

## How to Increase the Efficiency of the Photoinduced Electron Transfer in Porphyrin-Fullerene Compounds

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We have recently studied intramolecular photoinduced electron transfer reactions in several types of porphyrin-fullerene dyads, PF, where the fullerene (F) unit is covalently linked to one of the porphyrin (P) phenyls by using different linkers yielding compounds with different donor-acceptor distances and conformers (1, 2, 3,...).

An universal mechanism (Fig. 1), independent of detailed structures of the used linker, was found to be applicable for all the studied donor-acceptor pairs. An essential transient component was an intramolecular exciplex, (PF)\*, which was observed experimentally by applying both the femto second transient absorption pump-probe and the fluorescence up-conversion methods. In some cases the exciplex was found also by using steady state fluorescence method.

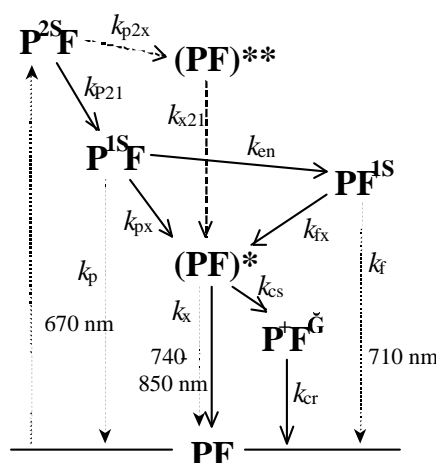


Figure 1

Evidently the excimer formation depended on the distance between the donor and acceptor and on their mutual configuration. This conjured up a vision of an ideal donor-acceptor pair, where an optimal geometry and distance could be achieved. The first example is a dyad (DHI), where the fullerene (F) unit is covalently linked with two linkers to the opposite phenyls of the porphyrin (P).

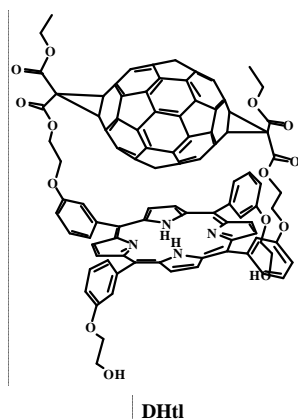


Figure 2

Practically the same mechanism as presented in Fig. 1, was applicable for this compound as was for the compounds studied earlier. The fluorescence lifetime, i.e. the exciplex formation took place in 170 ps. The lifetime of the exciplex was in non polar toluene, where the charge transfer (CT) state formation is prevented, 3 ns, but in polar benzonitrile, where it yielded the CT state, only 10 ps. Thus, the exciplex formation promotes the formation of the CT state.

The dyad presented in Fig. 3, because the polar tails linked to the phenyl rings, can form good quality Langmuir-Blodgett films. In LB-film the the exciplex emission is less intense than in toluene, as shown in Fig. 4. This is an indication of the fast and efficient CT state formation, which was proved by photo-voltage measurements demonstrating the vectorial electron transfer process.

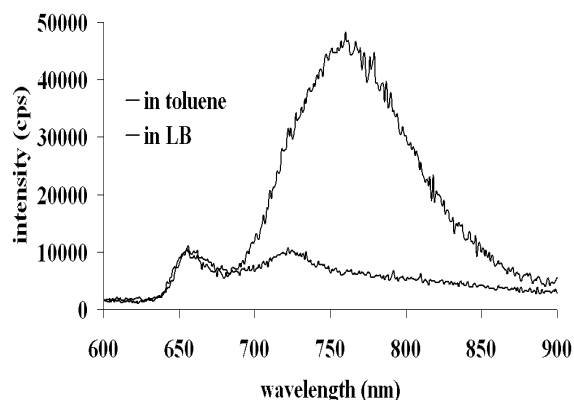


Figure 3.

A full analysis of the kinetics in solutions and the suitability of the studied compounds for building of photochemical devices will be presented.

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