

# Two-Photon Absorption in Neutral and Cationic Porphyrin-Chalcone Derivatives: Insights to a Biological Evaluation

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Organic molecules exhibiting nonlinear optical responses have key advantages because of their potentially increasing depth of light penetration in tissue, which is the primary set for photosensitizers in photodynamic therapy (PDT). Porphyrins are especially attractive for this nonlinear study considering their triplet formation efficiency, producing reactive singlet oxygen, the key to PDT. In this work, we report on the study of two-photon absorption (TPA) spectra of a series of tetraphenyl porphyrin with chalcone derivatives groups in its neutral and cationic forms. It was expected that the electronic nature of porphyrins leads to a significant change in two-photon absorption cross-sections due to different electron-accepting groups and symmetry changes, influencing the TPA magnitude with distinct chalcone derivatives, which is extremely important in applications such as fluorescent bioprobes. As it is known, so far, in the literature a few works report measurements on TPA cross-sections in porphyrins molecules, which is known to be difficult because of the easy aggregation of those at low molar concentrations. Thus, to circumvent this problem, we have set up a technique based on monitoring the fluorescence induced by a two-photon absorption that can be used for solutions at very low concentrations, avoiding aggregation. It was established in a pulsed laser system with 200 fs pulse width, which pumps an Optical Parametric Amplifier, allowing to tune of the two-photon excitation wavelengths. Furthermore, the measurements were done with a well-known reference sample (TPP) to calibrate the geometry of the experiment.

As a result of the measurements in chalcone porphyrin dissolved in DMSO, it was observed an increase in the TPA cross-section in the Soret band may be due to the Q-band one-photon resonance enhancement region or due to a gerade parity state nearby Soret band. Also, in the Q-bands, a maximum absorption cross-section of about 10 GM was measured at 570 nm, explained by TPA-allowed transitions (gerade-like state) into vibronic states, observed in non-centrosymmetric molecules. Corroborating that the attached chalcone groups to the TPP may increase the distortions in the molecular geometry and symmetry.