Dynamics of Photoinduced Electron Transfer of Porphyrin-Fullerene Dyads

Nikolai V. Tkachenko, Visa Vehmanen, Tero J. Kesti,
Alexander Efimov, Hiroshi Imahori,* Shunichi
Fukuzumi,** Helge. Lemmetyinen

Institute of Materials Chemistry, Tampere University of
Technology, P.O. Box 541, FIN-33101 Tampere, Finland
* Department of Molecular Engineering, Graduate School
of Engineering, Kyoto University, PRESTO, 34-4,
Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103,
Japan
** Department of Material and Life Science, Graduate
School of Engineering, Osaka University, CREST, Suita,
Osaka 565-0871, Japan

Porphyrin-fullerene (PF) donor-acceptor systems have gained a considerable attention during past decade. Their distinguishing features are high quantum yield of the electron transfer, fast charge separation (CS) and slow charge recombination. It was also recognized that the complete CS state of PF dyads is achieved via an additional intermediate state, which was identified as an exciplex (or emitting CS state). The focus of this presentation will be elucidation of the nature and role of this intermediate state.

Typical time constants of CS of the PF dyads with a short and moderate distance between donor and acceptor ($R_{cc} \leq 1.2$ nm) lie in sib-picosecond to tens of picosecond time interval. Commonly used techniques to investigate such fast processes are pump-probe transient absorption and emission up-conversion methods. Analysis of the measurements provides one with the spectra and lifetimes of the transient states, which can be used to build up a kinetic model of the photoreactions (1).

An exciplex transient state can also be observed as weak absorption and emission bands in the near infrared part of the spectrum. Then, the spectra can be analyzed in the framework of the Marcus ET theory and energetic parameters of corresponding transition, e.g. Gibbs and reorganization energies, can be evaluated (2). Thus, both energetic and dynamic parameters characterizing behavior of the PF systems can be obtained.

In order to compare the electron transfer properties of different DA systems in different environments a common reaction scheme can be proposed (1). The scheme includes singlet excited states of both chromophores, i.e. of the porphyrin and fullerene, an exciplex and a complete CS state. The appearance of the intermediate states and the direction of the reactions flow depend on the compound and environment. Compounds with a short separation between the donor and acceptor are usually characterized by a relatively low energy of the exciplex, e.g. 1.75 eV for a compact PF dyad (3). For this reason the complete CS state is not observed in non-polar solvents, but the exciplex emission can be clearly seen using an infrared sensitive fluorimeter. A relatively high electronic coupling of the locally excited and exciplex states (~0.03 eV) is another characteristic feature of these dyads.

Increase in the distance between the donor and acceptor results in a lower coupling and increases the energy of the exciplex, making formation of the complete charge separated state possible also in non-polar solvents (4).

A small variation in one of the energetic parameters of PF dyad can be used to probe the scheme and to gather missing information. For example, substitution of the hydroxyl group at poison 13^1 of the phytochlorin macro-cycle does not change the general behavior of the phytochlorin-fullerene dyad. The variations in reaction rates can be associated with the change in phytochlorin oxidation potential, which allowed us to estimate reorganization energies for the exciplex and complete CS states (4).

A high rate of the primary steps of the excited state relaxation (e.g. exciplex formation and intra-molecular energy transfer) makes possible for the reactions to occur from the second excited state of the porphyrin chromophore. This relaxation mechanism was proposed for phytochlorin-fullerene dyads characterized by a close proximity of the donor and acceptor. Recently, subpicosecond studies of porphyrin-[70]fullerene dyad with moderate DA distance ($R_{cc} \sim 1$ nm) have demonstrated that the intramolecular energy transfer and/or exciplex formation may compete successfully with internal conversion of the locally excited second singlet state of porphyrin chromophore. This results in formation of the exciplex in a few hundreds of femtosecond, and, potentially, can be used to increase the rate of complete CS state formation.

REFERENCES

1. T. J. Kesti, N. V. Tkachenko, V. Vehmanen, H. Yamada, H. Imahori, S. Fukuzumi, H. Lemmetyinen, J. Am. Chem. Soc., **124**, 8067 (2002).
2. H. Imahori, N. V. Tkachenko, V. Vehmanen, K. Tamaki, H. Lemmetyinen, Y. Sakata, S. Fukuzumi, *J.* Phys. Chem. A, **105**, 1750 (2001).
3. V. Vehmanen, N. V. Tkachenko, H. Imahori, S. Fukuzumi, H. Lemmetyinen, Spectrochim. Acta A, **51**, 2229 (2001).
4. V. Vehmanen, N. V. Tkachenko, A. Efimov, P. Damlin, A. Ivaska, H. Lemmetyinen, J. Phys. Chem. A, **106**, 8029 (2002).