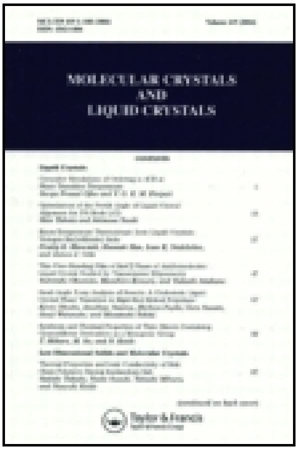

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Photoinduced Electron Transfer Dynamics for Self-Assembled Porphyrin Arrays in Solutions and Films

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Photoinduced Electron Transfer Dynamics for Self-Assembled Porphyrin Arrays in Solutions and Films

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Electronic excitation energy deactivation in self-assembled porphyrin triads has been studied by the time correlated single photon counting technique as a function of the solvent polarity (toluene-acetone mixtures), temperature (77–350 K), and mutual spatial arrangement of the donor and acceptor subunits. The donor (Zn-octaethylporphyrin chemical dimer) fluorescence quenching with time constant of 1.7÷10 ps is due to competing energy migration and electron transfer processes to the acceptor (dipyridyl substituted tetrapyrrole extra-ligand). The quenching of the acceptor fluorescence (by ~1.3–1.6 times) does not significantly depend on the mutual spatial arrangement of the triad subunits and increases with the solvent polarity rising and the decrease of the temperature. The obtained experimental data are analyzed using the reduced density matrix formalism in the frame of Haken-Strobl-Reineker approach taking into account the energy transfer, charge separation, and the dephasing of coherence between the excited electronic states of the triad.

Keywords: fluorescence lifetime shortening; donor-acceptor interactions; electron transfer; reduced density matrix formalism; coherence dephasing

INTRODUCTION

At present, it is well known that the initial energy conversion in photosynthetic reaction centers is the photoinduced electron transfer (PET) from chlorophyll special pair to monomeric pheophytin [1]. Correspondingly, a number of research groups have undertaken studies of PET between large π-conjugated tetrapyrrole molecules in various model systems [2-4]. According to [3] PET in this case can be characterized by a relatively small reorganization energy and a small inverse temperature dependence, Herein, we discuss the peculiarities of PET processes competing with the energy transfer in porphyrin triads on the basis of the experimental findings and theoretical calculations. Self-assembled triads of various but controllable geometry (Figure 1) were formed (using the extra-ligation effect [4]) from a covalently linked Zn-octaethylporphyrin dimer (ZnPD) as the energy and electron donor and dipyridyl-substituted free base porphyrin (P) as the acceptor.

FIGURE 1 Optimized structures of porphyrin triads with various arramgement of the extra-ligand (HyperChem, release 4.0, PM3).

The time-resolved dynamics (10 ps-nanosecond time scale) of the deactivation of the triads electronic excited states was performed with the time correlated single photon counting (TCSPC) technique.

EXPERIMENTAL RESULTS

As follows from the analysis of steady-state absorption, fluorescence and fluorescence excitation spectra of the triads reported in [4], the ZnPD strong fluorescence quenching in toluene at 293 K is attributed to the effective dissipative singlet-singlet energy transfer ZnPD→P (theoretical rate constant $F^{SS}=3\cdot10^{10}$ s^{-1}, Forster model). In these conditions the energy transfer may be considered as the main deactivation process for ZnPD S_1-state in all triads under consideration. The same situation was found for the triads in rigid polymethylmetacrylate films at 293 K. Upon the solvent polarity increase the fluorescence excitation spectra for the triad is transformed to those for the extra-ligand only while the ZnPD fluorescence remains strongly quenched. It means that the sensibilization effect disappears and the other process (PET ZnPD...P→$ZnPD^+$...P^-) becomes dominant. In addition, the quenching of the extra-ligand P fluorescence intensity is observed upon the increasing polarity and the temperature lowering (Figure 2). TCSPC results obtained from a global analysis fit using three or four time constants (Figure 3) reveal that the amplitude spectra of the extra-ligand P in the triad are characterized by smaller lifetimes (6.2-7.7 ns) in toluene even with respect to those obtained for individual free bases (9.3-10.0 ns). This lifetime shortening does not significantly depend on the mutual spatial arrangement of the triad subunits (Figure

1) but becomes essential upon the solvent polarity increase. Thus, the simultaneous decrease of the extra-ligand P fluorescence intensity and lifetime shortening reveal that in the triad the non-radiative deactivation of its S_1-state takes place.

THEORETICAL ANALYSIS

For the triads, the dynamics of the excited states $1 = \mathrm{ZnPD}^* - \mathrm{H_2P}$, $2 = \mathrm{ZnPD}^+ - \mathrm{H_2P}^-$, and $3 = \mathrm{ZnPD} - \mathrm{H_2P}^*$ is described by the equation of motion for the relevant reduced density matrix [5,6] with neglecting of the vibrational substructure of the electronic states [7]

$$\begin{aligned}\frac{\partial}{\partial t}\sigma_{\kappa\lambda} = &-\frac{i}{\hbar}\left([H_S,\sigma]\right)_{\kappa\lambda} + 2\delta_{\kappa\lambda}\left\{\Gamma_{\mu\kappa}\left[n(\omega_{\mu\kappa})+1\right]+\Gamma_{\kappa\mu}n(\omega_{\kappa\mu})\right\}\sigma_{\mu\mu}\\ &-\Sigma_\mu\left\{\Gamma_{\mu\kappa}\left[n(\omega_{\mu\kappa})+1\right]+\Gamma_{\kappa\mu}n(\omega_{k\mu})+\Gamma_{\mu\lambda}\left[n(\omega_{\mu\lambda})+1\right]+\Gamma_{\lambda\mu}n(\omega_{\lambda\mu})\right\}\sigma_{\kappa\lambda}\\ &+\left\{\Gamma_{\lambda\kappa}\left[2n(\omega_{\lambda\kappa})+1\right]+\Gamma_{\kappa\lambda}\left[2n(\omega_{\kappa\lambda})+1\right]\right\}\sigma_{\lambda\kappa}.\end{aligned}$$

Here the triad Hamiltonian H_S includes the energies E_λ of the corresponding states and couplings between them, $n(\omega) = \left[\exp(\hbar\omega / k_B T) - 1\right]^{-1}$ denotes Bose-Einstein distribution, $\Gamma_{\kappa\lambda}$ the damping constant, and $\kappa, \lambda, \mu = 1,2,3$. The energies E_1=2.1 eV and E_3=1.91 eV are taken from [4]. The energy of state 2 depending on the solvent polarity can be calculated using so-called Weller's formula [8]

$$E_2(\varepsilon) = E_2(\varepsilon_t) + \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_t}\right)\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}}\right).$$

In our case the solvent mixture consists of toluene (the basic component, a static dielectric constant ε_t=2.38) and a small concentration c of acetone (the static dielectric constant ε_a=10). In accordance with [9] the effective dielectric constant of the mixture of solvents reads:

$$\varepsilon = \varepsilon_l + c\,\frac{3(\varepsilon_a - \varepsilon_l)\varepsilon_l}{\varepsilon_a + 2\varepsilon_l}.$$

For each parameter set we calculate the relevant reduced density matrix $\sigma_{\kappa\lambda}(t)$ numerically. At $t = \infty$ the diagonal elements of density matrix arrive to the quasiequilibrium values. These values correspond to the fluorescence intensity of the triad subunits as presented in Figure 2.

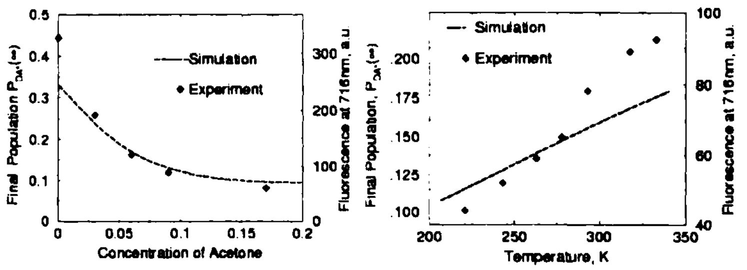

FIGURE 2. Solvent (left, 293 K) and temperature (right) induced fluorescence quenching for the extra-ligand P, $C_{acetone}$=7% vol.

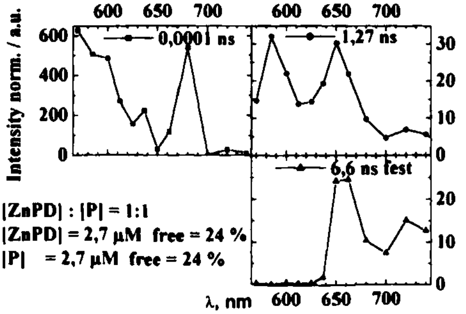

FIGURE 3. Amplitude spectra of time components of the fluorescence decay (λ_{ex}=545 nm) for triad ZnPD-P (toluene, 293 K).

CONCLUSIONS

It has been shown that calculated dependencies of the extra-ligand P (acceptor) population in the S_1-state reflecting the intensity of its fluorescence on temperature and solvent polarity are in a reasonable accordance with experimental data. On the base of the performed experimental and theoretical investigations one concludes that the charge transfer processes induce the quenching of the singlet locally excited states of the triad. The dimer S_1-state quenching is caused by the electron transfer from Zn-porphyrin dimer to the extra-ligand. The quenching of the extra-ligand S_1-state originates from the hole transfer to the Zn-porphyrin dimer from the extra-ligand being weakened by thermal exchange of the close lying charge transfer and extra-ligand locally excited S_1-states.

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