Covalent Multicomponent Models of the Photosynthetic Reaction Center

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Photosynthesis is the process by which green plants and photosynthetic bacteria convert sunlight into the high-energy chemicals which are the basis for life. The basic feature of all photosynthetic organisms is their abilty to absorb sunlight and the subsequently convert singlet excited state energy to chemical potential [1,2]. Chemical potential in the form of a long lived (~100 ms) charge separated state is produced in the reaction center (RC) which spans a lipid bilayer membrane (~30 Å) [1,2]. The RC is composed of a protein matrix which precisely holds an array of chromophores in the proper geometry [1]. The long distance charge separated state is formed through a series of short-range, rapid electron transfer (ET) steps starting at the excited state and proceeding down a stepped potential gradient [1,2].

Covalently linked multicomponent molecules (CLMM) have been designed and synthesized to mimic the long distance ET of the natural photosynthetic RC [5-7,12-16,18]. Current research uses ET theory as a guide to synthesize CLMMs that maximize the lifetime and quantum yield of charge separation as a means of capturing and storing solar energy.

Wasielewski and co-workers covalently linked a porphyrin (P) donor to a napthoquinone (NQ) acceptor through a rigid polycyclic cage. Excitation of the porphyrin to the singlet excited state was followed by quenching of the singlet state by ET to yield a short lived (370 ps) charge separated state, (P)+(NQ)⁻ [3,4]. The lifetime was increased by linking N,N-dimethylaniline (D) to the porphyrin to act a secondary electron donor (Figure 1a). Efficient two-step electron transfer resulted in the formation of (D)+(P)(NQ)⁻ with a lifetime of 2.45 μ s [5] (Figure 1b). The increase in lifetime was attributed to the longer restricted distance (~25 Å) between the cation and anion than in the dyad (~10Å) [5].



Figure 1:

(a) Molecular structure of aniline (D) - porphyrin (P) - napthoquinone (NQ) triad [5]
(b) Energetics and kinetics of electron transfer in triad [3-5]

A confomationally less rigid dyad was synthesized by Maruyama and co-workers that used a zinc porphyrin (ZnP) donor connected to a pyromellitimide (Im) acceptor [10-12]. Transient absorption and emission studies monitored the formation and decay of a $(ZnP)^+(Im)^-$ ion pair (IP) from decay of the ZnP singlet excited state [10]. The choice of solvent proved to be important in controlling the lifetime the IP and quantum yield of the charge separation (CS) [6,7]. The rate of IP charge recombination (CR), a relatively exothermic reaction, decreased with decreasing solvent polarity due to the smaller solvent reorganization energies [8-10].

A triad was synthesized by connecting a more easily reduced quinone (Q) to the Im [10-12]. A $(ZnP)^+(Im)(Q)^-$ ion pair was shown to be thermodynamically and kinetically accessible by two short ET steps from the decay of the porphyrin singlet excited state [10]. The relatively short lifetime of the triad was attributed to its conformational flexibility [10]. The quantum yield of charge separation to the IP increased (0.75 to ~1) by increasing the CS rate between the Im and the Q [10]. The higher rate was achieved by increasing the driving force of the (ZnP)⁺(Im)⁻(Q) \rightarrow (ZnP)⁺(Im)(Q)⁻ reaction by chlorinating the quinone[10].

In an attempt to maximize the IP distance and model energy transfer between porphyrins a pentad (Figure 2) was synthesized by Gust and co-workers. The pentad undergoes ET from the porphyrin singlet excited state to form a charge separated state, $CP_{Zn}P^+Q^-Q$ [15,16]. Competing with CR are additional ET reactions which operate both in series and parallel to converge on a final IP, $C^+P_{Zn}PQQ^-$ which was characterized by transient absorption [15,16], emission [15,16], and EPR [17]. The pentad used light energy to achieve net electron transfer over ~80 Å with a high quantum yield (0.83) and long lifetime (55 ms) [16].



Figure 2: Molecular structure, block diagram, for a covalently linked molecular pentad [13]

Modeling some of the ET events found in the photosynthetic reaction center is possible with CLMMs. A long lived IP can be formed by separating the ions with a large restricted distance. The long distance can be spanned with a series of short range and fast ET reactions with high efficiency. The efficiency of the overall charge separation reaction will depend on the ability to increase CS rates and decrease CR rates. This requires careful attention to the distance, orientation, solvent, and electronic coupling between the electron donor and acceptor.

The ultimate goal of these artificial RCs is to efficiently capture and store solar energy. By interfacing these systems into an organized assembly the stored oxidizing and reducing potential can be used to drive other chemical reactions [6,7,18].

References

1. Feher, G.; Allen, J. P.; Okamura, M. Y.; Rees, D. C., "Structure and Function of Bacterial Photosynthetic Reaction Centers," *Nature* 1989, 339, 111-116.

- 2. Barber, J.; Anderson, B., "Revealing the Blueprint of Photosynthesis," *Nature* **1994**, *370*, 31-34.
- 3. Wasielewski, M. R.; Niemczyk, M. P., "Photoinduced Electron Transfer in meso-Triphenyltriptycenylporphyrin-Quinones. Restricting Donor-Acceptor Distances and Orientations," J. Am. Chem. Soc. 1984, 106, 5043-5045.
- 4. Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B., "Dependence of Rate Constants for Photoinduced Charge Separation and Dark Charge Recombination on the Free Energy of Reaction in Restricted-Distance Porphyrin-Quinone Molecules," J. Am. Chem. Soc. 1985, 107, 1080-1082.
- Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B., "High-Quantum-Yield Long-Lived Charge Separation in a Photosynthetic Reaction Center Model," J. Am. Chem. Soc. 1985, 107, 5562-5563.
- 6. Wasielewski, M. R., "Photoinduced Electron Transfer in Supramolecular Systems for Artificial Photosynthesis," *Chem. Rev.* **1992**, *92*, 435-461.
- Balzani, V.; Scandola, F., Supramolecular Photochemistry; Ellis Horwood: New York, 1991; pp 89-150.
- 8. Closs, G. L.; Miller, J. R., "ntramolecular Long-Distance Electron Transfer in Organic Molecules," *Science* 1988, 240, 440-449.
- Bowler, B. E.; Raphael, A. L.; Gray, H. B., "Long-Range Electron Transfer in Donor (Spacer) Acceptor Molecules and Proteins," *Prog. Inorg. Chem: Bioinorganic Chemistry* 1990, 38, 259-321.
- Masaya, O.; Takahashi, A.; Mataga, N.; Okada, T.; Osuka, A.; Yamada, H.; Maruyama, K., "Direct Observation of a Consecutive Two-Step Electron Transfer in Some Zinc Porphyrin-Pyromellitimide-Quinone Triads Which Undergo the Same Mode of Electron Transfers as the Bacterial Photosynthetic Reaction Center," J. Am. Chem. Soc. 1993, 115, 12137-12143.
- Osuka, A.; Nakajima, S.; Takahashi, A.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K., "1,2-Phenylene-Bridged Diporphyrin Monomer and Pyromellitimide as a Model for a Photosynthetic Reaction Center: Synthesis and Photoinduced Charge Separation," J. Am. Chem. Soc. 1993, 115, 4577-4589.
- Maruyama, K.; Osuka, A.; Mataga, N., "A Chemical Approach Towards Photosynthetic Reaction Center," Pure and Appl. Chem. 1994, 66, 867-872.
- 13. Gust, D.; Moore, T. A., "Photosynthetic Model Systems," Top. Curr. Chem. 1991, 159, 103-151.
- Gust, D.; Moore, T. A.; Moore, A. L., "Molecular Mimicry of Photosynthetic Energy and Electron Transfer," Acc. Chem. Res. 1993, 26, 198-205.
- Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S.; Bittersman, E.; Luttrull, D. K.; Rehms, A. A.; DeGraziano, J. M.; Gao, F.; Ma, X. C.; Xiaochun, C. M.; Trier, T. T.; Belford, R. E., "Photoinduced Electron and Energy Transfer in Molecular Pentads," *Sience* 1990, 248, 199-201.

- Gust, D.; Moore, T. A.; Moore, A. L.; Macpherson, A. L.; DeGraziano, J. M.; Gouni, I.; Bittersman, E.; Seely, G. R.; Gao, F.; Nieman, R. A.; Ma, X. C.; Demananche, L. J.; Hung, S.; Luttrull, D. K.; Lee, S.; Kerrigan, P. K., "Photoinduced Electron and Energy Transfer in Molecular Pentads," J. Am. Chem. Soc. 1993, 115, 11141-11152.
- Hasharoni, K.; Levanon, H.; Tang, J.; Bowman, M. K.; Norris, J. R.; Gust, D.; Moore, T. A.; Moore, A. L., "Singlet Photochemistry in Model Photosynthesis: Identification of Charge Separated Intermediates by Fourier Tranform and CW-EPR Spectroscopies," J. Am. Chem. Soc. 1990, 112, 6477-6481.
- 18. Meyer, T. J., "Chemical Approaches to Artificial Photosynthesis," Acc. Chem. Res. 1989, 22, 162-170.