

# Mimicking the Primary Events of Photosynthesis

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## 1. Introduction

Photosynthesis is the process by which plants and some types of bacteria convert light energy into chemical energy.[1] The photosynthetic reaction center consists of chromophore arrays, which upon interaction with a specific wavelength of light, become excited to their singlet excited state. The energy is then funneled to the reaction center by a singlet-singlet energy transfer mechanism, whereby the excited electron undergoes several subsequent electron transfer steps to generate a long-lived charge-separated state. The stored energy, in the form of the charge-separated state, is later converted to useful chemical energy.

In order to gain a greater understanding of these relatively complex photo-chemical processes many synthetic mimics have been prepared and studied.[2] Most of these systems consist of porphyrin derivatives linked with one or more energy and/or electron transfer entities. These different entities may be connected by covalent and/or supramolecular type linkages.

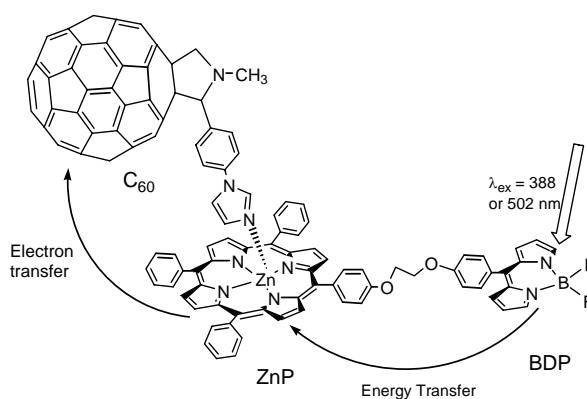
Here, we have synthesized a covalently linked dyad composed of a zinc porphyrin and boron dipyrin entities (ZnP-BDP). A supramolecular triad was then assembled by the addition of imidazole appended fulleropyrrolidine ( $C_{60}$ Im) which bound to the zinc atom at the center of the porphyrin macrocycle (Scheme 1). Upon selective excitation of the boron dipyrin entity of the triad ( $\lambda_{ex}=502$  nm), photo-induced energy transfer from the singlet excited state of boron dipyrin to the zinc porphyrin was observed. The singlet excited zinc porphyrin then undergoes electron transfer to the fullerene entity, thus producing a charge-separated species. This is the first reported example of a working model of the photosynthetic antenna-reaction center complex, constructed via self-assembled supramolecular methodology.

## 2. Discussion

The studied compounds were synthesized via procedures described in the paper discussing this project that has already been published.[3] The studied compounds (ZnP-BDP and  $C_{60}$ Im) were characterized by  $^1H$  NMR, UV-vis absorption spectroscopy, and ESI-MS. Energy transfer for the dyad (ZnP-BDP) was probed by steady-state and time resolved fluorescence spectroscopy. Upon excitation of the BDP entity of the dyad ( $\lambda_{ex}=502$  nm) the fluorescence emission of BDP was quenched and two new emission peaks were observed in the spectrum at 600 and 650 nm. These peaks correspond to the emission of zinc porphyrin. Time-resolved fluorescence also confirmed the occurrence of singlet-singlet energy transfer in the dyad. Upon laser excitation of the BDP entity of the dyad ( $\lambda_{ex}=388$  nm), the fluorescence emission was monitored on the picosecond time scale. Time profiles of the experiment show the decay of the BDP emission and the simultaneous enhancement of the ZnP emission. These results are in agreement with the steady-state fluorescence emission data. Energy transfer in the studied dyad was found to be an efficient process ( $k_{ENT}^{singlet} = 9.2 \times 10^9 s^{-1}$ ;  $\Phi_{ENT}^{singlet} = 0.83$ ).

Formation of the supramolecular triad (ZnP-BDP- $C_{60}$ Im) was monitored by UV-vis spectroscopy. Upon addition of  $C_{60}$ Im to a solution containing ZnP-BDP the Soret absorption band of the zinc porphyrin decreases in intensity and becomes shifted to a longer wavelength. This shift in the Soret band of the zinc porphyrin is a typical spectral feature of the zinc atom becoming a five coordinate species. Several isosbestic points were revealed which indicates that the metal binding is an equilibrium process. The UV-vis absorption data was analyzed via the Scatchard method to arrive at a binding constant for the supramolecular complex ( $K=16,500 M^{-1}$ ).[4]

Scheme 1



Electron transfer in the supramolecular triad was monitored by steady-state and time-resolved fluorescence, as well as transient absorption spectroscopy to characterize the excited state species. Upon excitation of the BDP entity of the triad ( $\lambda_{\text{ex}}=502$  nm) the steady-state fluorescence revealed quenching of both the BDP and ZnP emission. The BDP is quenched due to energy transfer to zinc porphyrin, while subsequent electron transfer to the fullerene causes the quenching of the ZnP emission. Time-resolved fluorescence decay profiles revealed accelerated decay of the zinc porphyrin emission in the triad versus pristine ZnP. This accelerated fluorescence emission decay is a result of electron transfer to the fullerene entity. The excited state species were characterized by transient absorption spectroscopy. Bands for triplet excited zinc porphyrin and fullerene were observed in the spectrum at 850 and 700 nm, respectively. Also, a broad band at 1000 nm was observed which is characteristic of  $\text{C}_{60}$  anion radical, thus indicating that electron transfer is occurring in the triad. This was found to be an efficient process in the triad ( $k_{\text{CS}}^{\text{singlet}} = 4.7 \times 10^9 \text{ s}^{-1}$ ;  $\Phi_{\text{CS}}^{\text{singlet}} = 0.9$ ).

### 3. Conclusions

The first example of a working model of the photosynthetic antenna-reaction center complex, constructed via self-assembled supramolecular methodology has been achieved. For this, a supramolecular triad was assembled by axially coordinating imidazole appended fulleropyrrolidine ( $\text{C}_{60}$ ) to the zinc center of a covalently linked zinc porphyrin-boron dipyrin dyad, ZnP-BDP. Selective excitation of the boron dipyrin moiety in the boron dipyrin-zinc porphyrin dyad results in efficient energy transfer creating singlet excited zinc porphyrin. Upon forming the supramolecular triad, the excited zinc porphyrin undergoes efficient electron transfer to the coordinated fullerene resulting in a charge-separated state. The observed energy transfer followed by electron transfer in the present supramolecular triad mimics the events of natural photosynthesis.

### 4. Acknowledgements

The authors are thankful to the Petroleum Research Fund administered by the American Chemical Society and the NIH for funding. PS is thankful to the DOE-GAANN fellowship. The authors would also like to thank Dr. Melvin E. Zandler and Dr. Osamu Ito and coworkers for their collaboration.

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