Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 196 (2008) 99–105
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Characterizing the functional dynamics of zinc phthalocyanine from femtoseconds to nanoseconds

Janne Savolainen[a,*], Dennis van der Linden[a], Niels Dijkhuizen[a], Jennifer L. Herek[a,b,*]

[a] *FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*
[b] *Optical Sciences Group, Department of Science and Technology, MESA+Institute for Nanotechnology, University of Twente, Enschede 7500 AE, The Netherlands*

Received 9 August 2007; received in revised form 20 November 2007; accepted 22 November 2007
Available online 16 January 2008

Abstract

A promising photosensitizer, zinc phthalocyanine, is investigated by means of steady-state and time-resolved pump-probe spectroscopies. Spectrally resolved pump-probe data are recorded on time scales ranging from femtoseconds to nanoseconds. Global analysis yields the excited-state absorption spectra and lifetimes, as well as the pathways and efficiencies of the competing relaxation processes from the initially excited S_1 state. In addition to the expected nanosecond-scale processes of fluorescence, internal conversion and inter-system crossing that follow the generally accepted kinetic scheme, we also resolve ultrafast dynamics. The nature of these fast processes and their implications to the functional pathway involving triplet formation are discussed.

Keywords: Photosensitizer; Ultrafast dynamics; Energy-flow diagram; Triplet yield; Zinc phthalocyanine

1. Introduction

The functionality of photosensitizer molecules arises from their ability to react with molecular oxygen to produce highly reactive singlet oxygen and other radical species. Among the applications are photodynamic therapy, blood sterilization and sunlight activated herbicides and insecticides [1,2]. A good photosensitizer should have a high absorption cross-section at a wavelength suitable for the application, e.g. the optical window of tissue in photodynamic therapy [3]. Singlet oxygen species are created by the interaction between a photosensitizer in its triplet state and oxygen molecule, hence the quantum yield of the triplet state is a key factor when searching for or designing new photosensitizers. Other important factors include the rate of photodegradation, solubility, and the tendency to aggregate [3].

In the end, the efficiency of all these applications depends on the photophysics of the photosensitizer molecule. Improving the photosensitizer to enhance the functional pathway and suppress loss channels is an attractive route to explore by coherent control experiments using shaped ultrafast laser pulses [4]. In this approach, an optimisation experiment is designed with the goal of finding a pulse shape that will improve the yield of a chosen photophysical process in comparison to that obtained with a transform-limited (i.e. unshaped) laser pulse. Improving the triplet yield, and correspondingly the efficiency of the photosensitizer molecule in generating singlet oxygen, is a clear target for an optimisation experiments on photosensitizers. However, prior to these experiments a detailed understanding of photophysical processes involved in the excited-state deactivation, as well as their manifestation to the transient spectral signals used as feedback in the control experiments, must be acquired. Here, we report transient absorption experiments and detailed global analysis to extract the pathways, spectral signatures and efficiencies of energy flow in a prototype photosensitizer molecule.

Amongst the most promising second-generation photosensitizers for photodynamic therapy (PDT) are the phthalocyanines [1]. In this study, zinc phthalocyanine (ZnPc) is chosen to serve as a model photosensitizer to study the efficiency of the triplet yield as well as other processes occurring after the initial excitation of the chromophore (see Fig. 1). ZnPc has been in clinical trials [5,6], is easy to obtain, stable, produces singlet oxygen with

---

[*] Corresponding authors. Tel.: +31206081234; fax: +31206684106.
E-mail addresses: savolainen@amolf.nl (J. Savolainen), j.l.herek@tnw.utwente.nl (J.L. Herek).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2007.11.018

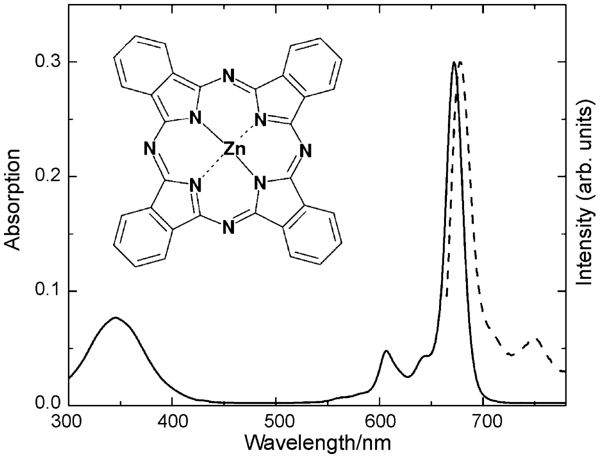

Fig. 1. Absorption (solid curve) and fluorescence (dashed) of ZnPc in DMSO. For the latter, the excitation wavelength was 660 nm. Inset: chemical structure of ZnPc.

high yield [7], and has a high absorption cross-section in the far-red part of the visible spectrum close to the optical window of tissue. To fully explore the photosensitising qualities of ZnPc, a detailed description of the intramolecular processes, occurring on time scales ranging from femtoseconds to microseconds, is required. We begin by reviewing results from related studies obtained during the last decade, which we will later compare to our own results.

Several experimental studies on the photophysics of ZnPc and similar compounds (derivatives or different metallophthalocyanines) in solution have been reported [8–19], but so far the results fail to depict a coherent picture of the overall photophysics. The generally accepted energy-flow model includes three major intramolecular relaxation pathways from the initially excited S_1 state. The competition between these processes can be summarized by the modified Gouterman's equation [20]:

$$\Phi_{\rm F} + \Phi_{\rm IC} + \Phi_{\rm ISC} = 1, \tag{1}$$

where $\Phi_{\rm F}$, $\Phi_{\rm IC}$ and $\Phi_{\rm ISC}$ are the quantum yields of fluorescence, internal conversion and inter-system crossing, respectively.

For the most part, first excited-state (S_1) lifetimes (often called fluorescence lifetime ($\tau_{\rm F}$) due to the direct relation between detected fluorescence intensity and S_1 population) and fluorescence quantum yields, obtained from fluorescence measurements in different environments, are consistent, and similar values are reported in various studies. Measured S_1 lifetimes are in the order of few nanoseconds, for example $\tau_{\rm F} \sim 2.88$ ns with a quantum yield of $\Phi_{\rm F} \sim 0.277$ for zinc phthalocyanine tetra sulfonate (ZnPcTS) in DMF [6]. For the sample used in this study, ZnPc in DMSO, a $\Phi_{\rm F}$ of 0.20 ± 0.03 is reported by Ogunsipe et al. [18]. Fluorescence yields and decays of the same order have been reported in different environments like proteins, cell suspensions and in vesicles [21,22], and they are found to be dependent on the surroundings of the chromophore, yet always displaying nanosecond-scale behaviour.

A more complete picture of the nanosecond dynamics is depicted by Bishop et al. in a study of ZnPc (and its 16-deuterated derivative) in toluene by various photophysical methods [23]. The authors report rate constants of 9.1, 38.5, and 5.6 ns, with corresponding quantum yields of 0.34 ± 0.03, 0.08 ± 0.11 and 0.58 ± 0.08 for F, IC and ISC, respectively. However, as an example of the wide variation in the reported nanosecond dynamics, we note a study by Frackowiak et al. These authors found the quantum yield for the inter-system crossing to be even as high as 0.98 ± 0.18 for ZnPc in air-saturated DMSO [12], using a photothermal measurement technique.

The triplet-state lifetime ($\tau_{\rm T}$) is strongly affected by the presence of molecular oxygen, which drastically reduces $\tau_{\rm T}$ due to efficient intermolecular energy transfer. Grofscik et al. [9] find a $\tau_{\rm T}$ of 220 ± 22 ns for ZnPc in air-saturated ethanol; Lang et al. [22] report 1.6 μs for $\rm ZnPcS_3$ in aerated aqueous protein solution and 205 μs without the presence of oxygen.

In addition to the nanosecond dynamics described above, also femtosecond and picosecond processes have been reported. The S_1 lifetime of ZnPc in toluene is claimed to be ~35 ps by Rao and co-workers, a value obtained by degenerate four-wave mixing using incoherent light [13]. The setup used, however, was inadequate for quantify components exceeding 100 ps. In addition, the authors report a ~3.5 ps component that is assigned to vibrational relaxation in the S_1 state, as well as a S_n dephasing time of <170 fs. Howe and Zhang report an S_1 lifetime of ~160 ps and an S_2 lifetime of ~10 ps for tetrasulfonated $\rm ZnPcS_4$ in DMSO [10]. The data were obtained by femtosecond pump-probe measurements, where excitation was to the second excited state. In explaining the multi-exponential behaviour of the kinetics authors introduce an energy-flow model that includes an uphill climb from S_1 to the S_2 state at room temperature and an inverse saturable absorber model. Recently, in a study of artificial light-harvesting complexes where ZnPc is covalently linked to a carotenoid molecule, ultrafast branching of the energy flow in the singlet manifold with time scale of <100 fs has been reported by Berera et al. [24].

Collectively, the various observations from the ultrafast studies suggest that the conventional energy-flow model (Eq. (1)) fails to depict the entire picture of the kinetics, and that faster processes may also play an important role in the photophysics of ZnPc and its derivatives. However, the previous results from the ultrafast studies performed on ZnPc in solution are extremely divergent, and motivate further studies in order to resolve the intramolecular dynamics of this system.

Here, we employ pump-probe spectroscopy from femtosecond to nanosecond time scales in order to deliver a more consistent picture of the kinetic processes following the excitation of the photosensitizer. Using a state-of-the-art pump-probe setup and global analysis of the spectrally broad data we focus on the intramolecular dynamics of ZnPc in DMSO, determining the excited-state spectra, deactivation pathways, time constants and efficiencies. Besides resolving the nanosecond-scale dynamics that follow the conventional energy-level scheme, we show that there indeed are ultrafast processes present. In this context, we also address the role of the solvent, and how solvation dynamics may complicate the analysis of dynamics on ultrafast time scales [25–30]. Global analysis of the temporally and spectrally resolved data allows us to extract a complete picture of the branching ratios between the three competing intramolecular