

Transient absorption spectroscopy study of Zinc Phthalocyanine in different solvents

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Abstract

Zinc Phthalocyanine (ZnPc) is a promising Photodynamic therapy (PDT) photosensitiser that exhibits photodynamic activity. ZnPc has suitable photophysical properties for PDT. The high yield of molecules in the triplet state results in a high yields of singlet oxygen, which leads to the destruction of the tumor. It has been suggested that the energy transfer from the singlet excited state to the triplet excited state transition is influenced by photophycal process that take place on ultrafast timescales. The photophysical processes of Zinc Phthalocyanine in different solvents and using different pump wavelengths have been measured by femtosecond pump-probe spectroscopy. The femtosecond transient absorption measurements reveal new results in picoseconds timescale which is due to solvent dynamics. It has been shown that there is a high signal loss which could be due to solvent dynamics and demonstrates the need for further investigation.

Background on solvent effect



When ZnPc are dissolved in solvent, at room temperature, there is a formation of solvent shell around the ZnPc molecules. This equilibrium state is perturbed when excited states of these molecules are created by pulsed laser. The excited state molecule will interact with the surrounding solvent molecules, depending on their polarity. There will be reorientation of the solvent molecules in order to establish the solvation equilibrium before returning to the ground state. These solvation effects occur in femtosecond to picosecond timescales.

Pump-probe technique

In order to investigate the fast dynamics in ZnPc, pump-probe technique was used. Figure 2 present briefly the pump-probe technique whereas Figure 3 shows the experimental layout of femtosecond pump-probe setup used to carry out the investigation of these fast dynamics.



Figure 2: The basic principle of the pump-probe spectroscopy technique illustrated with probe pulse arriving at the sample a delay time $t_{\rm p}$ after the pump pulse, indicating the basic energy level diagram of a hypothetical system under investigation and showing how the ground state concentration are monitored

Figure 3: Pump-probe experimental setup used to measure Figure 3: Pump-probe experimental setup used to measure transient absorption in liquid samples. BS0, BS1, BS2 and BS4: Beam splitters. M1, M2, M3, M4, M5, M6, M7, M8, M9, M10, M11, M12, M13 and M14: Coated mirrors. WP: Wave plate. P: Polariser. SP: Sapphire plate. F: Cut off filter. S: Sample. PD1 and PD2: Photoidodes. L1 and L2: Focusing lenses. OF1 and OF2: Optic fibres. PDA: Photodiode arrays. NOPA: Noncolinear avital correction among the second seco optical parametric amplifier.

Results

A study of ultrafast processes in ZnPc was done not only by exciting ZnPc at different pump wavelengths, but also by investigating the ZnPc ultrafast processes in different solvents, namely DMSO and DMF. In addition white light continuum was used as probe. Figure 4 and 5 present the transient absorption kinetics results obtained at different concentrations and different solvents respectively. Table 1 summarises all the results obtained



Figure 4: Transient signals of ZnPc in DMSO at 672 nm pumped at 630 nm for different concentration: 1.3*10.6 mol.dm 3, 5.2*10.6 mol.dm 3 and 10*10.6 mol.dm 3



Figure 5: Transient absorbance change of ZnPc in DMF at 6.3 µM pumped at 660 nm (in black square) and transient absorbance change of ZnPc in DMSO at 5 µM pumped at 672 nm (circle).



Figure 6: Transient absorption spectra of ZnPc in Figure 6: Transient absorption spectra of ZnPc in DMSO (at a concentration of 10 M) pumped at 630 nm, indicating the wavelength peak of the Q-band moving toward the red. At 0 ps (green curve), 4.68 ps (red curve) and 24.92 ps (black curve) the peak was at 671.9 nm, 674.9 nm and 676 nm, respectively.



Figure 7: Variation of the area luder 672 nm peak as function of time for ZinPc in DMSO with a concentration of 4*10⁻⁶ mol.dm⁻³ pumped at 672 nm.

Table 1: Decay times of ZnPc in DMSO and DMF pumped at 630 nm, 660 nm and 672 nm for different concentrations and probes

Solvent	ZnPc concentration (µM)	Pump wavelength (nm)	Probe wavelength (nm)	Time constant (ps) $\tau_1 \tau_2$
DMSO	10.4	672	686	47+1.6 45.1+7.5
			672	1.82 ± 0.1 38.9 ± 2.6
			668	1.5 ± 0.1 , 29.3 ± 3.9
			630	1.4 ± 0.3, 17 ± 2.6
			485	1.4 ± 0.5 , 14 ± 1.8
DMSO	10.4	630	672	1.8 ± 0.1, 34.2 ± 2.3
			630	2.7 ± 0.3
			485	2.5 ± 0.3, 38.4 ±0.6
DMSO	5.2	630	672	1.3 ± 0.3, 39.6 ± 8.3
DMF	6.3	660	690	38.5 ± 7.4
			670	45.7 ± 5.7
			660	42.9 ± 3.8
			624	44.8 ± 5.7
			480	38.3 ± 2.1

The investigation of the solvent effect on ZnPc for different solvents revealed a red shift of the Q-band. Figure 6 shows the red shift of the Q-band of ZnPc in DMSO.

In addition, It was found that there is signal loss within 100 ps. The study of this loss was done by looking at the variation of the area under the Q-band peak (672 nm) in function of time as shown in figure 7. A loss of about 35% of the signal was found.

Conclusions

The transient decay dynamic of 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. The longer time constant (in the order of 40 ps) is related to the dielectric solvent dynamic relaxation of S1. In addition the investigation of the solvent effect revealed that there is a longer red shift of the Q-band peak of ZnPc in DMSO than in DMF. This due to the difference in the polarity of the two solvents. Furthermore a signal loss of 35% due to solvent effect was observed. This value is high compare to what is reported in literature. However more work is required in order to confirm this.

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