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)$_2$] 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$_{60}$) as an electron acceptor to construct the ferrocene-meso.meso-linked porphyrin dimer-fullerene system (Fc-(ZnP)$_2$-C$_{60}$). Photolysis of Fc-(ZnP)$_2$-C$_{60}$ results in photoinduced electron transfer from the singlet excited state of the porphyrin dimer $|{1}\text{(ZnP)}_2\rangle$ to the C$_{60}$ moiety to produce the porphyrin dimer radical cation-C$_{60}$ radical anion pair, Fc-(ZnP)$_2$'$^+$-C$_{60}$'$^-$.

In competition with the back electron transfer from C$_{60}$'$^-$ to (ZnP)$_2$$^+$ to the ground state, an electron transfer from Fc to (ZnP)$_2$$^+$ occurs to give the final charge-separated (CS) state, i.e., Fc$^+$-(ZnP)$_2$-C$_{60}$'$^-$, which is detected as the transient absorption spectra of the dimer radical cation-C$_{60}$ radical anion pair. This indicates that the relatively strong electronic coupling without methylene linkage in ZnP$^+$-Im$^-$-C$_{60}$' and ZnP$^+$-Im$^-$-CH$_2$-C$_{60}$' exhibits an Arrhenius-like temperature dependence with an activation energy of 0.13 eV which corresponds to the energy difference between ZnP$^+$-Im$^-$-CH$_2$-C$_{60}$' and ZnP$^+$-Im$^-$-CH$_2$-C$_{60}$'.

This indicates that the relatively strong electronic coupling without methylene linkage in ZnP$^+$-Im$^-$-C$_{60}$' whereas the sequential ET predominates in the triads with the methylene linkage.

References