

Bis(porphyrin)-Quinone Triad as a Model of the Photosynthetic Reaction Center

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The photosynthetic reaction center (PRC) is of considerable interest owing to its ability to harness light energy. It efficiently (quantum yield ~ 1) undergoes electron transfer via a multistep pathway forming a long-lived (seconds timescale) charge-separated state. Bacterial photosynthetic reaction centers are made up of a cofacial dimer of bacteriochlorophylls called the special pair (P), two monomeric bacteriochlorophylls (B), two bacteriopheophytins (H), two quinones ($Q_{a/b}$), and a non-heme iron(II), as shown in Figure 1. The two bacteriochlorophyll units in the special pair, which are separated by $\sim 3.3 \text{ \AA}$, serve as the primary electron donor and the quinones serve as the electron acceptor. We aimed to synthesize a structural model incorporating these features.

Our laboratory has previously described the synthesis of the first bis(porphyrin) sandwich quinone complex $\text{Zr}(\text{TTP})(\text{TTP-NH-CO-AQ})$, ($\text{TTP} = 5,10,15,20$ -tetratolylporphyrin, $\text{AQ} = \text{anthraquinone}$).^{3,4} Electron transfer studies of this compound showed evidence of the formation of the charge-separated state; however, the lifetime could not be measured owing to rapid charge recombination back to the ground state.⁵

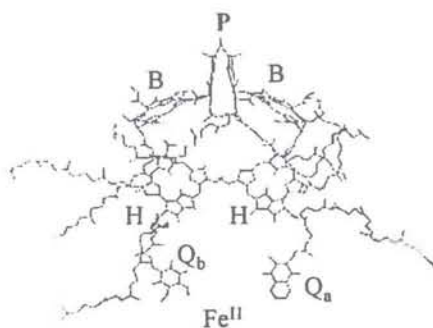


Figure 1. Photosynthetic reaction center *Rhodobacter viridis*.⁶

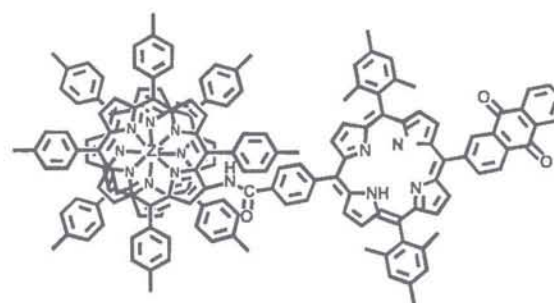


Figure 2. Structure of triad molecule of $\text{Zr}(\text{TTP})(\text{TTP-NH-PAQ})$.

Increasing the distance between the bis(porphyrin) sandwich and quinone should increase the lifetime of the charge-separated state and decrease the rate of charge recombination. We have designed and synthesized the first bis(porphyrin)-quinone triad, $\text{Zr}(\text{TTP})(\text{TTP-NH-PAQ})$, that mimics structural and electronic features of the photosynthetic reaction center (Figure 2):

- 1) The bis(porphyrin) interplanar separation of $\sim 3 \text{ \AA}$ is similar to the separation of the special pair.
- 2) The oxidized bis(porphyrin), $\text{Zr}(\text{TTP})_2^+$, has a near IR band at 1074 nm, which is similar in energy to that of the oxidized special pair.

- 3) The porphyrin spacer molecule mimics the bacteriopheophytins of the reaction center and provides for the possibility of a multi-step electron transfer pathway.
- 4) The quinone molecule mimics the quinone electron acceptor in natural reaction centers.

One of the challenging aspects of coupling a bis(porphyrin) metal subunit with a porphyrin-quinone molecule is synthesizing and purifying a *trans*-substituted porphyrin containing three different *meso*-substituents. We have accomplished this goal by condensing a mixture of two aldehydes with a sterically hindered dipyrromethane starting material.^{7,8} Analytical HPLC and FAB-MS were utilized to determine the yields of the different porphyrin molecules that formed during the reaction. Preparative HPLC can be used to purify the anthraquinone porphyrin spacer molecule (PAQ methyl ester); however, it is not cost and time effective to purify the porphyrin in this manner. We found the best purification method to be the hydrolysis of PAQ methyl ester to PAQ carboxylic acid, which can be isolated by a series of extraction and chromatography steps.

The AQ triad, Zr(TTP)(TTP-NH-PAQ) was synthesized by coupling Zr(TTP)(TTP-NH₂)^{9,10} with PAQ carboxylic acid using oxalyl chloride as the coupling agent, Figure 3. Other common coupling agents such as DCC and thionyl chloride were not effective in coupling these starting materials. Column chromatography was used to separate AQ triad from the starting materials. Zr(TTP)(TTP-NH-PAQ) was analyzed by FD-MS, ¹H-NMR, UV-vis spectroscopy, and HPLC.

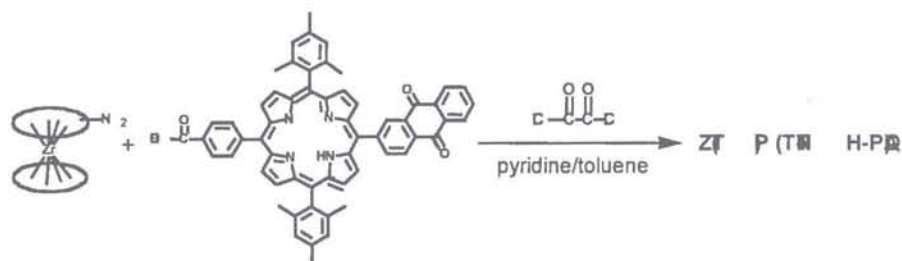


Figure 3. Preparation of AQ triad, Zr(TTP)(TTP-NH-PAQ).

Photophysical measurements were carried out in collaboration with Professor Dewey Holten and Robin Lammi at Washington University. The expected electron transfer pathway for the triad is shown in Figure 4. In toluene, benzonitrile, and DMF, we observed a bleaching of the Soret band upon excitation. Kinetic plots in these solvents show that the lifetime of the initial photoexcited state is not significantly dependent on solvent: 800 ± 150 ps in toluene, 610 ± 70 ps in benzonitrile, and 1150 ± 150 ps in DMF. Control experiments were also carried out with Zr(TTP)(TTP-NH-PHBQ dimethyl ester), the protected BQ triad. The lifetimes for the initial photoexcited states of the triad, protected triad, and Zr(TTP)(TTP-NH₂) in a given solvent are the same within experimental error. This result means that an electron is not transferring to the monomeric spacer porphyrin in high yield. Presumably, the DG for this process is too unfavorable. Instead, the excited zirconium bis(porphyrin) sandwich complex simply returns to the ground state, Figure 5.

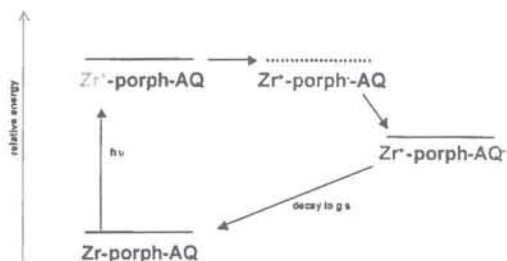


Figure 4. Expected electron transfer pathway in AQ triad.

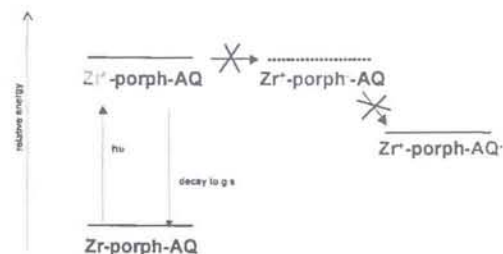


Figure 5. Actual electron transfer pathway in AQ triad.

In conclusion, the first bis(porphyrin)-quinone triad has been successfully synthesized. Photophysical measurements show that incorporating a bis(porphyrin) dimer into a triad system did not provide enough driving force for electron transfer to occur. One way to improve upon this system would be to make the bridging porphyrin a better electron acceptor by replacing the mesityl substituents with pentafluorophenyl groups.

References:

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