PHOTOINDUCED CHARGE TRANSFER VIA "SUPEREXCHANGE" MECHANISM IN PORPHYRIN TRIADS WITH ELECTRON ACCEPTORS

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Molecular self-assembly, namely the spontaneous or driven association of molecules, is the basis of many successful strategies to produce nano- and mesoscopic structures that adopt thermodynamic minima. In this respect, the interest in nanostructures based on tetrapyrrolic macrocycles may be explained by two reasons: i) they are good models for the mimicking the primary photo-events *in vivo,* and ii) they are used as promising building blocks for advanced multifunctional nanocomposites with potential applications in nanotechnology and nanoelectronics.

Here, we discuss pathways and mechanisms of energy relaxation in nano-composites based on self-assembled porphyrin triads and covalently linked electron acceptors (quinone, Q or pyromellitimide, Pim, Fig. 1).
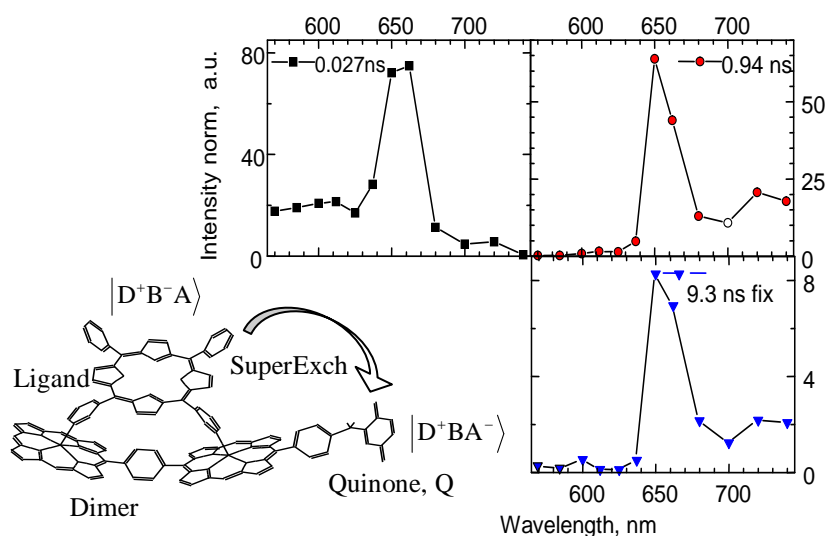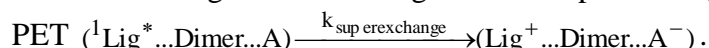

Fig. 1 Chemical structure of the triad $(ZnOEP)_2Ph$-$Q \otimes H_2P(m\char94 Pyr)_2$-$(iso$-$PrPh)_2$ with Q and decay-associated spectra (toluene, 293 K, λ_{ex} = 546 nm) for this triad derived from global analysis of 12 TCSPC time-resolved fluorescence measurements. Arrow denotes a bridge-mediated long-distance superexchange

$$PET\ (^1Lig^*...Dimer...A) \xrightarrow{k_{superexchange}} (Lig^+...Dimer...A^-).$$

Main results have been obtained using laser picosecond fluorometry (Global analysis fit) and femtosecond transient spectroscopy. Experimental set-up, preparation strategy, structural properties and spectral-kinetic characteristics of

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these complexes have been described in details earlier [1]. It was shown also that in self-assembled porphyrin triads the non-radiative relaxation of the porphyrin chemical dimer $(ZnOEP)_2Ph$ is governed by two main processes: i) Foerster resonance energy transfer (FRET) dimer→ligand and ii) the photoinduced electron transfer (PET) from the dimer to ligand [1]. The existence of an additional electron acceptor of non-porphyrin nature (Q or Pim) covalently linked to the dimer $(ZnOEP)_2Ph$ leads to the more complex dynamics of the excitation energy relaxation in these triads.

The main feature observed upon triad formation with covalently linked acceptors is that the fluorescence of complexed ligands is essentially quenched compared to the same ligands in the corresponding triads without Q or Pim in toluene at 293 K. The decrease of φ_F values is more pronounced for the Q-containing triad as compared to the Pim-containing one (Table 1).

Table 1.

Measured and estimated parameters for superexchange PET in self-assembled triads of the same geometry with electron acceptors (A) Pim or Q and various extra-ligands (toluene, 293 K)

Triad Composition Ligand⊗Dimer-A	r_{DB} nm	r_{DA} nm	$E(D^+B^-A)$ eV	τ_{S0}^D ns	τ_S^D ns	$k_{PET}/10^8$ s^{-1}
$H_2P(m{^\wedge}Pyr)_2 \otimes (ZnOEP)_2Ph$-Pim	0.91	2.42	3.08	7.7	2.67	2.5
$H_2P(m{^\wedge}Pyr)_2 \otimes (ZnOEP)_2Ph$-Q	0.91	2.08	3.08	7.7	0.95	9.2
$H_2Chl(m{^\wedge}Pyr)_2 \otimes (ZnOEP)_2Ph$-Q	0.82	1.80	3.05	6.6	1.24	6.5
$H_2THP(m{^\wedge}Pyr)_2 \otimes (ZnOEP)_2Ph$-Q	0.82	1.80	3.07	4.3	1.04	7.3

Notes: The symbol $\otimes$ shows what interacting subunits are bound together; r_{DB}, r_{DA} are inter-center distances; $E(D^+B^-A) = e(E_D^{OX} - E_A^{RED}) + \Delta G_S$ is the energy of a bridge (dimer) level; τ_{S0}^D and τ_S^D are fluorescence decays for ligands in triads without and with A's; $k_{PET} = (\tau_S^D)^{-1} - (\tau_{S0}^D)^{-1}$ is the rate constant of a bridge-mediated long-distance superexchange PET.

The reason of ligands fluorescence quenching in this case is explained by the fact that the dimer $(ZnOEP)_2Ph$ plays the role of the bridge which does not directly participate in the PET process but lowers the barrier for its realization. Distant donor, *D* and acceptor, *A* can exchange their charges through the bridge, that is a high-lying "spectator" state $|D^+B^-A\rangle$ (see Fig. 1) mediates the electron transfer from a donor state $|D^*BA\rangle$ to a charge transfer state $|D^+BA^-\rangle$.

1. *Zenkevich E.I., von Borczyskowski Ch.W.* Formation Principles and Excited States Relaxation in Self-Assembled Complexes: Multiporphyrin Arrays and "Semiconductor CdSe/ZnS Quantum Dot-Porphyrin" Nanocomposites. /Handbook of Porphyrin Science with Application to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine. Volume 22 – Biophysical and Physicochemical Studies of Tetrapyrroles / edited by K. Kadish, K.M. Smith, R. Guilard. Singapore: World Scientific Publishing Co. Pte. Ltd. 2012. Chapter 104. P. 68–159.