EPJ Web of Conferences **41**, 07006 (2013)
DOI: 10.1051/epjconf/20134107006

Ultrafast dynamics and Raman imaging of metal complexes of tetrasulphonated phthalocyanines in human cancerous and noncancerous breast tissues

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Abstract. A promising material in medicine, electronics, optoelectronics, electrochemistry, catalysis and photophysics, Al(III) phthalocyanine chloride tetrasulfonic acid ($AlPcS_4$) is investigated at biological interfaces of human breast tissue by means of time-resolved spectroscopy. The nature of fast processes and pathways of the competing relaxation mechanisms from the initially excited electronic states of a photosensitizer at biological interfaces have been studied. Comparison between the results in the biological environment of the breast tissues and in aqueous solutions demonstrates that the photochemical mechanisms become dramatically different. The presented results provide a basis for a substantial revision of the commonly accepted assumption that photochemistry of the bulk properties of photosensitizers in solutions can be translated to the interfacial region. First, in solution the dynamics of the photosensitizer is much slower than that at the biological interface. Second, the dynamics of the photosensitizer in the cancerous tissue is dramatically slower than that in noncancerous tissue. Our results provide evidence that molecular structures responsible for harvesting of the light energy in biological tissue find their ways for a recovery through some special features of the potential energy surfaces such as conical intersections, which facilitate the rate of radiationless transitions and maintain the photostability in the biological systems.

1. Introduction

Ultrafast spectroscopies have played an important role in the study of a number of biological processes and have provided unique information about primary events and the mechanism of energy relaxation [1-3]. Although interactions at cellular surfaces involve large numbers of forces and molecular interactions, the successful use of time resolved laser spectroscopy to achieve measurable biological responses indicates that it is indeed possible to probe dynamics at the nano-bio interface experimentally. Here we explore such interfaces from the perspective of dynamics of photosensitizers at biological interface and compare it with the dynamics in aqueous solutions. Ever since photodynamic therapy (PDT) has emerged as an alternative and promising noninvasive

treatment for cancer, experimentalists and theoreticians have tried to unravel the molecular details of primary events occurring upon excitation. An open question is how the biological environment affects the topography of the potential energy surfaces of the ground and the excited state of the photosensitizer. To answer this important question we have selected one of the most favored candidates for consideration in photocatalysis and photosensitization, Al(III) phthalocyanine chloride tetrasulfonic acid ($AlPcS_4$). In this paper we focus on biological interfaces that photosensitizer may encounter after suspension and adsorption in a biological medium of noncancerous and cancerous human breast tissue. We will present dynamics of phthalocyanine at biological interface in the time window ranging from femtosecond to nanoseconds and compare it with the dynamics in aqueous solutions. Detailed understanding the paths of energy dissipation will reveal mechanisms that mediate light-induced signal transduction as well as the role of photoreceptors in photostability protection in living cells and tissues.

2. Experimental methods

Pump-probe transient absorption spectroscopy: the source of femtosecond pulses was mode-locked titanium sapphire femtosecond laser (MIRA, Coherent, 800 nm, 76 MHz, 9 nJ, < 200 fs) pumped with diode-pumped solid-state laser (VERDI V5, Coherent, 532 nm). The fundamental beam was amplified with Ti: Sapphire regenerative amplifier (Coherent Legend USP, 800 nm, 1 kHz, 3 mJ, 50 fs). The regenerative amplifier was pumped with diode-pumped Nd: YLF laser (JADE, Thales Laser, 527 nm, 1 kHz, 20 mJ, < 200 ns). The pulse was split in two and further amplified in a dual single pass amplifier (Coherent Elite-Duo, 800 nm, 1 kHz, 2 × 4.5 mJ, 50 fs).

3. Results

To get an insight into mechanisms of energy dissipation and dynamical alterations in the phthalocyanine structure at biological interface of human breast tissue, a system was triggered with pump laser pulse at 677 nm, which promotes the $S_0(a_{1u})\rightarrow S_1(e_g)$ transition in the Q-band (Fig.1A), and monitored by delayed laser pulses of various wavelengths and pulse duration of 50 fs. In this paper we focused on the probe at 602 nm. Figure 1 shows the comparison of the transient absorption signal $\Delta A(t)$ of $AlPcS_4$ as a function of time delay in the noncancerous, cancerous human breast tissues, and aqueous solution.

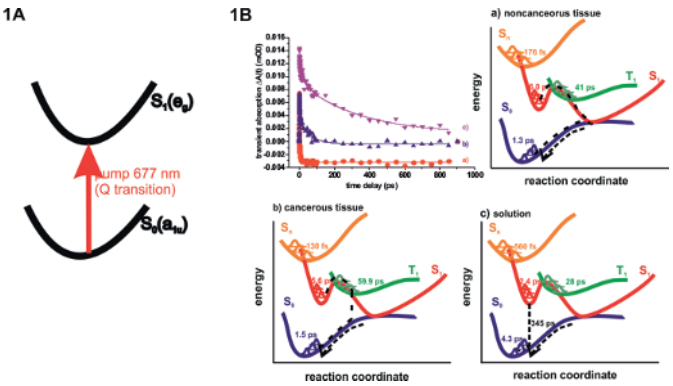

Fig.1. A Excitation of the electronic states pumped with the pulse at 677 nm. B Comparison of the transient absorption signal $\Delta A(t)$ of $AlPcS_4$ as a function of time delay in noncancerous (●) (a), cancerous (▲) (b) human breast tissues (pumped at 677 nm and probed at 602 nm), and aqueous solution (▼) (c) (concentration 10^{-3} M, pumped 678 nm, probed at 570 nm). The main channels of energy dissipation of photosensitizer ($AlPcS_4$) at interfacial region of the noncancerous and cancerous tissues and in solution.

The picture that emerges from the presented results provides a basis for a substantial revision of the commonly accepted assumption that photochemistry of the bulk properties of photosensitizers in solutions can be translated to the interfacial region. First, in solution the dynamics of the photosensitizer is much slower than that at the biological interface. Second, the dynamics of the photosensitizer in the cancerous tissue is dramatically slower than that in noncancerous tissue. Detailed results are presented in Table 1.

Table 1. Comparison of time constants of $AlPcS_4$ at biological interfaces of the noncancerous and cancerous tissues, and solution.

	Time constants				
Noncancerous tissue for pump 677 nm, probe 602 nm	176 ± 20 fs	847 ± 422 fs	6.03 ± 1.92 ps		
Cancerous tissue for pump 677 nm, probe 602 nm		810 ± 40 fs	5.63 ± 5.49 ps	59.90 ± 12.85 ps	
Solution for pump 678 nm, probe 570 nm	560 ± 94 fs		2.37 ± 0.71 ps	28.07 ± 24.18 ps	345.81 ± 107.87 ps

In the view of the results presented in this report we propose the following picture for the primary events occurring in the noncancerous and cancerous tissues. After photon absorption in aqueous solution, the excited state S_1 relaxes rapidly within 560 fs in the Franck-Condon region followed by return to the ground state S_0 via fluorescence with the excited state lifetime of 345 ps. The second channel of energy dissipation goes through intersystem crossing to the triplet state T_1 relaxing to the ground vibrational state with the time constant of 28 ps followed by return to the ground state S_0 via phosphorescence (at longer time scale which is not recorded in the time window up to 1 ns). The situation becomes different when the photosensitizer molecules attached to the biological interface are exposed to light. In the noncancerous tissue the main channel of energy dissipation is radiationless decay via conical intersection with the time constants of 176 fs and 847 fs corresponding to the rapid relaxation in the Franck-Condon region down to the local minimum of the excited state S_1, crossing the local barrier followed by the relaxation to the conical intersection, respectively. The constant of 1.3 ps along this pathway corresponds to the vibrational relaxation in the ground state S_0 reflected by the recovery of the absorption at 602 nm in Table 1. The second channel active in the noncancerous tissue is intersystem crossing to the triplet state T_1 with the time constants of 6 ps, and 41 ps corresponding to and the intersystem crossing $S_1 \rightarrow T_1$ lifetime, and the vibrational relaxation in the excited state T_1, respectively. In the cancerous tissue the main channel is intersystem crossing within 59 ps followed by relaxation to the ground vibrational state of the triplet state T_1 with the time constant of 5.6 ps followed by return to the ground state S_0 via phosphorescence. The second channel goes through a conical intersection within 810 fs followed by radiationless transition to the ground state S_0 and vibrational relaxation in the ground state within 1.5 ps.

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