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Electron Transfer in Porphyrin Multimolecular Self-Organized Nanostructures

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On the base of of covalent and non-covalent bonds nanoscale self-assembling multiporphyrin arrays with well-defined geometry, the controllable number of interacting components and their spectral and photophysical properties were formed. The deactivation of excited singlet and triplet states was studied using steady-state, time-resolved picosecond fluorescence ($\Delta_{1/2}\approx$30 ps) and femtosecond pump-probe ($\Delta_{1/2}\approx$ 280 fs) spectroscopy in solvents of various polarity at 77-300 K. It has been found that the competition between the non-radiative energy transfer (within $\leq$10 ps) and charge transfer (within 300 fs - 700 ps) processes in the systems depends on the structure, spectral and redox properties of interacting subunits and may be driven by the distance, temperature and solvent polarity. The possible pathways and mechanisms of the electron transfer in the systems of various types are discussed (Marcus theory for the "normal" region and the non-adiabatic case,. the "superexchange" mechanism).

Keywords Electron transfer, porphyrin dimers, fluorescence quenching, electron acceptors

INTRODUCTION

During the past decade the majority of supramolecular porphyrin arrays have been used quite intensively in order to model energy and electron transfer (ET) processes taking place *in vivo*[1-3] or to gain insight into the principal possibilities of molecular electronics[4]. Apart from covalent linking the desired supramolecular subunits the strategy of self-assembly, using different kinds of non-covalent linkage of the subunits, has attracted a lot of interest[5]. Recently, we applied the complexation of Zn-porphyrin chemical dimers by pyridyl-substituted porphyrins as extra-ligands to form triadic[6] or even pentadic[7] porphyrin arrays. Complexation constants of the order of 10^6 to 10^7 M^{-1} were found for this two-point self-assembly effect[6].

In the present paper we carry out the comparative analysis of the electronic excitation deactivation processes for the elucidation of the main ET pathways in some multicomponent systems based on Zn-octaethylporphyrin chemical dimer with a phenyl spacer, (ZnOEP)Ph(ZnOEP) which, in its turn, is covalently linked in *meso*-position to various electron acceptors [*p*-benzoquinone (Q) or pyromellitimide (Im)] and/or is self-assembled with tetrapyrrolic extra-ligands such as dipyridyl substituted porphyrin (P) or dipyridyl-pentafluor-substituted porphyrin (P_F). The corresponding structures of the systems are presented below. In addition to steady-state data, the time-resolved dynamics of electronic excited states deactivation was studied. Fluorescence experiments were carried out using laser picosecond fluorescent setup with 2-D (wavelength-time) registration based on a dye laser (repetition rate 4 MHz, 10 ps pulses) and a Streak-Scope (Hamamatsu Model C4334, $\Delta_{1/2} \approx 30$ ps). Pump-probe experiments involved a Coherent MIRA 900 Ti:sapphire laser with a regenerative amplifier and a parametric oscillator running at 1 kHz. Excitation in the 400-800 nm range was used, the experimental response was $\Delta_{1/2} \approx 280$ fs.

EXPERIMENTAL FINDINGS AND DISCUSSION

ET in (ZnOEP)Ph(ZnOEP) with covalently linked acceptors

At 295 K in toluene the (ZnOEP)Ph(ZnOEP) dimers with Q and Im have the same absorption and fluorescence spectra with respect to those for the pure dimer, but the fluorescence is essentially quenched and S$_1$ state lifetime is found to be 21 ps for Q and ~ 60 ps for Im. Increasing the environment polarity (addition of acetone) accelerates the Zn-dimer fluorescence quenching in the case of Q but does not influence on the observed quenching for Im. Pump-probe experiments show that for the system (ZnOEP)Ph(ZnOEP)-Im the Im$^-$ radical absorption band at ~715 nm appears (Fig. 1) as a result of the Zn-dimer S$_1$-state quenching and decays with lifetime of ~100 ps. Together with the 715 nm band a weaker absorption at ~660 nm is detected, that corresponds to the (ZnOEP)Ph(ZnOEP)$^+$ radical. On the base of kinetic data, redox properties and structural parameters of the systems it was shown that Im is a weaker electron acceptor that Q, and ET from the dimer to both acceptors is described by Marcus theory [8] (the "normal" region, the non-adiabatic case, the electronic coupling term V<200 cm^{-1}). These results were used for the analysis of ET processes between large tetrapyrrole subunits in more complex systems.

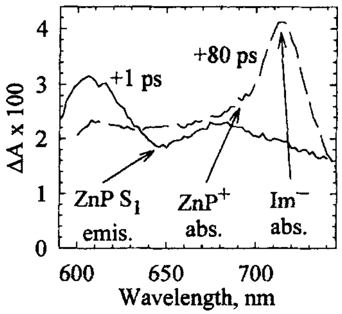

FIGURE 1. Transient absorption spectra of (ZnOEP)Ph(ZnOEP)-Im at 295 K in toluene.

ET in the Triad Containing (ZnOEP)Ph(ZnOEP)-Q and P Extra-Ligand

In non-polar methylcyclohexane at 295 K the two-point interaction of P extra-ligand with the Zn-dimer having a covalently linked Q leads to the formation of the triadic self-assembled complex (Fig. 2). In this case the additional fluorescence quenching of the (ZnOEP)Ph(ZnOEP)-Q subunit is observed with an efficient fluorescence sensitization effect for P. The derived results show that the Zn-dimer fluorescence quenching ($\tau_S \leq 1$ ps) is due to the effective S-S energy transfer Zn-dimer→P with the probability $F \geq 7 \cdot 10^{10}$ s^{-1} and to ET process Zn-dimer→Q. Thus, the energy transfer and ET from Zn-dimer to P is faster than the considered above ET process from Zn-dimer to Q. Nevertheless, the interaction of the excited states of Zn-dimer and P is followed by the P S_1-state formation. It is noteworthy that the extra-ligand P fluorescence lifetime shortening from $\tau_{S0}=11$ ns to $\tau_S=460$ ps is observed, and this process becomes faster in more polar medium and slower at low temperatures The observed facts are attributed to the photoinduced ET via the "superexchange" mechanism where a "spectator" CT state of the triad, H_2P^+-(Zn-dimer)$^-$-Q, mediates the direct ET from P to a distant Q (R≈17.5-19 E) resulting in the efficient charge transfer within the nonadiabatic limit[9].

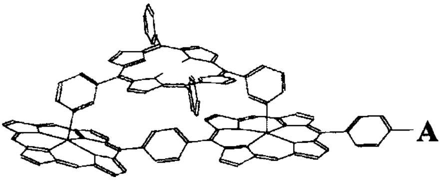

FIGURE 2. Computer-simulated structures of self-organized triads with the covalently linked acceptor A. A: CH_2-Q or CH_2-Im.

ET in the Triad Containing (ZnOEP)Ph(ZnOEP)-Im and P Extra-Ligand

In the triad the ultrafast quenching of the Zn-dimer S_1-state is also observed with $\tau \approx 1$ ps (Fig. 3) accompained by the P ground state absorption bleaching. However, the ground state absorption of the Zn-dimer does not recover simultaneously. Thus, the Zn-dimer S_1-state depopulates due to the efficient ET from Zn-dimer to P mainly. The following formation of P S_1-state and the Zn-dimer ground state recovering are observed within 5 - 100 ps. In contrast to the similar triad with Q, the P fluorescence quenching is weak and its S_1-state decay in a ns time scale. Consequently, a distant ET from P to the weaker electron acceptor Im is essentially slower than in the case of Q.

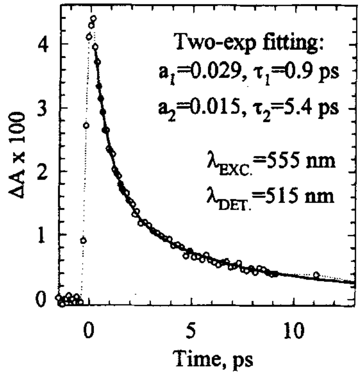

FIGURE 3. Transient absorption kinetics of the triad containing Im and P in toluene at 295 K. The decay fit is shown by solid line.

ET in the Triad Containing (ZnOEP)Ph(ZnOEP) and P_F or P Extra-Ligands

These triads are characterized by similar structures (Fig. 4) differing by the nature of the extra-ligand (P or P_F). For the triad formed with P, the competition between S-S energy transfer and ET from the Zn-dimer to P is observed upon the excitation of the former. Upon excitation into the P absorption band at 645 nm its fluorescence intensity is about twice lower in the triad as compared to that for individual P at the same concentration. Nevertheless, time-resolved fluorescence data show no indication of any pronounced porphyrin free base lifetime shortening (7.9 ns) in the triad. This means that the P S_1-state quenching is negligible similar to the case of the triad with covalently linked Im.

In the case of the triad formed with P_F (stronger electron **A** than P) ET is observed even from the excited P_F and the charge separated state P_F^+-Zn-dimer$^-$ is detected (Fig. 5). It reveals that the ultrafast ET with $k_{ET}\geq 10^{12}s^{-1}$ at 295 K competes with the S-S energy transfer and results in the strong fluorescence quenching of both Zn-dimer and P_F subunits. This ET process remains very efficient yet at 120 K. In addition, at 77 K fluorescence excitation spectra of the system upon the registration in the vibronic band of P_F ($\lambda\geq 750$ nm) show the noticeable sensitization effect, that is the dimer excited S_1-state deactivation (within ≤ 10 ps) is due to both ET and the energy transfer. This explanation is consistent with the conclusions made for covalently linked porphyrin diads (intercenter distance R=18.7 A^0) containing fluorinated porphyrin[10]. But in our case, because of smaller R=8.2 A^0 the vectorial interporphyrin ET is faster essentially in the comparison with that for the porpphyrin P-P_F diad[10] where $k_{ET}=4.1\cdot 10^7$ s^{-1}. Pump-probe experiments show that the charge separated state transforms within ~2 ns to the long-lived P_F T_1-state (Fig. 5). Upon the equivalent excitation conditions at $\lambda_{ex}=532$ nm the triplet state parameters of P_F ($\tau_T\approx 350$ ns in the presence of O_2, T-T absorption amplitude) for the (ZnOEP)Ph(ZnOEP)-P_F triad are close to those for the (ZnOEP)Ph(ZnOEP)-P triad at the same concentrations. It means that the intermediate P_F^+-Zn-dimer$^-$ radical-ion state is presumed to be higher than the extra-ligand P_F triplet state.

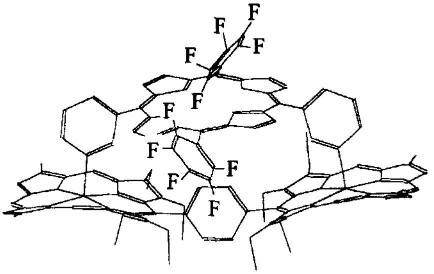

FIGURE 4. Computer-simulated structure of the self-organized triad with P_F extra-ligand.

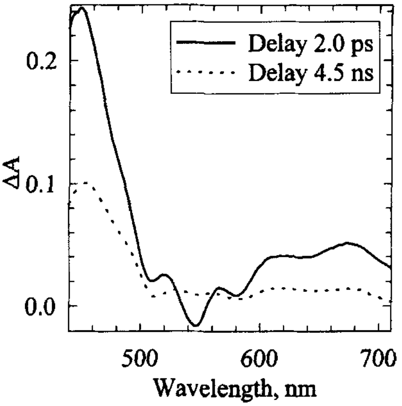

FIGURE 5. Transient absorption spectra of the triad with P_F in toluene at two delays, T=295 K.

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