Identification of ultrafast processes in ZnPc by pump-probe spectroscopy

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Abstract. The transient absorption of Zinc phthalocyanine (ZnPc) has been studied by femtosecond pump-probe spectroscopy. We present results on the ultrafast spectroscopy of ZnPc, specifically three ultrafast components were observed and identified. These are the inertial solvation dynamics (~1.8 ps), the dielectric solvation dynamics (~39 ps) and vibrational relaxation (~2.7 ps) in the electronic excited state. Interpretation of results using different pump wavelengths, different sample concentrations and different solvents help to clarify the mechanisms resulting in the observed signals. The red shift of the ground state (Q band) spectra is also discussed.

1. Introduction

Zinc phthalocyanine (ZnPc) is a promising photosensitiser for Photo Dynamic Therapy (PDT) that exhibits a photodynamic activity. A strong absorption band in the near–infrared in close proximity to the optical window of human tissue [1,2] and a triplet state near resonance with the transition of the oxygen from ground to excited singlet state make ZnPc a suitable candidate for PDT. ZnPc has been reported to have suitable photophysical properties [2]. It has a relatively long lifetime excited singlet state (3–8 ns) in DMSO and a long lifetime of triplet state with a high-quantum yield. These long lifetimes constitute an important advantage for ZnPc. Long lifetimes enhance the number of interactions between the ZnPc excited triplet state and the ground state of the environmental oxygen, thereby increasing the singlet oxygen quantum yield.

Several femtosecond studies have indicated that phthalocyanines in solution exhibit ultrafast excited-state dynamics [2, 3]. Understanding these dynamics is relevant to research on PDT. Femtosecond transient absorption pump–probe spectroscopy has shown the existence of ultrafast energy transfers in phthalocyanines [2, 3]. These ultrafast energy transfers play an important role in the photophysics of ZnPc. Before looking at the energy transfer, the lifetime of the first excited state is an important factor that one needs to consider. The first excited state (S_1) lifetime, or

fluorescence lifetime, measurement has been obtained in diverse environments. The measured value of fluorescent lifetime of ZnPc in DMSO is approximately 2.8 ns [2, 4]. Extensive work done on ZnPc in toluene has indicated that the decay rate constant of fluorescence (F) is around 9.1 ns [7]. In addition, the decay rate constants of the non–radiative pathways are 38.5 ns for the internal conversion (IC) and 5.6 ns for the intersystem crossing [7]. It has been reported in literature that work done on $ZnPcS_4$ in DMSO shows that the first excited-state decays with a time constant of 160 ps [5] whereas the first excited state decays with a time constant of 35 ps for ZnPc in DMSO [6]. Note that intersystem crossing (ISC) contributes to the decay time, as well as the internal conversion (IC). However, it has been demonstrated that the time constants of picosecond range cannot be attributed to the depopulation of the first excited state because of the long lifetime of fluorescence (~3 ns) [2]. There constants might be associated to solvation dynamics.

In the present paper we report on selected results for ZnPc in DMSO investigated by transient absorption spectroscopy. We focus on the results when pumping at 630 nm, not at the generally used 672 nm, as this has not been investigated before.

2. Experimental setup

A standard transient absorption pump probe spectroscopy technique was applied and our experimental setup has been described in detail elsewhere [9]. Briefly, this consists of a tunable visible pump pulse of ~ 150 fs and a delayed, chirped white light continuum probe pulse. The amplified beam is split by a beam splitter into two. These are the pump and probe beams respectively. The probe beam is sent to a variable optical delay line and then focused on a sapphire plate to generate a white light continuum. A short pass filter is placed after this in the probe path in order to suppress the strong residual peak at 795 nm from the Ti:Sapphire laser. The probe beam is split into two beams, reference and signal. The signal is focused on the sample in such a way it that overlaps spatially with the pump beam in the liquid sample while the reference beam is also sent through the sample. The pump pulse is sent through an optical parametric amplifier (TOPAS C - OPA) in order to obtain a wide tuning range of the pump beam (530-20000 nm). After the OPA a chopper is inserted in the pump beam path in order to record spectra that are classified as pumped and not-pumped, thereby reducing background effects. The probe reference and signal beams are focused on optical fibres which guide the beams into the entrance slit of an imaging spectrometer. The experiments were not done at the so-called magic angle between the polarisation directions of the pump and probe.

3. Results

A steady state absorption spectrum of ZnPc in DMSO at a concentration of 10 μM was acquired using a Xe-Kr lamp combined with USB2000 ocean optics spectrometer (figure 1) in order to confirm the optimum pump pulse wavelength. A strong absorption peak near 672 nm was observed as expected - this can be explained as the transition from the singlet ground state to the first singlet excited state $(S_0 \rightarrow S_1)$.

In the work done here, the pump was set at different wavelengths, 672 nm, 660 nm and 630 nm with pulse energy of 3-6 μJ. In addition a range of concentrations of ZnPc, from 1.3 μM to 10 μM, and different solvents (DMSO and DMF) were used in our experiments.
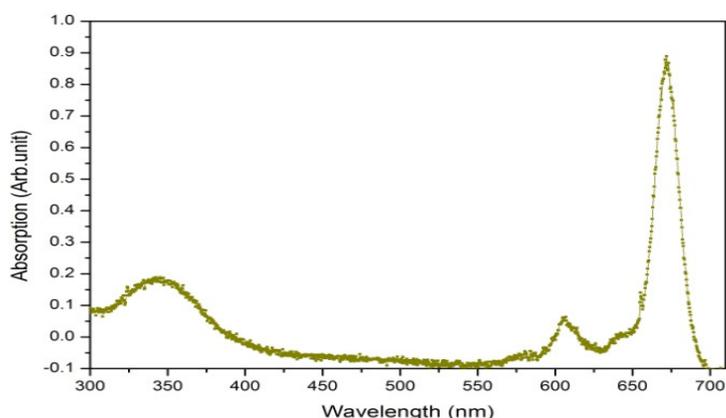
Figure 1: Steady-state absorption spectrum of ZnPc in DMSO at a concentration of 10 μM in a 10 mm path length cuvette recorded using using a Xe–Kr lamp combined with a USB2000 Ocean Optics spectrometer

Figure 2 illustrates the typical transient absorption contour plot measurement of ZnPc. This result was obtained for a pump wavelength set at 630 nm. This figure shows three main bands. The first band has a peak at 672 nm which relates to the ground state bleach dynamics. It exhibits a negative absorbance changes and shows how the ground state is repopulated after excitation ($S_1 \rightarrow S_0$). However this broadband feature also includes stimulated emission. The second band has a peak at 630 nm which is due to the excited state absorption ($S_1 \rightarrow S_{n1}$). This peak overlaps with the scattering of the pump light (630 nm). The third one has a broadband ranging from 500 nm to 600 nm. This broadband is a potential combination of two processes: the triplet-triplet state excited absorption ($T_1 \rightarrow T_n$) and the singlet-singlet excited absorption ($S_1 \rightarrow S_{n2}$). However, if the lifetime of the singlet state is ~3 ns then the T_1 state is still practically empty and therefore only S_1-S_{n2} absorption will be observed.
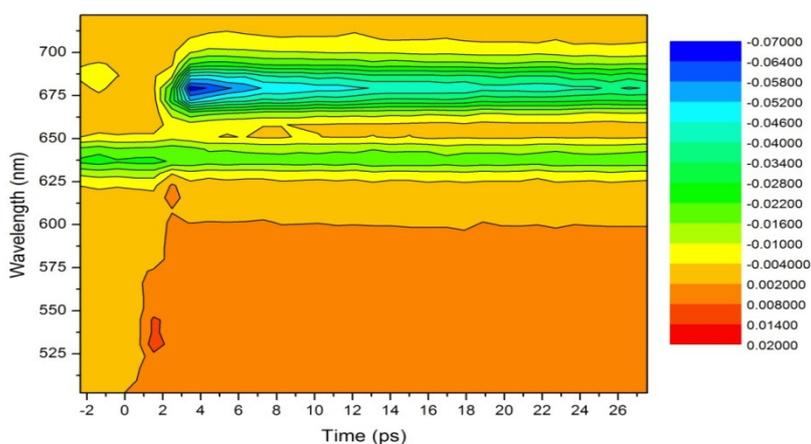

Figure 2: Transient absorption contour plot of ZnPc in DMSO (at a concentration of 10μM) pumped at 630 nm, indicating measured absorbance changes for a range of delay times between pump and probe pulses

The results obtained in our experiments show a good fit to a bi-exponential decay at the 672 nm band peak as shown in Figure 3. The bi-exponential comprises a fast process with a time constant of 1.82 ± 0.06 ps and a slower process with a time constant of about 38.9 ± 2.6 ps . These times decay are attributed to solvation dynamics (inertial and dielectric salvations dynamics). The solvation process is a non-exponential process and can be characterised only by approximation by a set of exponential decay times. Additional, the red shift of the ground state (Q band) spectra was studied. After excitation at 630 nm, it was observed that the ground state wavelength peak of the Q-band was extended further toward the red. At zero delay, the GSB peak was at 671.9 nm, whereas after 4.68 ps and 24.92 ps, the peak was sitting at 674.9 nm and 676 nm, respectively. We could notice that after 24.92 ps there was a red shift of 4 nm for the Q-band peak, whereas a 2 nm red shift was observed for the sample pumped at 672 nm. This red shift indicates the decrease of energy of the excited state (S_1) due to solvent redistribution and the shift depends on the pump wavelength. In the region with the band near 630 nm, we were able to resolve a mono-exponential fast process as shown in Figure 3 in spite of the scattering of the pump wavelength that overlaps with the $S_1 \rightarrow S_{n1}$ excited state absorption expected at this wavelength. The time constant of this mono-exponential fit is 2.7 ± 0.5 ps. A similar time constant of 2.5 ± 0.3 ps has been observed at 485 nm where $S_1 \rightarrow S_{n2}$ excited state absorption is expected. These time constants could be attributed to vibrational relaxation. Upon excitation at 630 nm, the molecules relax from the vibrational levels into which they were pumped down to lower vibrational levels of the excited singlet state. This vibrational relaxation has been reported to be around 3 ps [2, 6].
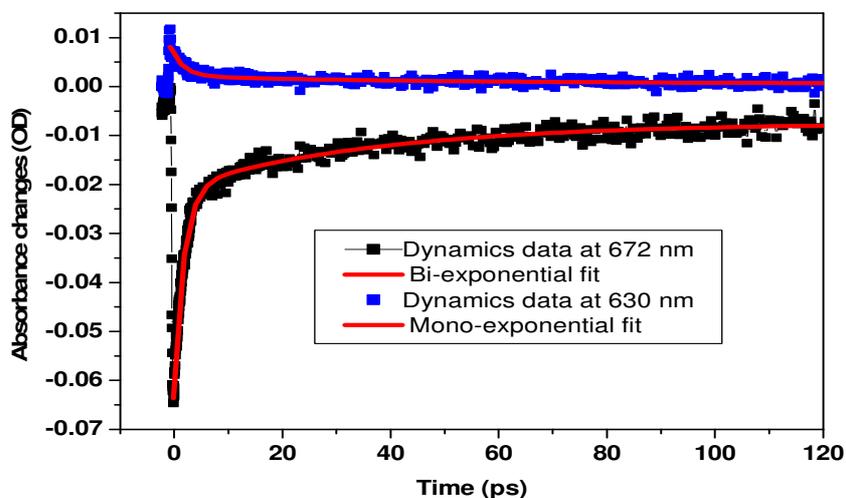

Figure 3: Transient signals of absorbance changes of ZnPc in DMSO at a concentration of 10 μM pumped at 630 nm and probed at 630 nm and 672 nm

4. Conclusion

We studied the transient absorption of ZnPc in DMSO and DMF using the pump–probe setup. Our study of the transient absorption dynamics of the ZnPc in DMSO and DMF revealed that the dynamics observed on a timescale of a few picoseconds are associated with solvent relaxation and vibrational relaxation.

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