

Thesis:

Photoinduced Electron Transfer in Dyads and Triads of Porphyrins, Phthalocyanines and Fullerenes

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Abstract

Developing environmentally sustainable solutions to the increasing energy demand of the world is one of the most important goals of research. The ultimate renewable energy source is the sun, which emits more than enough (120 000 TW) energy onto Earth to cover the current energy need (13 TW) completely. The reason why solar energy is utilized to a much lower degree (2 GW) than possible is the lack of inexpensive and efficient technology for the purpose.

Mimicking nature's complex photosynthesis system in detail is not feasible, but a simpler approach needs to be taken. The essential tasks of the system are light harvesting and electron transfer. Thus the simplest mimic is a dyad molecule consisting of an electron donor (D) and an electron acceptor (A) with at least one of the moieties being able to absorb the light.

In photosynthetic reaction centres the chromophores are held together in a membrane by a protein. In the artificial systems the close contact between the electron donor and acceptor is usually achieved with a covalent linker joining the chromophores. A single linker can either be rigid, keeping the donor and acceptor in fixed orientation, or flexible, allowing the chromophores some freedom to move with respect to each other. In either case an advantageous symmetric structure with face-to-face orientation can be difficult to obtain. To realize a more stable, symmetrical dyad structure, two-linker strategies have been developed. Such dyads have also been modified to form solid films in which the molecules are oriented controllably. This is of special interest for application in photovoltaic devices such as solar cells.

In this study both dyad and triad structures were studied. Porphyrins and phthalocyanines were selected as the electron donor part of the molecules. Fullerene was used as the acceptor in all the compounds. The two-linker approach was followed in both the dyad and triad molecules. Focus of the study was on detailed determination of the reaction schemes for the compounds after photoexcitation using mainly time-resolved spectroscopic methods. The desired efficient ET was achieved in all of the studied compounds and the increase in the CS distance in the triads compared to corresponding dyads resulted in a longer-living CS state. The phthalocyanine-fullerene dyads were found to behave similarly to the previously studied porphyrin- and phytychlorin-fullerene dyads with comparable organization of the donor and acceptor, i.e. the ET reaction proceeds via an intramolecular exciplex. The triad structures were also studied in solid state examining specially the possibility of using the compounds in photovoltaic applications. Enhancement of both photovoltage and photocurrent generation was observed, compared to the corresponding porphyrin-fullerene dyad samples, as was expected on the basis of the study of the triads in solutions.

Photoinduced electron transfer of several dyads and triads, consisting of porphyrins or phthalocyanines as electron donors and fullerene as acceptor, was studied. Efficient electron transfer was observed in the studied compounds due to two important approaches in the design of the molecular structure: (i) appropriate selection of the donor and acceptor moieties and (ii) controlled orientation and distance of the moieties achieved with two covalent linkers connecting the donor and acceptor.

Mainly spectroscopic methods were used to determine the reaction schemes of the photo-induced reactions. Time-resolved spectroscopy revealed the transient states of electron transfer and it was confirmed that the intermediate exciplex state precedes the charge-separated state in all the studied compounds. Rate constants of the transitions and energies of the states were evaluated in both polar and non-polar solvents.

To test the possibility to use the studied compounds in solid state photovoltaic devices, thin films with porphyrin-porphyrin-fullerene triad structures were attached on glass substrates covered with a transparent indium tin oxide layer. The triad structures were obtained by building successive self-assembled monolayers (SAM) of porphyrin and porphyrin-fullerene dyad on top of each other. Because of the presence of the secondary electron donor, the triad structures were found to enhance both photocurrent and photovoltage generation compared to the corresponding porphyrin-fullerene dyad SAM.

The following conclusions can be drawn based on the reported results:

1. Photoinduced electron transfer of the various phthalocyanine-fullerene dyad and porphyrin-porphyrin-fullerene triad compounds studied was found to be very efficient even in a non-polar solvent, such as toluene. The rapid electron transfer reactions observed in all the compounds are consistent with the symmetric, double-linker design strategy of the molecular structures.
2. Attaching a side porphyrin unit to the previously studied porphyrin-fullerene dyad to form a triad molecule resulted in the expected prolongation of the lifetime of the charge separated state.
3. The inner porphyrin and fullerene of the studied triads were found to act as a unit behaving in the same manner as in the corresponding dyad molecules, e.g. forming an exciplex with distinct emission in non-polar solvent.
4. Consistently with the studies of the triads in solutions, the photovoltaic behaviour of solid monolayer film samples of Zn porphyrin-free-base porphyrin-fullerene triads is improved considerably compared to the corresponding dyad films due to the higher absorbance and the longer charge separation distance.
5. The phthalocyanine-fullerene dyads follow the same general reaction scheme of photo-induced electron transfer as the previously studied porphyrin- and phytychlorinfullerene dyads. The scheme includes an intermediate exciplex state preceding the charge-separated state.
6. Because of the rapid electron transfer forming the charge-separated state in the phthalocyanine-fullerene dyads, the characteristic exciplex emission is quenched efficiently and observed only weakly in the steady state emission spectra.