

PHOTOINDUCED ELECTRON TRANSFER IN FERROCENE-PORPHYRIN OLIGOMER-FULLERENE SYSTEMS

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The three-dimensional structures of the antenna complex and the bacterial reaction center have provided an important structural basis for understanding the light-harvesting and subsequent primary charge separation processes in photosynthesis. Namely, visible light is harvested by the antenna complexes, including a wheel-like array of chlorophylls and carotenoid polyenes, and the collected energy is funneled efficiently into the chlorophyll dimer (i.e., special pair) in the reaction center. The subsequent multistep electron transfer (ET) event takes place unidirectionally along the well-arranged chromophores that are embedded in the transmembrane protein in the sequence of special pair, accessory chlorophyll, pheophytin, and quinones. The resulting second lasting, charge-separated state with nearly 100% quantum yield eventually leads to the conversion of light into usable chemical energy. The importance and complexity of energy transfer (EN) and ET reactions in photosynthesis have inspired many synthetic chemists to design and prepare donor-acceptor linked systems that mimic the EN or ET processes.

Since porphyrins and metalloporphyrins are essential components in photosynthetic electron transfer, they have been frequently employed in donor-acceptor linked molecules. Some of the covalently linked porphyrin-containing arrays, such as triads, tetrads, and pentads, have successfully exhibited efficient EN or ET processes like photosynthesis. However, the synthetic difficulty has precluded integration of two functions, light-harvesting and charge separation, into one artificial system. So far there have been few examples of donor-acceptor linked systems mimicking both EN and ET processes in photosynthesis.¹⁻³ As such, model system comparable to natural photosynthetic systems has yet to be reported.

Recently we have achieved the longest-lived charge-separated state in ferrocene-zincporphyrin-freebaseporphyrin-fullerene tetrad which reveals a cascade of photoinduced energy transfer and multistep electron transfer within a molecule in frozen media as well as in

solutions.⁴ The lifetime of the resulting charge-separated state (i.e., ferricenium ion-C₆₀ radical anion pair) in a frozen benzonitrile is as long as 0.38 s, which is comparable to that observed for the bacterial photosynthetic reaction center. However, the quantum yield for formation of the charge-separated state is rather low ($\Phi = 0.24$) in benzonitrile. Thus, the charge separation efficiency has remained to be further improved. Moreover, the light-harvesting efficiency should also be increased. In this context, *meso,meso*-porphyrin arrays are good candidates to improve the both values, since the length of *meso,meso*-porphyrin arrays can be extended easily by facile oligomerization of the porphyrin monomer. In addition, they can absorb visible light more widely than a linear combination of the corresponding porphyrin monomer due to the exciton coupling of the porphyrins, which is similar to molecular assemblies of chlorophylls in antenna complex. We have previously reported that incorporation of *meso,meso*-linked porphyrin dimer [(ZnP)₂] as an improved light-harvesting chromophore as compared to the monomer porphyrin into photosynthetic ET model to construct the ferrocene-*meso,meso*-linked porphyrin dimer-fullerene triad (**Fc-(ZnP)₂-C₆₀**) where the C₆₀ and the ferrocene (Fc) are tethered at both the ends of (ZnP)₂.⁵ The quantum yield of formation of the final CS state is indeed improved to 0.80 in PhCN. However, the final CS state decays obeying first-order kinetics with a lifetime of 19 μ s in benzonitrile at 298 K. The lifetime is far shorter than expected from the long edge-to-edge distance ($R_{ee}=38.6$ Å) as compared to the triad in the **Fc⁺-ZnP-C₆₀⁻** radical ion pair ($R_{ee}=30.3$ Å) which has a lifetime of up to 16 μ s.

We report herein incorporation of an additional porphyrin moiety to construct the ferrocene-*meso,meso*-linked porphyrin trimer-fullerene pentad (**Fc-(ZnP)₃-C₆₀**) where the C₆₀ and the ferrocene (Fc) are tethered at both the ends of (ZnP)₃ ($R_{ee}=46.9$ Å). The lifetime of the final CS state is expected to be prolonged without lowering the charge separation efficiency when a similar stepwise ET occurs in **Fc-(ZnP)₃-C₆₀**. In fact we have succeeded in achieving not only a high quantum yield for formation of a final CS state, but also the extremely long lifetime of the CS state. The ET dynamics of **Fc-(ZnP)₃-C₆₀** have been investigated in full detail by electron spin resonance spectroscopic method as well as time-resolved transient absorption spectroscopy and fluorescence lifetime measurements. The synthesis and photophysical properties of **Fc-(ZnP)₃-C₆₀** and the related systems will be presented.

References

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