

# Photoinduced Stepwise Charge Separation and Charge Recombination in Porphyrin-Fullerene Linked Triads and Tetrads

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Investigations of photoinduced electron transfer (ET) in donor-acceptor linked molecules have attracted enormous interest, motivated by desires to address basic mechanistic problems on ET chemistry and biology as well as to develop artificial photosynthetic systems for light energy conversion. In particular, porphyrin-fullerene linked systems have revealed the occurrence of long-lived charge separation (CS) with a high quantum yield due to the small reorganization energies of porphyrins and fullerenes. Such a long-lived charge-separated state is expected to offer an excellent experimental opportunity for examining the charge recombination pathways. In this talk we present synthesis and photophysical properties of novel porphyrin-fullerene linked triads and tetrads.

*Meso-meso*-linked porphyrin dimer [(ZnP)<sub>2</sub>] as a light-harvesting chromophore has been incorporated into a photosynthetic multistep electron transfer model including ferrocene (Fc) as an electron donor and fullerene (C<sub>60</sub>) as an electron acceptor to construct the ferrocene-*meso,meso*-linked porphyrin dimer-fullerene system (Fc-(ZnP)<sub>2</sub>-C<sub>60</sub>). Photoirradiation of Fc-(ZnP)<sub>2</sub>-C<sub>60</sub> results in photoinduced electron transfer from the singlet excited state of the porphyrin dimer [<sup>1</sup>(ZnP)<sub>2</sub>\*] to the C<sub>60</sub> moiety to produce the porphyrin dimer radical cation-C<sub>60</sub> radical anion pair, Fc-(ZnP)<sub>2</sub><sup>•+</sup>-C<sub>60</sub><sup>•-</sup>. In competition with the back electron transfer from C<sub>60</sub><sup>•-</sup> to (ZnP)<sub>2</sub><sup>•+</sup> to the ground state, an electron transfer from Fc to (ZnP)<sub>2</sub><sup>•+</sup> occurs to give the final charge-separated (CS) state, i.e., Fc<sup>+</sup>-(ZnP)<sub>2</sub>-C<sub>60</sub><sup>•-</sup>, which is detected as the transient absorption spectra by the laser flash photolysis. The quantum yield of formation of the final CS state is determined as 0.80 in benzonitrile. The final CS state decays obeying first-order kinetics with a lifetime of 19 μs in benzonitrile at 295 K. The activation energy for the charge-recombination (CR) process is determined as 0.15 eV in benzonitrile which is much larger than the value expected from the direct CR process to the ground state. This value is rather comparable to the energy difference between the initial CS state (Fc-(ZnP)<sub>2</sub><sup>•+</sup>-C<sub>60</sub><sup>•-</sup>) and the final CS state (Fc<sup>+</sup>-(ZnP)<sub>2</sub>-C<sub>60</sub><sup>•-</sup>). This indicates that the back electron transfer to the ground state occurs via the reversed stepwise processes, i.e., a rate-limiting electron transfer from (ZnP)<sub>2</sub> to Fc<sup>+</sup> to give the initial CS state (Fc-(ZnP)<sub>2</sub><sup>•+</sup>-C<sub>60</sub><sup>•-</sup>), followed by a fast electron

transfer from C<sub>60</sub><sup>•-</sup> to (ZnP)<sub>2</sub><sup>•+</sup> to regenerate the ground state, Fc-(ZnP)<sub>2</sub>-C<sub>60</sub>. This is in sharp contrast with the extremely slow direct CR process of bacteriochlorophyll dimer radical cation-quinone radical anion pair in bacterial reaction centers.

A homologous series of zincporphyrin (ZnP)-pyromellitimide (Im)-C<sub>60</sub> linked triads where the pyromellitimide (Im) moiety is incorporated as an intermediate acceptor between the above two chromophores with a linkage of different spacers, ZnP-Im-CH<sub>2</sub>-C<sub>60</sub>, ZnP-Im-C<sub>60</sub> and ZnP-CH<sub>2</sub>-Im-C<sub>60</sub> as well as the reference dyads (ZnP-Im-CH<sub>2</sub>-ref, ZnP-Im-ref and ZnP-CH<sub>2</sub>-Im-ref) have been prepared to investigate linkage dependence of photoinduced electron transfer (ET) and back ET to the ground state in the triads. Time-resolved transient absorption spectra of the triads measured by picosecond laser photolysis as well as the fluorescence lifetimes in THF reveal the occurrence of photoinduced ET from the singlet excited state of the ZnP to the Im moiety to give the initial charge-separated state, i.e., the zincporphyrin radical cation (ZnP<sup>•+</sup>)-imide radical anion (Im<sup>•-</sup>) pair, followed by a charge shift (CSH) to produce the final charge-separated state, the ZnP<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> pair. The transient absorption spectra of the final charge-separated state, the ZnP<sup>•+</sup>-C<sub>60</sub><sup>•-</sup> pair have also been measured by nanosecond laser photolysis. It has been found that the rate constant of charge recombination (CR) of ZnP<sup>•+</sup>-Im-C<sub>60</sub><sup>•-</sup> is temperature independent, but that the CR rate constants of ZnP<sup>•+</sup>-Im-CH<sub>2</sub>-C<sub>60</sub><sup>•-</sup> exhibit an Arrhenius-like temperature dependence with an activation energy of 0.13 eV which corresponds to the energy difference between ZnP<sup>•+</sup>-Im<sup>•-</sup>-CH<sub>2</sub>-C<sub>60</sub> and ZnP<sup>•+</sup>-Im-CH<sub>2</sub>-C<sub>60</sub><sup>•-</sup>. This indicates that the relatively strong electronic coupling without methylene linkage in ZnP-Im-C<sub>60</sub> results in the preference of the tunneling superexchange ET over the sequential ET in the CR process which requires the thermal activation to reach the higher energy state (i.e., ZnP<sup>•+</sup>-Im<sup>•-</sup>-C<sub>60</sub>), whereas the sequential ET predominates in the triads with the methylene linkage.

## References

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