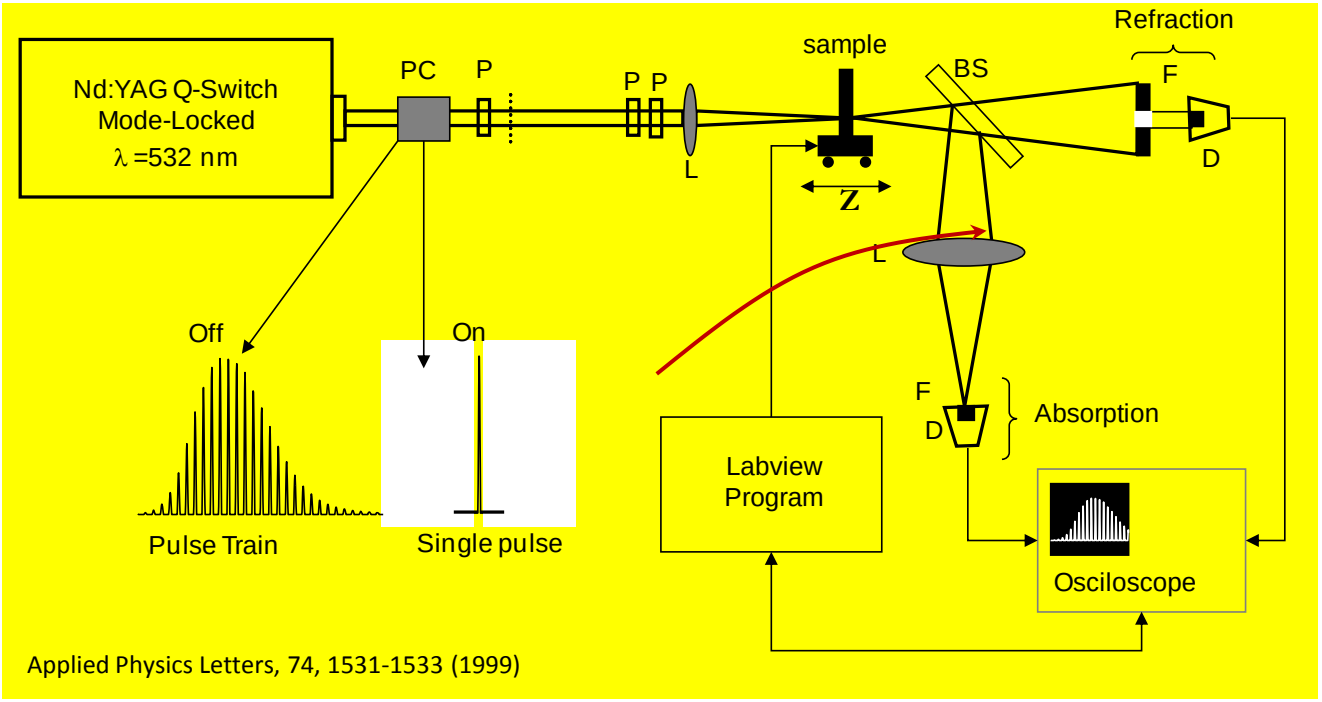
J. Mater. Chem., 2010, **20**, 2882 - 2886



✓ Changes in the linear absorption
✓ Increases in the vibrational modes;
✓ Decreases in the fluorescence QY

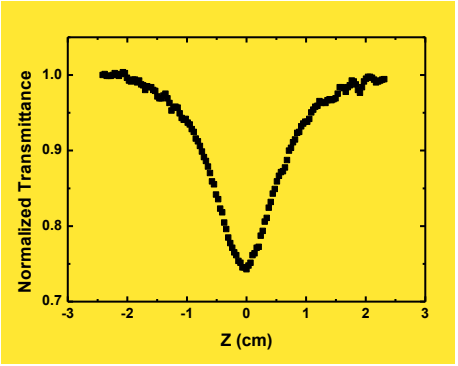
¿ Nonlinear absorption ?

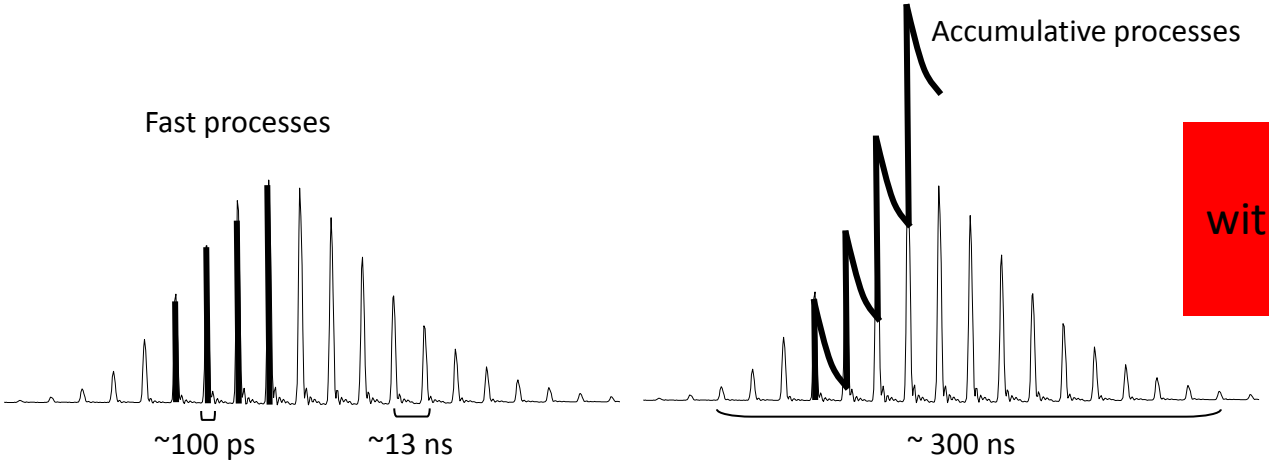
The Pulse Train Z-scan Technique



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

Typical Z-scan curve



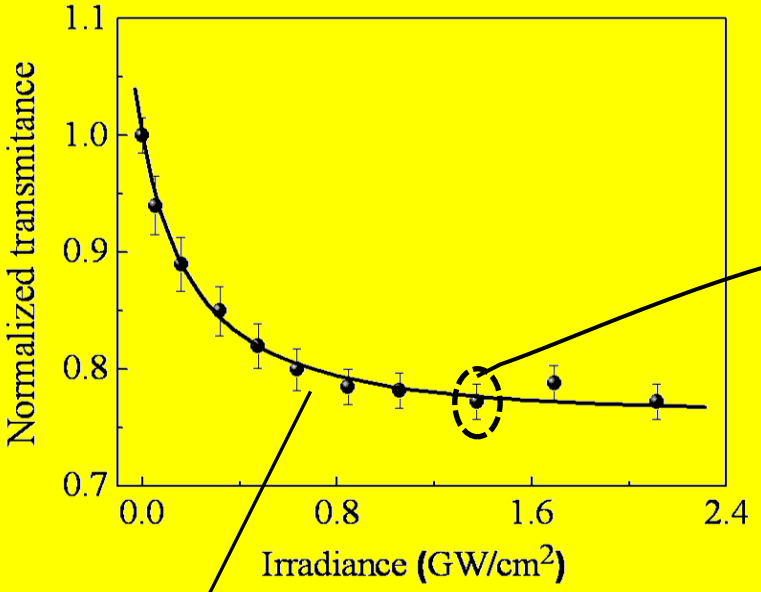


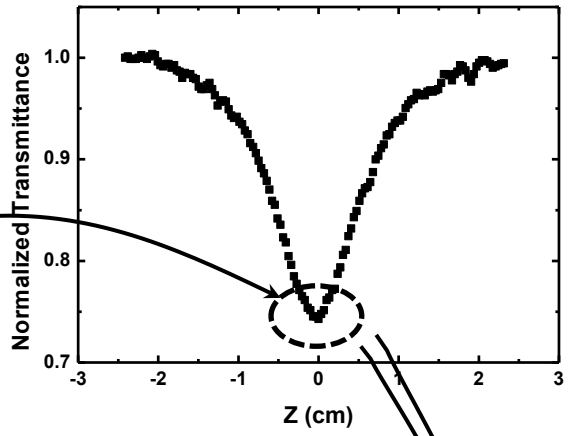
Measurements
with single and pulse train
Z-scan

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

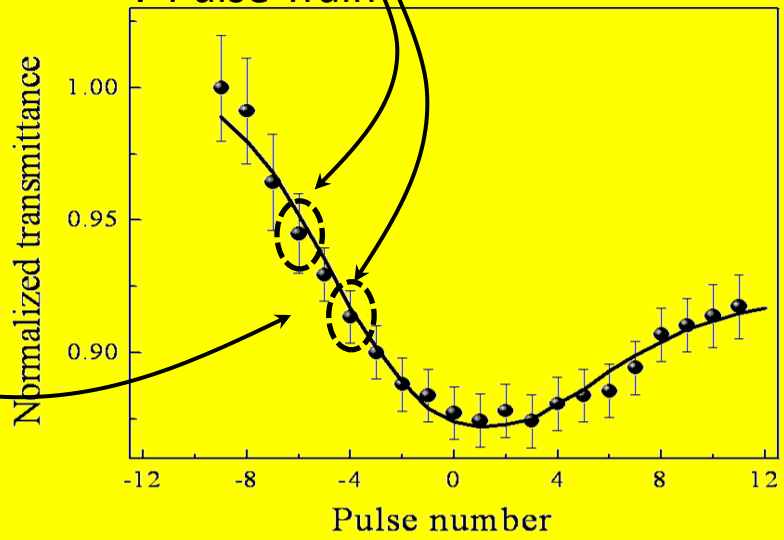
Experimental Results

† Single pulse





† Pulse Train

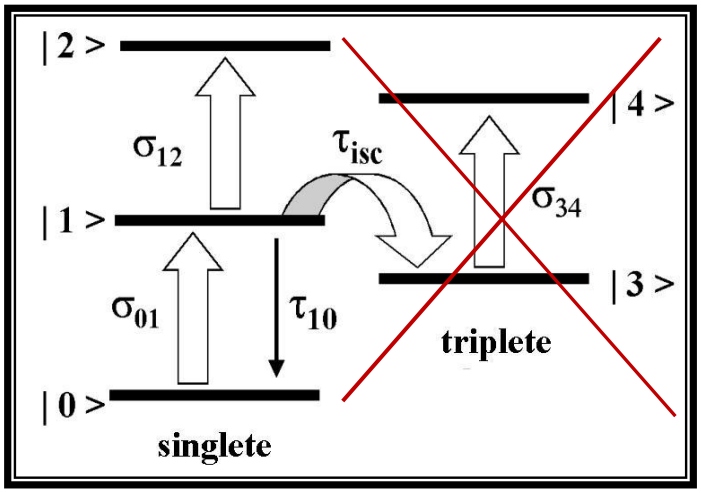


☑ Able to characterize singlet excited state absorption

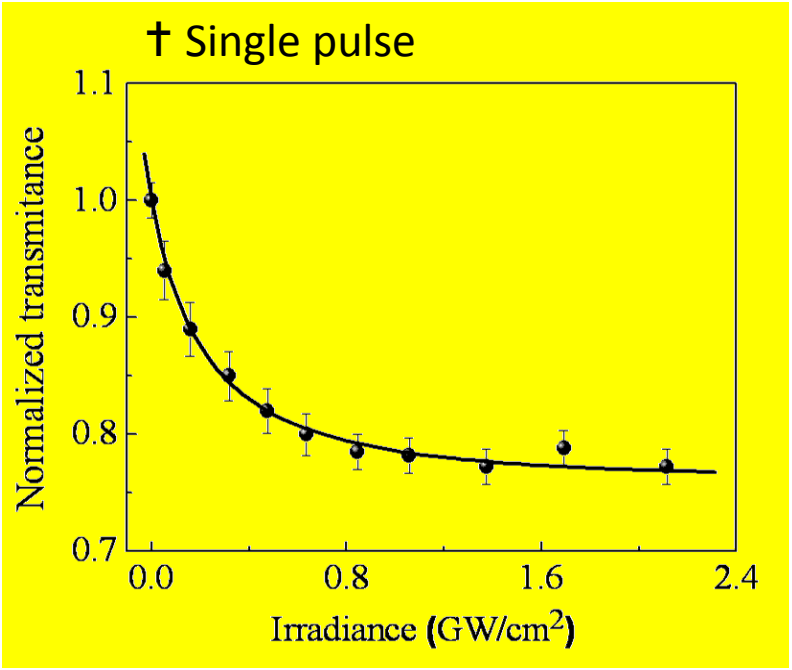
☑ Able to characterize triplet excited state absorption

Results are fitted by rate equation

Results and Discussions



☑ Triplet states are not considered



$$\frac{dn_0}{dt} = -W_{01}n_0 + \frac{n_1}{\tau_{10}}$$

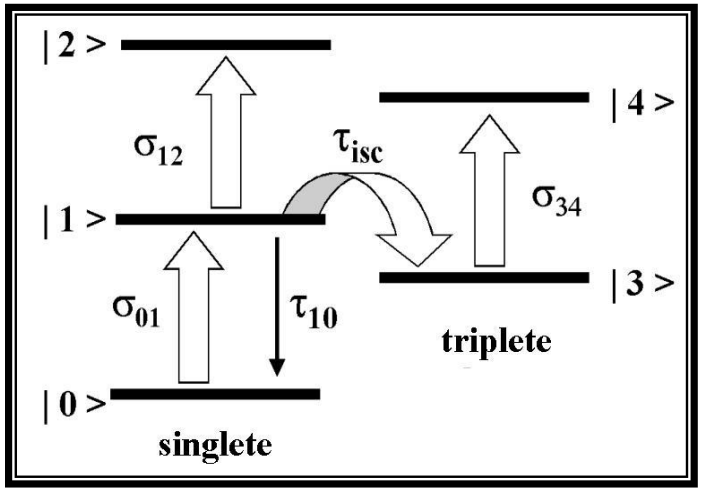
$$\frac{dn_1}{dt} = W_{01}n_0 - W_{12}n_1 - \frac{n_1}{\tau_{10}}$$

$$\frac{dn_2}{dt} = W_{12}n_1 - \frac{n_2}{\tau_{21}}$$

Absorption coefficient

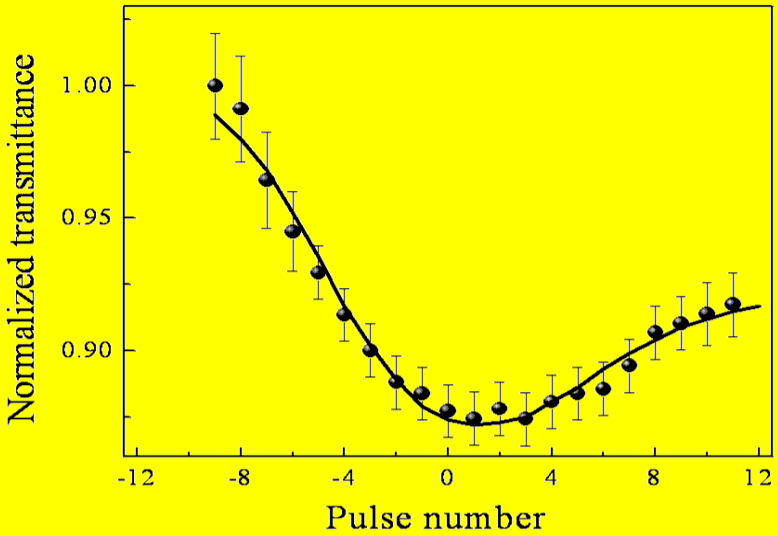
$$\alpha(t) = n_0\sigma_{01} + n_1\sigma_{12}$$

Results and Discussions



☑ Triplet states are considered

† Pulse Train



$$\frac{dn_0}{dt} = -W_{01}n_0 + \frac{n_1}{\tau_{10}}$$

$$\frac{dn_1}{dt} = W_{01}n_0 - W_{12}n_1 - \frac{n_1}{\tau_{10}} + \frac{n_2}{\tau_{21}} \quad \frac{-n_1}{\tau_{isc}}$$

$$\frac{dn_2}{dt} = W_{12}n_1 - \frac{n_2}{\tau_{21}}$$

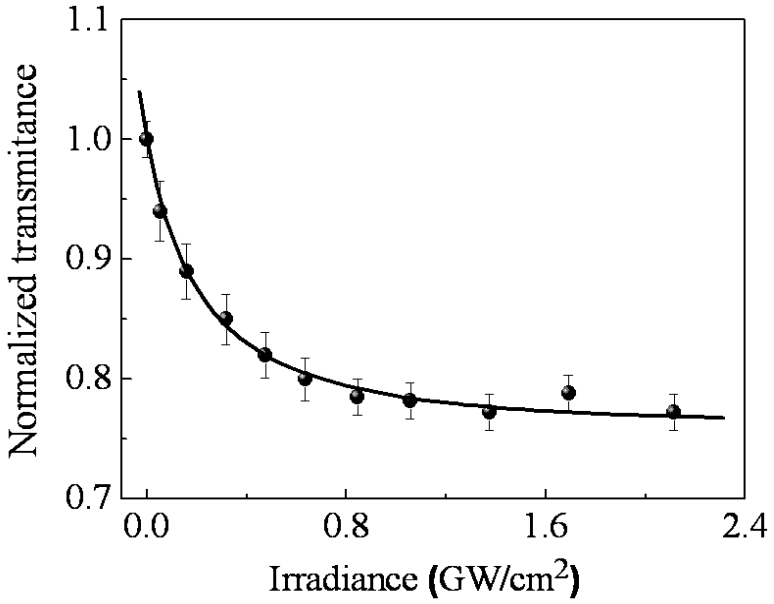
$$\frac{dn_3}{dt} = -W_{34}n_3 + \frac{n_4}{\tau_{43}} + \frac{n_1}{\tau_{isc}}$$

$$\frac{dn_4}{dt} = w_{34}n_3 - \frac{n_4}{\tau_{43}}$$

Absorption coefficient

$$\alpha(t) = n_0\sigma_{01} + n_1\sigma_{12} + n_3\sigma_{34}$$

Results and Discussions



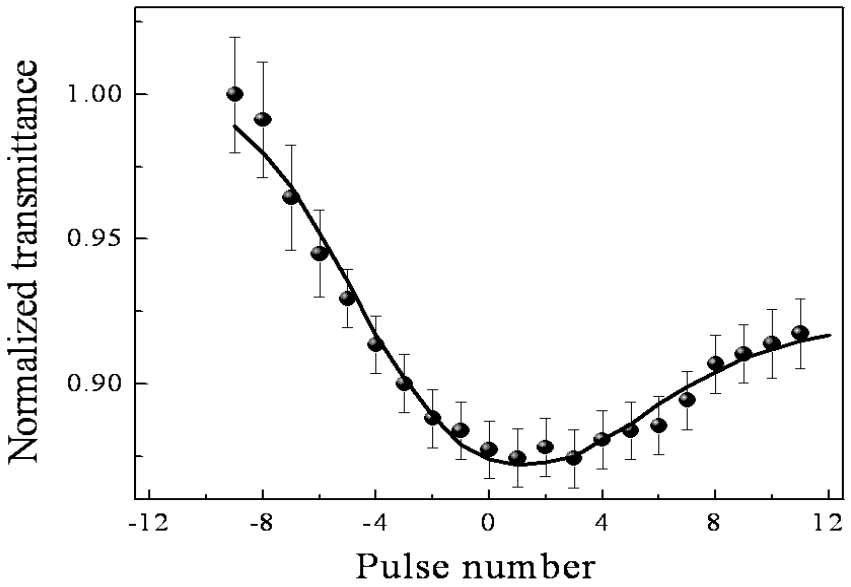


TABLE. Photophysical parameters obtained for J-aggregate and monomer of $TPPS_4$.

Sample	σ_{01} 10^{-17} cm^2	σ_{12} 10^{-17} cm^2	σ_{34} 10^{-17} cm^2	$\frac{\sigma_{12}}{\sigma_{01}}$	$\frac{\sigma_{34}}{\sigma_{01}}$	τ_{s_1} ns	τ_{isc} ns	φ_{isc}	φ_{fl}	φ_{ic}
Monomer[a]	0.8	7.4	7.6	9.25	9.25	3.6	10	0.36	0.16	0.48
J-aggregate	2.0	6.5	3.5	3.25	1.75	0.105[b]	1.4	0.08	0.001[b]	0.92

(a) Gonçalves, P. J.; De Boni, L.; Barbosa Neto, N. M.; Rodrigues Jr., J. J.; Zilio, S. C.; Borissevitch, I. E. *Chem. Phys. Lett.* **2005**, *407*, 236-241.
(b) Miura, A.; Shibata, Y.; Chosrowjan, H.; Mataga, N.; Tamai, N.; *J. Phototochem. Photobiol. A* **2006**, *178*, 192-200.

Conclusion

- aggregates formation x monomer
  - reduction in τ_{S1}, τ_{isc};
  - increases in σ_{01} at 532 nm, however, there is a decrease in σ_{12} and σ_{34};
  - decreases in σ_{12}/σ_{01} ~ 3 folds and σ_{34}/σ_{01} ~ 9 folds;
  - strong decreases in φ_{isc}, from 0.36 to 0.08
  - it´s still having RSA effect

In summary

- Aggregates decreases the intersystem crossing yield: not important for PDT;
- An increase in the vibronic relaxation reduces the lifetimes of the states and reflect in an increase of the internal conversion pathway;
- Could be used as a fast optical limiter;

Acknowledgements

FAPESP

CNPq

CAPES

Thank you