Synthetic Analogs of the Photosynthetic Reaction Center

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Our understanding of the chemistry and physics of the photosynthetic reaction center (PRC) has been greatly assisted by studies of synthetic models. For example, remarkably long-lived charge separated states have been observed in synthetic porphyrin-quinone tetrads and pentads. Also, the physiological significance of chromophore orientation and donor-acceptor energetics in reaction centers has been addressed through studies of gable porphyrin dimers and porphyrin-quinone complexes, respectively.[1] The distinctive structural feature of the RC, however, is the closely-stacked "special pair" of bacteriochlorophylls that act as the primary photoelectron donor (Figure 1). Unfortunately, prior model compounds lacked such a closely-spaced cofacial porphyrin dimer.[2,3]

Much better building blocks for synthetic analogues of the RC are bis(porphyrin) complexes in which the porphyrin-porphyrin separations are ≈ 3 Å.[4] We have synthesized compounds that combine two key structural features present in the reaction center of photosynthetic organisms: a donor consisting of a cofacial arrangement of two porphyrinic macrocycles held ≈ 3 Å from each other, and electron accepting agents like quinone and pyromellitimide (Figure 2). These strongly-interacting porphyrin subunits closely resemble the "special-pair" dimer of chlorophylls in the PRC, in their cofacial architecture, spacing, and electronic properties.
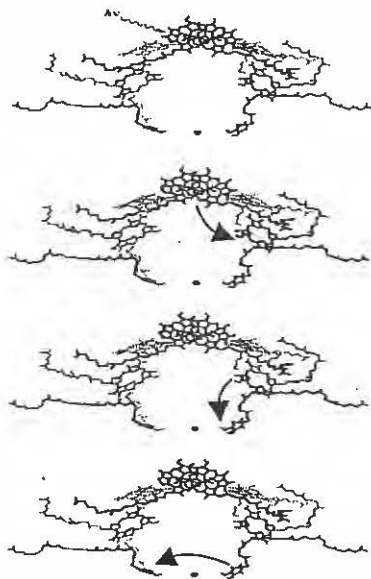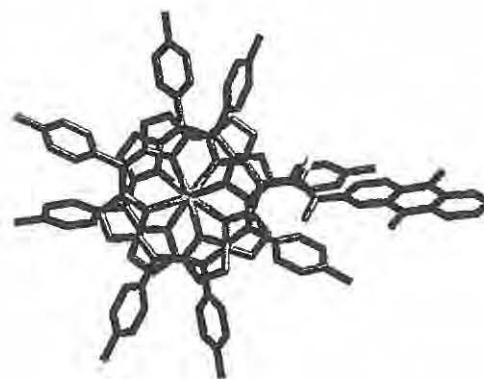

Figure 1   **Figure 2**

The cyclic voltammogram of the quinone-derivatized complex Zr(TTP)(TTP-NHCOAQ) contains two oxidation and four reduction waves. The first two reduction waves involve the anthraquinone unit, while the third and fourth involve the bis(porphyrin) π-system, as judged from comparisons with the redox potentials of related species. The porphyrin π-system in Zr(TTP)(TTP-NHCOAQ) is ≈ 100 mV harder to oxidize than the related amine-substituted

sandwich complex. Furthermore, the reduction potentials for the anthraquinone substituent in Zr(TTP)(TTP-NHCOAQ) are shifted cathodically by ≈ 40 mV relative to those seen for 2-(phenylamidocarbonyl)anthraquinone. These perturbations in the redox potentials suggest that the quinone substituent is electron-withdrawing. The reduction potentials of the porphyrin π-system in anthraquinone-substituted bis(porphyrin) species remain nearly unchanged.

Oxidized dimeric porphyrins exhibit characteristic near-IR absorptions due to electronic transitions between bonding and antibonding molecular orbitals of the new supermolecule. Treatment of Zr(TTP)(TTP-NHCOAQ) with phenoxathiinylium hexachloroantimonate yields the salt of the double-decker quinone monocation, $[Zr(TTP)(TTP-NHCOAQ)]^+[SbCl_6]^-$. Both chemical and electrochemical oxidation takes place from the porphyrin HOMO. The near-IR absorption band due to the monocation occurs at 1096 nm. Such electronic transitions are of particular interest since a broad transition (1300 nm) is also found for the special pair dimer of bacteriochlorophyll-b, $[(BChl)_2]^+$.

Porphyrin-pyromellitimide complexes are ideal systems in which to study light-induced charge separation processes because reduced pyromellitimide absorbs strongly at 715 nm, a wavelength at which the bis(porphyrin) subunit is optically transparent.[5] We have developed synthetic routes towards several pyromellitimide-substituted bis(porphyrin) metal complexes. Upon irradiation of these species, a transient charge-separated complex is generated in which the photoexcited bis(porphyrin) zirconium unit reduces the pyromellitimide substituent.

The decay of the fluorescence due to the singlet excited state of Zr(TTP)(TTP-NHCOAQ) allows us to calculate the rate of charge separation in this complex. We find that charge separation occurs in 28 ps in acetonitrile (Figure 3) but 625 ps in diethyl ether. For comparison, the lifetime of Zr(TTP)(TTP-NH2) varies by only 30% with solvent polarity, from 1100 ps in toluene to 700 ps in DMF, which more than covers the range of solvent polarities in which the Zr(TTP)(TTP-NHCOAQ) complex was studied. Thus, the lifetime of the excited singlet state (*P) of the bis(porphyrin)-anthraquinone (and bis(porphyrin)-pyromellitimide) complex changes by a much larger percentage over a slightly smaller range of solvent polarity. Electron transfer from the excited singlet state to the acceptor is followed by very rapid charge-recombination of the charge-separated state to the ground state. There is no evidence for buildup of the charge-separated state. Electron transfer becomes more efficient in both complexes as the solvent polarity increases, a result which is consistent with a larger driving force for electron transfer. Electron transfer is more facile for the anthraquinone complex than the pyromellitimide complex even though the driving force should be larger for the pyromellitimide complex. This may indicate that the anthraquinone complex is in the Marcus activated (normal) region while the pyromellitimide complex is in the inverted region.[6]
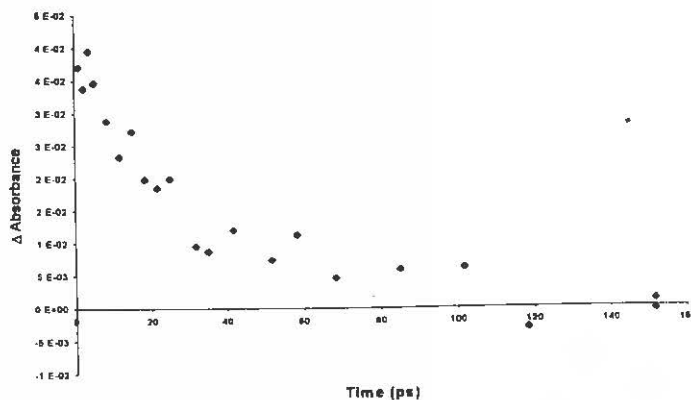

Figure 3

The role of the accessory bacteriochlorophyll chromophore is an active point of biophysical research.[7] In order to gain insight into its role, we have constructed triad complexes in which the bis(porphyrin)metal and quinone units are separated by a monomeric porphyrin spacer. These triad complexes are the first porphyrin-based triad system featuring a electron donor that has properties similar to that of the special pair in photosynthesis.

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