Nonlinear absorption dynamics in tetrapyridyl porphyrins

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Abstract

Nonlinear absorption dynamics in a group of tetrapyridyl porphyrins solutions was investigated at 532 nm with Z-scan and a set of complementary techniques, such as linear absorption and time resolved fluorescence. Using either three- or five-energy-level diagram we determine their excited state spectroscopic parameters.

Introduction

The search for new organometallic complexes that exhibit large and fast nonlinear optical process have attracted a considerable interest because of their potential applications in photonic devices. Among organic materials, porphyrin (PPh) complexes have deserved a significant attention as good candidates for passive optical limiters. These materials present nonlinear effects such as reverse saturable absorption (RSA) or saturable absorption (SA) processes, depending on the atom at the central position. In order to estimate the prospects of this class of materials for photonic applications, a characterization of the excited state absorption is necessary.

Tetrapyridyl porphyrins (TPyP) are macrocyclic aromatic molecules having four pyrrole rings connected by unsaturated methine carbons with a pyridyl group linked to them. To assure structural stability, the PPh ring presents a central part constituted by either two protons or a metal ion, this molecule is showed in Figure 1. The properties of porphyrins are highly influenced by central substituted, which is responsible for their classification as regular or irregular [1]. In our measurements, regular TPyPs have two protons (free base) or Zn^{2+} as central substituted and irregular TPyPs have either Cu^{2+} or Ni^{2+}.

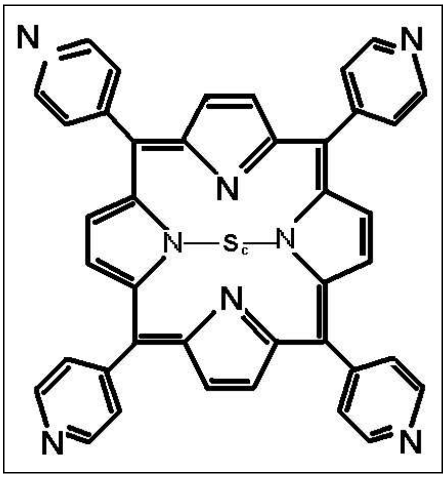

Figure 1 – The TPyP molecule. For our case the central substituted S_c is: $2H^+$, Zn^{2+}, Ni^{2+}, Cu^{2+}

In this work we have investigated the nonlinear absorption dynamics of TPyPs using the Z-scan technique with single 100 ps pulses as well as with pulse trains (PTZ-scan) [2], in association with others complementary techniques such as UV-VIS absorption spectroscopy and time-resolved fluorescence.

Experimental Setup

The porphyrin molecules were diluted in a ether/chloroform solution to a concentration around 10^{17} molecules/cm^3, being their absorption spectra obtained from a Carry-17 UV-VIS spectrophotometer. To obtain the time resolved fluorescence the sample was pumped with a 100 ps laser pulse at 532 nm operating at 10 Hz of repetition rate and the fluorescence signal was acquired by a fast detector, with 0.5 ns of rise time, connected in a 1 GHZ digital TEKTRONIX oscilloscope. This measurements just were performed in regular porphyrins, once the irregular ones present fluorescence signals below our detection threshold. The nonlinear absorption process was investigated by mean of Z-scan technique with both a single 100 ps pulse and a mode locked Q-switched pulse train at 532 nm. The pulse trains were delivered by a second harmonic of a mode locked and Q-switched Nd:YAG laser at a 10 Hz of repetition rate and the single pulses were extracted from pulse trains using a Pockel's Cell.

Results and Discussions

In this work we have obtained the values of excited state spectroscopy parameters, such as absorption cross sections, decay and intersystem crossing times using the Z-scan with single pulse and pulse trains associated with others complementary techniques. We have observed reverse saturable absorption process (RSA) for regular TPyPs ($2H^+$, Zn^{2+}), and both fluorescence lifetime and intersystem crossing time were on the order of nanoseconds. For irregular TPyPs (Cu^{2+}, Ni^{2+}) we have observed saturable absorption effects (SA) with fast decay times and a very small fluorescence signal. Just single pulse nonlinear absorption effect was observed for irregular TPyPs and no one cumulative triplet process was observed with PTZ-scan, thus the triplet parameters could not be determined for them. The PTZ-scan results were fitted with a singlet-triplet five-energy-level diagram, while for single pulse Z-scan we adjusted the normalized transmittance against pulse intensity with a three-energy–level model because we assume that there is no enough time for the triplet states to be populated in 100 ps [3]. In the single pulse Z-scan we have observed clear saturation process of the nonlinear absorption effects with the intensity, for all types of porphyrins studied. In the figure 2 we show typical results for single pulse and PTZ-scan.

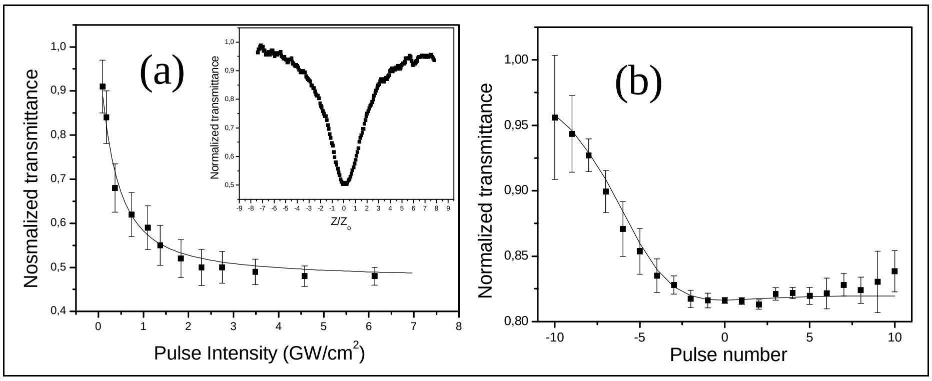

Figure 2 – Single pulse (a) and PTZ-scan results (b) for H_2TPyP. The solid lines are the theoretical fitting. The insert in (a) is typical open aperture Z-scan signal for RSA process.

The excited state spectroscopy parameters are listed i the table 1.

Table 1 –Excited state spectroscopic parameters for TPyPs.

	H_2TPyP	ZnTPyP	NiTPyP	CuTPyP
$\sigma_g\,(10^{-17}cm^2)$	1.6	2.1	5.5	5.3
$\sigma_{exc}^S\,(10^{-17}cm^2)$	4	4.7	3	3.5
$\sigma_{exc}^T\,(10^{-17}cm^2)$	2.1	3.8	—	—
τ_f (ns)	8	1.6	$5x10^{-3\,*}$	$55x10^{-3\,*}$
τ_{isc} (ns)	14	6	—	—

* Time estimated from theoretical fitting

Conclusions

The results clearly indicate that the presence of the central metal determines the nonlinear properties of this family of materials. As expected, regular TPyPs present long excited singlet lifetimes and, consequently, a macroscopic population of the triplet state. The Central metal for regular PPhs presents a closed shell, give rise to a small spin-orbit coupling. On the other hand, the metal ion in irregular PPhs allows a strong spin-orbit coupling, shortening their state lifetime [1]. In summary we have observed a marked difference in nonlinear absorption process between regular and irregular TPyPs due to presence of different central ions

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