Dynamic and orbital factors affected on electron transfer and light energy conversion in proteins

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Probing environment with dual fluorophore-nitroxide supermolecules (FNS) in which fluorophore is tethered with nitroxide, a fluorescence quencher, opens unique opportunities to study molecular dynamics and micropolarity of the medium which affect intramolecular fluorescence quenching (IFQ), electron transfer, photoreduction and light energy conversion [1]. In such molecules, the excited fragment of the chromophore can serve as an electron donor, and the nitroxide fragment as an electron acceptor. The same groups allow monitoring of dynamics and micropolarity of the medium in the vicinity of the donor (by fluorescence technique) and acceptor (by ESR) moieties. In the present work, two FNS were incorporated in a binding site of bovine serum albumin. On the basis of experimental data and the Marcus model of the electron transfer between the excited dansyl fluorophore (donor) and nitroxide group (acceptor) and, the mechanism of the electron transfer in the dual molecules. It was shown that dual FN molecules in the protein meet main requirements for an efficient light energy conversion system.

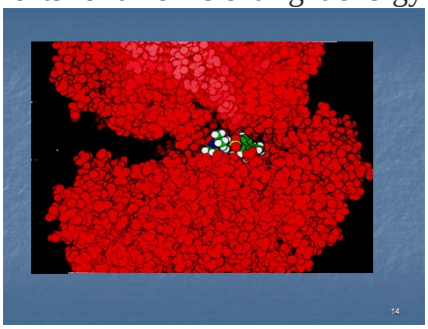

Figure. Model of the bovine serum albumin incrusted with a dual fluorescence nitroxide probe

For fast estimation the rate constant of electron transfer (ET) in DA pairs, we suggest the following equations [1]

$$J_{SE} = J_0 \rho_{S1} \rho_{S2} \prod^i \gamma_i^{-1}$$
$$k_{ET} = k_0 \rho_D \rho_A \prod^i \gamma_i^{-1}$$

where $J_0 = 10^{14} s^{-1}$ exchange integral at Van der Waals contact , $\rho_{S1,2}$ - spin density at Van der Waals contact, γ_i - decay factors, $k_0 = 5x10^{10} s^1$ rate constant of ET in a notbridged DA pair

The values of SE and ET estimated for the photosynthetic and model donor-accaptor pairs were found to be in a reasonable agreement with corresponding experimental data.

[1] Likhtenshtein G. I. Electron Spin Interaction in Chemistry and Biology. Fundamentals, methods, reactions mechanisms, magnetic phenomena, structure investigation. Springer, 2016