

**OPTICAL PROPERTIES AND CHARGE
TRANSPORT IN NANOSCALE
MULTIPORPHYRIN SELF-ASSEMBLED ARRAYS**

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The preparation of multimolecular model assemblies with functional properties to mimic primary light-induced events in photosynthesis or to gain some insight into the principal possibilities of molecular electronics is the attractive tendency of supramolecular photochemistry.

In this report, we will discuss the optical properties and electronic excitation energy relaxation dynamics (energy migration, EM, and electron transfer, ET) in nanoscale self-assembled triads prepared via non-covalent binding interactions of dipyrridyl substituted tetrapyrrole extra-ligands (porphyrin, chlorin, tetrahydroporphyrin) with Zn-octaethylporphyrin dimers which, in its turn, are covalently linked to electron acceptors, quinone or pyromellitimide (Fig. 1), in solutions and polymeric (PMMA) films. Using static, time-resolved picosecond fluorescent (experimental response $\Delta_{1/2} \approx 30$ ps) and femtosecond pump-probe ($\Delta_{1/2} \approx 280$ fs) set-up, the dynamics of non-radiative relaxation has been studied in the triads with controllable geometry as a function of redox and photophysical properties of interacting subunits as well on the solvent polarity and temperature.

It has been shown that the strong quenching of the dimer fluorescence is due to energy and sequential electron transfer (ET) processes to the extra-ligand (~ 0.9 ps, Fig. 2), which are faster than a slower ET (34-135 ps) from the dimer to covalently linked acceptors, A, in toluene at 293 K. The extra-ligand S_1 -state decay ($\tau_s=940$ -2670 ps with respect to $\tau_{s0}=6.6$ -7.7 ns) is governed by competing processes: a bridge (dimer) mediated long-range ($r_{DA}=18$ -24 Å) superexchange ET to an acceptor, and photoinduced hole transfer from the excited extra-ligand to the dimer followed by possible superexchange ET steps to low-lying CT states of the triads. Being once created, CT state ($\text{Lig}^- \dots \text{Dimer}^+ \dots \text{A}$) may be deactivated via the following one-electron transfer reaction, ($\text{Lig}^- \dots \text{Dimer}^+ \dots \text{A}$) \rightarrow ($\text{Lig} \dots \text{Dimer}^+ \dots \text{A}^-$) or a two-electron ET process seems to be taken into account ($\text{Lig}^- \dots \text{Dimer}^+ \dots \text{A}$) \rightarrow ($\text{Lig}^+ \dots \text{Dimer} \dots \text{A}^-$).

The generalized Haken-Strobl-Reineker method has been applied to the calculation of the excited states dynamics for electrons and excitons in the triads with taking into account some important energetic parameters for the systems under study evaluated from the obtained experimental data. The coherent energy transport is described by the transition matrix elements between interacting subunits in the porphyrin triads. Calculated dependencies of the 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 (Fig. 3). In addition, the theoretical analysis predicts that in the presence of polar admixture (5-15 vol% of acetone) the increase of temperature induces the crossover from the coherent to the incoherent type of the quantum particle transport.

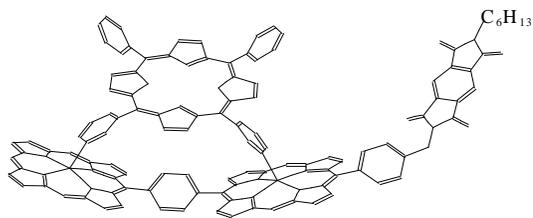


Fig. 1. Mutual arrangement of the interacting subunits in the triad $(\text{ZnOEP})_2\text{Ph-Pim}\otimes\text{H}_2\text{P}(\text{m}^\wedge\text{Pyr})_2-(\text{iso-PrPh})_2$ with electron acceptor, pyromellitimide (HyperChem, release 4, semiempirical method PM3).

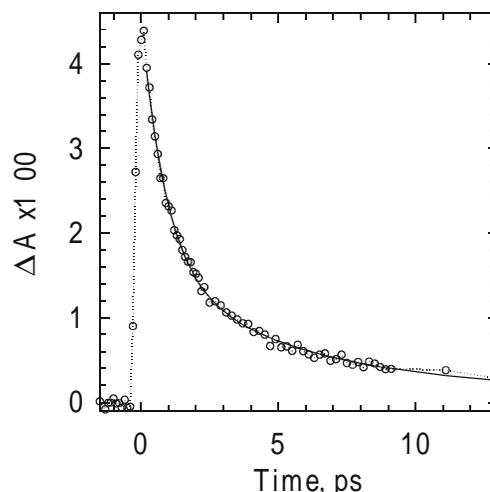


Fig. 2. Time evolution of the transient absorbance for the triad $(\text{ZnOEP})_2\text{Ph-Pim}\otimes\text{H}_2\text{P}(\text{m}^\wedge\text{Pyr})_2-(\text{iso-PrPh})_2$ in toluene at 293 K ($\lambda_{\text{pump}}=555$ nm, $\lambda_{\text{probe}}=515$ nm). Two-exponential fit: $I(t) = A_1 \cdot \exp(-t) + A_2 \cdot \exp(-t/\tau_2) + \delta(t)$ with $\tau_1=0.9$ ps ($A_1=0.029$) and $\tau_2=5.4$ ps ($A_2=0.015$).

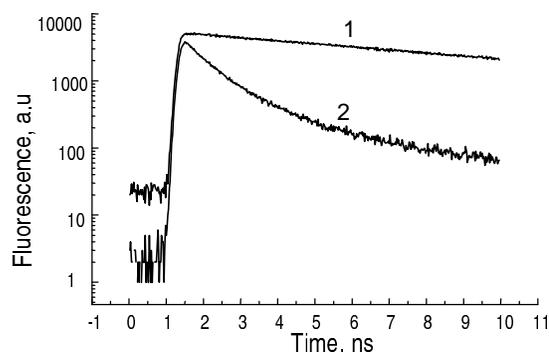


Fig. 3. Fluorescence decay profiles for a pure extra-ligand $\text{H}_2\text{Chl}(\text{m-Pyr})_2$ and the triad $(\text{ZnOEP})_2\text{Ph-Q}\otimes\text{H}_2\text{Chl}(\text{m-Pyr})_2$, (toluene, 293 K, $\lambda_{\text{exc}}=545$ nm, $\lambda_{\text{rec}}=650$ nm).

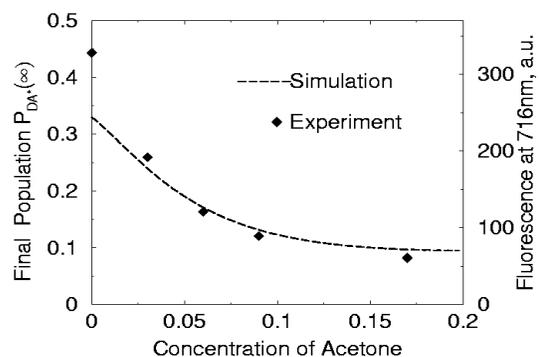


Fig. 3. Experimental (black dots) and simulated (dashed lines) dependencies on the solvent polarity for the extra-ligand fluorescence in the triad $(\text{ZnOEP})_2\text{Ph}\otimes\text{H}_2\text{P}(\text{m}^\wedge\text{Pyr})_2-(\text{iso-PrPh})_2$.