



## Research paper

# Picosecond dynamic of aqueous sodium-copper chlorophyllin solution: An excited state absorption study

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## ABSTRACT

This work reports on the singlet excited-state absorption spectrum of sodium-copper chlorophyllin using three distinct methods of Z-Scan measurement: white-light continuum Z-Scan technique ranging from 470 to 780 nm, tunable Z-Scan technique with femtosecond pulses (490–700 nm) and 532 nm Z-Scan technique with 100 ps pulse width. A transition from reverse saturation absorption (RSA) to saturable absorption (SA) was observed at 570 nm, and at 532 nm RSA was tested showing potential application as optical limiting device. Pump-probe technique was used to measure lifetime of the first singlet excited state (22 ps) and no evidence of triplet conversion was observed.

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## 1. Introduction

Chlorophyllin molecules are macrocyclic organic compounds in the class of porphyrins that exhibit large optical nonlinearities, making them a great candidate to be applied as sensitizers for photodynamic therapy (PDT) [1–4], in optical limiting devices [5,6] and solar photovoltaic cells [7,8]. So, the understanding of the excited state properties of these organic molecules is of great importance. Furthermore, the organic molecules can be chemically synthesized in several ways by adding different metals in the macrocyclic center or attaching functional or peripheral groups that changes their photo-chemical properties which can be suitable for a given application. In the present work, it was studied the sodium-copper chlorophyllin (Cu-Chl), a water-soluble salt that is semi-synthetic derivative of the natural green pigment chlorophyll in which a copper ( $\text{Cu}^{2+}$ ) ion is contained in the center of the porphyrin macrocycle. Even with its semi-synthetic nature, this compound is available as food colorant with some potential benefits [9] such as antimutagenic [10] and antioxidant [11]. Therefore, besides the nonlinear optical properties presented in this molecule, it is completely applicable in living systems for some specific purpose.

Remarkable in our results is the possibility of Cu-Chl molecule to work as a passive limiting device to the visible range. In such

application, when light intensity above a threshold reaches the target, the molecule limits this intensity and, therefore, protects an optical instrument or even the human eye from damage [12–15].

Singlet excited state absorption and picoseconds internal conversion relaxation were studied in Cu-Chl diluted in distilled water. To determine precisely the excited state absorption cross-section, we employed three distinct Z-Scan techniques, in which, each one uses different laser pulse widths. For example, fs tunable Z-Scan was used to determine the excited singlet state absorption. Using this system, the first excited state lifetime is not required to describe the population dynamics in the electronic state due to the short time interaction between the laser pulse and the sample. White-light continuum Z-Scan was employed to increase the spectral resolution of the first one. Finally, ps Z-Scan technique at 532 nm was used to indirectly determine the lifetime of the first excited state by knowing from the fs Z-Scan the excited state absorption cross section value at this wavelength. To corroborate the spectroscopic results, pump and probe measurements at Q-band region was made to confirm the obtained lifetime of the first excited state.

We identified that the main relaxation mechanism of the first excited state is through internal conversion because no fluorescence emission was observed. Besides, in according to the pump-probe measurements, a mono-exponential behavior describes the optical transmission as a function of the time, suggesting that no triplet states have being populated during the pump and probe beams. As final results, we tested the optical limiting application of sodium-copper chlorophyllin at 532 nm with 100 ps pulse width.

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## 2. Experimental section

Sodium-Copper chlorophyllin was commercially obtained from Sigma-Aldrich® (St. Louis, MO, USA) and diluted in water. In order to obtain the molar absorption coefficient, absorption spectra were acquired in different concentrations in the range of  $25\text{--}100 \times 10^{-6}$  M. For fluorescence measurements, a concentration of about  $1 \times 10^{-6}$  M ( $0.6 \times 10^{15}$  molecules/cm<sup>3</sup>) was used. For nonlinear absorption measurements, a concentration of about  $1.25 \times 10^{-3}$  M ( $7.5 \times 10^{17}$  molecules/cm<sup>3</sup>) was defined. No aggregation effect was observed. The linear absorption of the molecule was characterized with a Shimadzu UV-1800 spectrophotometer using a 2 mm path length quartz cuvette. One of the nonlinear measurements performed in this work is the Z-Scan technique using the same procedure proposed by Sheik-Bahae et al. [16] in order to measure the excited singlet state absorption. As source of pulsed and amplified light, an Optical Parametric Amplifier (OPA) that generates 120 fs of pulses ranging from 470 to 2000 nm working at 1 kHz was employed. To pump the OPA, a 775 nm Ti:sapphire laser was employed, also working at 1 kHz. The sample was translated at the z direction by a homemade LabView software controlled motor. The transmitted light is focused to a silicon photodetector that is amplified by a lock-in amplifier and acquired by the same computer software.

To reinforce the excited singlet state absorption with improved spectral resolution, it was used the white-light continuum (WLC) Z-Scan technique proposed by De Boni et al. [17], which uses the same Z-Scan procedure proposed by Sheik-Bahae et al. [16]. However, in this case, a broadband spectral pulsed beam was used instead of a single wavelength source. The white-light supercontinuum was generated in a 3 cm glass cell with distilled water by focusing with a 30 cm focal length lens pulses of 120 fs at 1110 nm from an OPA working at 1 kHz repetition rate. The OPA is pumped with a Ti:sapphire chirped pulse amplified system at 775 nm (CPA-2001 system from Clark-MXR Inc.) working at the same repetition rate. The WLC spectrum used in the experiment present a 300 nm bandwidth in the visible region ranging from 470 to 780 nm, with about 5 ps of positive chirp that must be considered under resonant conditions once spectral components will reach the sample at different times leading to cumulative effects due to absorption of excited states. After the white-light passed through the water cell, a low pass filter is used to remove any contribution of the pump pulse in the white light spectrum. After that, WLC passes by a pair of achromatic lenses, one to first collimate the WLC beam and other to focus the light in the studied sample. The sample was scanned along the focused WLC beam in the z direction in a way that the transmitted light is focused using a  $f = 10$  cm lens and directed to a 1 mm diameter core optical fiber connected to a spectrometer of  $\sim 5$  nm resolution. The transmittance as a function

of the z position was normalized by the transmittance far from the focus, yielding Z-Scan signatures for each wavelength in the WLC range. All experiment was controlled by a homemade LabView software.

Finally, the same single-pulse Z-Scan apparatus was used but now pumping the sample with a 100 ps laser at 532 nm, working at 100 Hz. This pulse width configuration was used in order to obtain possible contribution from longer-lived excited states, such as, triplet state. This system can be also employed to evaluate the excited state absorption and optical limiting behavior at this wavelength in the ps regime. This setup is composed by doubled wavelength 532 nm of Q-switched and mode-locked 1064 nm Nd:YAG laser, which hits a set of polarizers to preserve linear polarization and to control the power focalized and delivered to the sample. The sample can translate at the z direction by a homemade LabView software controlled motor. The transmitted light is focalized to a silicon photodetector that is amplified by a lock-in amplifier and acquired by the same computer software. Additionally, the variation of the normalized transmittance when increasing the deliver energy to the sample was evaluated in order to propose this molecule as an optical limiting candidate. Peak intensities used were ranged from  $0.5 \text{ GW/cm}^2$  up to  $5 \text{ GW/cm}^2$ .

In order to investigate the excited state relaxation time from the first singlet excited state, the pump and probe technique, as shown in Fig. 1, was employed. A 120 fs pulse at 640 nm, delivered by the same OPA described in the Z-Scan technique, passed through a beam splitter. The more intense beam (pump) of about 98% of the power, with vertical polarization, is directed to a pair of fixed mirrors while the less intense beam (probe) is directed to a pair of two moving mirrors. It makes the optical path of probe to be longer, changing its arrival time to be late in steps of 280 fs with respect to the fixed temporal pump. Polarization of the probe beam was rotated to a polarization of about  $54.7^\circ$  (magic angle) with achromatic  $\lambda/2$  waveplate (Optosigma). Both beams are focalized in the same spot in the sample by the same convergent lens. Only the probe beam hits a silicon photodetector that is amplified by a lock-in amplifier. Pump beam is blocked just after passes the sample. A homemade LabView program is responsible for the data acquisition and control the moving mirrors in right temporal steps.

This experiment works in the way that the intense beam (98%) excites a great population of molecules to the first excited state, changing the optical transmission (or absorption) of the probe as function of the time. Thus, for each temporal step set by the moving mirrors, the probe beam feels different population in the excited state that gives distinct levels of optical transmission. After one measurement, a typical exponential behavior is observed to the optical transmission, and adjusting it, the excited state lifetime is obtained.

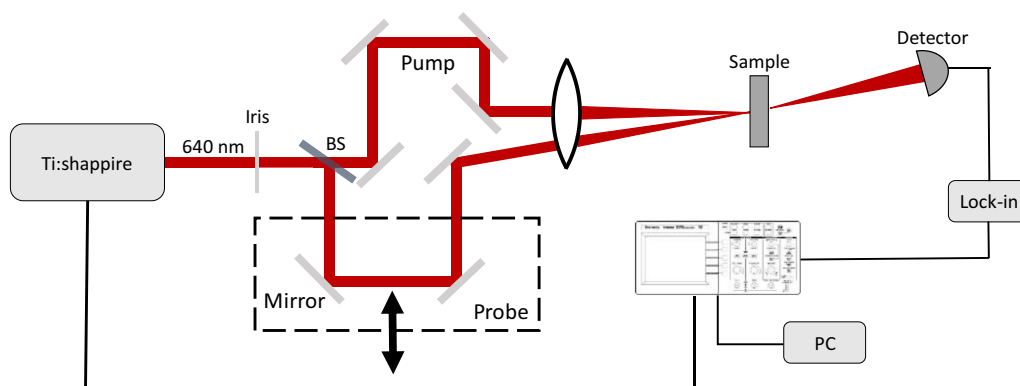


Fig. 1. Experimental setup used in pump and probe technique to measure internal conversion decay time by changes in the optical transmission over time.

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