

## The Effects of Polarity and Ligands on Electron Transfer in Porphyrin-Fullerene Dyad: A Quantitative Study

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At close proximity of porphyrin and fullerene the electronic interactions between the two chromophores result in appearance of a weak absorption band in the near infrared (NIR) part of the spectrum which is commonly called charge transfer (CT) band. The same interaction manifests itself in relaxation of the excited states by a new emission band in the NIR part of the spectrum associated with formation of an emissive intermediate between the locally excited and the charge separated (CS) states. This new state is usually called intramolecular exciplex. The shapes of both new bands, NIR absorption and emission, can be analyzed in frame of the Marcus semi-quantum electron transfer theory [1]. The theory operates with four quantities which can be obtained from the band analysis: the exciplex free energy,  $\Delta G_{ex}$ , the solvent reorganization energy,  $E_s$ , the energy of the fundamental vibrational mode,  $E_v$ , and the electronic vibrational coupling,  $S$ . Two values,  $\Delta G_{ex}$  and  $E_s$ , are sensitive to the dyad environment, e.g. solvent polarity, and two others,  $E_v$  and  $S$ , are properties of the molecule and virtually independent of the solvent polarity.

Although the exciplex is an important intermediate state in the excitation relaxation process, the goal of the donor-acceptor dyad design is the efficient formation of the complete charge separated state or the radical ion pair. For most porphyrin-fullerene dyads the complete CS can be achieved in polar media, but in non-polar environment the energy of the exciplex is lower than that of the complete CS state and the exciplex is observed as the longest lived state after the excitation. In media with moderate polarity the energy balance between the exciplex and the charge separated state controls the relaxation pathway and the efficiency of the complete CS. This equilibrium is difficult to study experimentally since the transient spectra of the exciplex and CS state are rather similar, and the number of experimentally available lifetimes is not sufficient to evaluate the intrinsic rate constants for all reactions taking place in this complex case. On the other hand, the semi-quantum ET theory can also predict the reaction rate constants using the same four quantities,  $\Delta G_{ex}$ ,  $E_s$ ,  $E_v$  and  $S$ , plus electronic coupling between the reactant and product,  $V$ . Furthermore, the polarity dependences of  $\Delta G_{ex}$  and  $E_s$  for the exciplex and CS state can be coupled by introducing the degree of charge separation of the exciplex relative to the complete CS state,  $\gamma$ . Using this approach we constructed a model which predicts polarity dependences of the intrinsic reaction rate constants for transitions from the exciplex to the ground state and from the CS state to the ground state. The model was used to fit the polarity dependence of experimentally observed lifetimes. The results of the fit are presented in Figure 1, which also shows the calculated dependences of the intrinsic time constants for the exciplex and CS state.

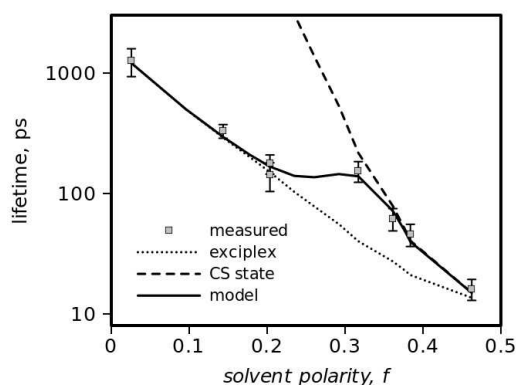


Figure 1. Solvent polarity ( $f$ ) dependences of the measured relaxation time constant (squares with error bars), modeled relaxation time constant (solid line), and intrinsic lifetimes of the exciplex (dotted line) and CS state (dashed line) [2].

The experimental lifetimes presented in Figure 1 were obtained from both emission decay measurements in non-polar solvents and pump-probe measurements in all solvents. In the latter case the excitation wavelength was 780 nm, which populates the intramolecular exciplex directly, and thus reduces the number of intermediate states involved in the relaxation process. The model best fit is achieved for the degree of charge transfer at the exciplex  $\gamma = 0.55$ . The electronic coupling is 0.012 eV for the CS state recombination, and 0.24 eV for the exciplex. The latter is a surprisingly high value, though it agrees with the relatively strong intensity of the CT absorption band.

Solvent polarity is not the only factor affecting the energetics of both the exciplex and the CS state. For example zinc porphyrin can ligate an anion, such as  $\text{Cl}^-$ , which lowers gradually the energy of CS state and reduces also the exciplex energy. As the result, the CT band shifts to the red [3], the conversion rate from the exciplex to the CS state increases due to the increased driving force, and the charge recombination rate increases by few times confirming that the charge recombination in porphyrin-fullerene dyads takes place in the inverted Marcus regime [4].

## References

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