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Insights into the photophysics of zinc phthalocyanine and photogenerated singlet oxygen in DMSO-water mixture

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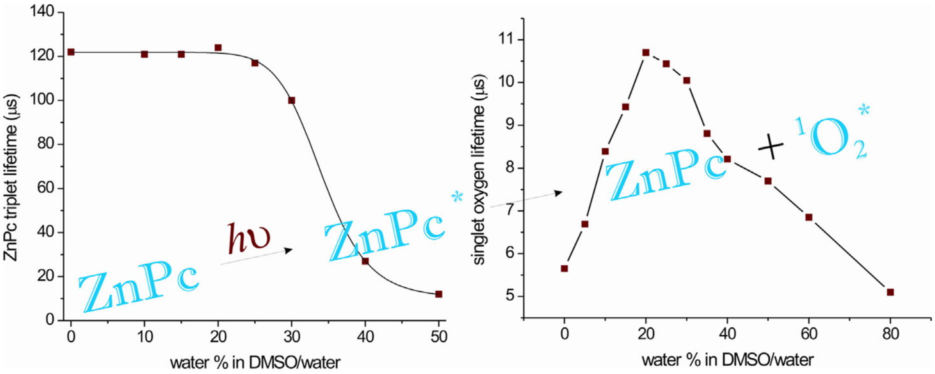
HIGHLIGHTS

- Photophysical properties of ZnPc and sensitized singlet oxygen in DMSO-(0–80%)water.
- Dye triplet follows sigmoid trace, 120 μs starting plateau untill 30% water.
- Singlet oxygen lifetime shows quasi-Gaussian behavior with maximum at 30% water.
- In DMSO, ZnPc quenches well its own triplets but does not quench singlet oxygen.

GRAPHICAL ABSTRACT



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ABSTRACT

This research was focused on the effects of DMSO-water ratio on the photophysics of the sensitizer Zn phthalocyanine (ZnPc) and on the photogenerated singlet oxygen. To reach this objective optical absorption, flash photolysis and time-resolved phosphorescence were used. Potential dye accumulation at the surface of the sample was studied by surface-tension measurements and at the chosen concentration no such effects were found. It was established that the sharp drop of dye absorbance at ~40% water content is produced by dye dimerization, probably induced by a re-clustering of molecules in the solvent composition. When water runs over 0–80% range the dye triplet lifetime follows a sigmoid evolution with an inceptive plateau at 120 μs and a sharp decrease in the 25–35% water range. Complementary experiments in neat DMSO established that while the ground dye molecules strongly quench the dye triplet states they do not significantly quench singlet oxygen. Experiments also showed that previous reported behavior of the lifetime of photosensitized singlet oxygen, exhibiting a prominent peak in the range 20–40% of water content is a common feature for both water soluble and insoluble solvates. The work outlines the hypothesis of a DMSO first solvation shell around the solvated dye molecules for a water content less than 25% and of a molecular re-organisation of the solvent taking place beyond this point, which induces important variations of photophysical quantities.

1. Introduction

This paper reports results pursuing the works presented in [1], discussing aspects of photo-excited dyes in DMSO-water mixtures and sensitized singlet oxygen.

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Among various applications of phthalocyanines, much research interest lies in life sciences – biology and medicine. In this field, and specifically in photodynamic therapy, even basic non-functionalized metallated phthalocyanines can be associated with carrier vectors such as nanoparticles and micelles or with different encapsulation ways [2] to circumvent one of their main drawback – water insolubility. This trend brought into light the basic metallated phthalocyanines.

On the other hand, DMSO (approved by the FDA for the treatment of a bladder inflammation – interstitial cystitis e.g.) is one of the most extensively used aprotic solvent in biology and medicine, especially in various combinations with water. Due to its property largely defined as membrane penetration it is frequently projected as a potential vector for the drug delivery, keeping high the interest for this compound in biology [3,4].

The DMSO-water mixtures are reported as showing strong non-linear and non-additive behavior in many aspects. This was often explained, documented with experimental data or theoretical models, through changings of the clusterization state of the component molecules (water and DMSO) [5–10].

Within this framework, the system constituted from Zinc Phthalocyanine (ZnPc) solvated in DMSO-water mixtures is of interest. In this respect we have previously reported [1] some data about non-linearity in the photophysics of the ZnPc and of the photosensitized singlet oxygen in DMSO-water mixtures. Briefly, a rather steep change of the values of some photophysical quantities of the system was observed in these mixtures within a quite narrow domain of cosolvent ratio beyond 30% water. This behavior was assigned to the effect of changing of solvent molecules clustering state occurring at some point of DMSO-water proportion. At that time, we could not decide that the absorbance behavior function of solvent composition is induced also by the dimerization.

Evidence of another interesting behavior regarding the lifetime of singlet oxygen in DMSO-water mixtures was given in [1]: although the lifetime of singlet oxygen is 3–4 μs in water and 6–7 μs in DMSO, a serious increasing of it was found when water content gradually increases until about 20% in the mixture. Singlet oxygen lifetimes longer than 10.5 μs are reached for about 20% water, followed by decay down to 6–7 μs beyond 50% water.

The current paper treats new aspects with respect to results obtained in a previous paper on photophysics of ZnPc solvated in DMSO-water mixtures [1]. Time-resolved NIR phosphorescence of singlet oxygen, laser flash photolysis and pendant droplets surface tension were techniques employed in finding out data regarding dye excited states behavior, photosensitized singlet oxygen behavior and study of fluidic properties of the system.

In this respect, absorption measurements were performed using a dis-stacking agent in order to elucidate if dimerization is the cause of absorption steep decrease at water content larger than 30% in solvent mixture. Surface tension measurements were made on ZnPc solvated in DMSO-water mixtures.

Also, flash photolysis studies were performed for different co-solvent ratios to reveal the behavior of dye triplet lifetime versus water content. In addition, studies about triplet lifetime behavior versus concentration in DMSO solvent were engaged, to identify possible quenching agents of triplet states. Lifetime of singlet oxygen for other two photosensitizers was measured (Verteporfin and Methylene Blue), to see whether the increase of lifetime of singlet oxygen in DMSO-water beyond the values for any of the co-solvents is common for soluble and insoluble (in water) dyes.

The research aimed to gain knowledge in the field of the impact of microenvironment on behavior of photosensitizer and of photogenerated singlet oxygen.

2. Materials and methods

The methods applied in this study were mainly spectroscopic – steady state absorption, flash photolysis and time-resolved near IR phosphorescence. Besides, surface tension measurements of pendant droplets containing DMSO/water mixture with or without ZnPc were performed.

Materials: DMSO was EMSURE grade (Merck), ZnPc dye was Sigma-Aldrich (97%), the distilled water was prepared with Merit Water Still W4000 equipment. Verteporfin® was from Kemprotec Ltd. UK, Methylene Blue was supplied by Sigma-Aldrich and Triton^{TM} X-100 BioXtra grade was obtained from Sigma-Aldrich.

The samples were in equilibrium with atmospheric air. ZnPc concentration was 5×10^{-6} M if not otherwise mentioned. Samples were prepared from ZnPc in DMSO stock ($c = 5 \times 10^{-5}$ M) by adding adequate volumes of DMSO and water to reach required proportion of co-solvents. Solvent composition is expressed as volume percent v/v% (water volume) to (solvent volume) × 100.

Steady-state absorption measurements were carried out on Lambda950 UV/Vis/NIR Spectrometer, PerkinElmer.

The 1270 nm dye photosensitized singlet oxygen phosphorescence was measured in a home-made experimental setup described in [1]. The photosenzitizer was excited by the third harmonic of the Nd:YAG laser (Minilite ML II, Excel Technology, 355 nm, 10 Hz, 6 ns pulse time width), a cooled NIR photomultiplier (Hamamatsu H-10330) fitted with appropriate band-pass cutting filters being employed to measure the singlet oxygen phosphorescence. The photomultiplier signal was digitized by an oscilloscope Tektronix DPO 7254 triggered by a TTL signal from laser pulse generator. Averaged waveforms for 1000 laser pulses were fitted with mono-exponential function to determine singlet oxygen decay time constant (lifetime). The zero-time value of the phosphorescence intensity was obtained by extrapolating the fitting curve to $t = 0$. In order to avoid non-linear effects, the energy of the laser pulse was kept within 1–2 mJ range. The laser pulse energy was monitored on-line with an energy meter (Quanta QE 25, Gentec) by proper beam splitting.

The transient absorption of the triplet states of ZnPc was achieved by using a home-made, right-angle geometry laser flash photolysis system [11], using the third harmonic (355 nm) of a YAG:Nd laser as the pump probe and a CW, 75 W Hamamatsu Xe-lamp as the monitoring probe. The energy of the laser pulse was kept within 1–2 mJ range for dye excitation. Samples were accommodated in 10 × 10 mm fluorescence-type cell. The suitable tailored Xe-lamp beam was conveyed by an optical fiber to a monochromator (SPM2, Carl Zeiss Jena) equipped with 600 tr/mm diffraction grating at 0.15 mm slits (0.06 nm bandwidth) and detected by a photomultiplier (H7732-10Hamamatsu). The photomultiplier signal was digitized by an oscilloscope, Tektronix DPO 7254. Raw signals were averaged over 1000 pulses. The average waveform was processed to obtain the triplet state decay time constant (lifetime) by mono-exponential fitting. Transient absorption of ZnPc triplet states was measured at the peak of the triplet absorption band (480 nm).

Given the known preference for surface of the DMSO molecules [12], their accumulation at surface can occur [13] altering the bulk concentration. The possible presence of DMSO solvation shells for this system would have as effect the carrying along of the dye molecules towards sample surface and a depletion of the dye in the bulk.

Consequently, it is important to evaluate the extent of which the DMSO accumulation is inducing ZnPc adsorption at the interface by monitoring the surface tension which is very sensitive to small solute concentration. Surface tension measurements were performed using the Drop Profile Analysis Tensiometer (PAT1 Sinterface Technologies, Germany). This equipment generates pen-

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