Molecular Mimicry of Photosynthetic Energy and Electron Transfer

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The design of electronic components with molecular dimensions is an area of active research and speculation. Not surprisingly, biology yields useful paradigms for this relatively unexplored realm. The reaction centers of photosynthetic organisms are in fact photovoltaic devices at the molecular level. These entities collect light of various wavelengths and use essentially every photon to initiate an electron-transfer process which culminates in a long-lived, energetic charge-separated state. The output of these solar cells is used to meet the energy needs of the organism and, indirectly, of almost all living things. In recent years, it has proven possible to prepare synthetic molecular devices which mimic certain aspects of natural solar energy conversion. In this Account, we will discuss the basic principles underlying the design of artificial reaction centers and illustrate progress using a few examples, most of which are drawn from our laboratories.

Photosynthesis is carried out by pigments and electron donor and acceptor moieties housed within proteins, which are in turn associated with biological membranes. Typically, these moieties include chlorophylls and their relatives, quinones, and carotenoid polyenes. They interact by three basic photochemical processes: singlet–singlet energy transfer, triplet–triplet energy transfer, and photoinitiated electron transfer. For example, antenna systems consisting of chlorophylls, carotenoids, and sometimes other pigments collect light and conduct excitation to the reaction center via singlet–singlet energy transfer.[1-3] Triplet chlorophyll can sensitize production of highly reactive, and therefore destructive, singlet oxygen. By rapidly quenching such triplets through triplet–triplet energy transfer, carotenoids provide photoprotection.[2,3] Photoinitiated electron transfer involving chlorophylls and quinones which transforms excitation energy into chemical potential in the form of long-lived, trans-

membrane charge separation is at the heart of photosynthetic energy conversion.[4-6]

There are two major aspects to the design of artificial reaction centers. The first consideration is the choice of pigments and electron donors and acceptors. Especially critical are excited-state energy levels and photophysical parameters, and the redox properties of all relevant states. The second is the selection of an organizing principle that will control the interactions among these components. These interactions play a major role in dictating the rates and quantum yields of the various transfer processes and are in turn determined by spatial separations, angular relationships, and the nature of the intervening medium.

Proper application of these design considerations can yield artificial photosynthetic devices which creditably mimic the three natural photochemical processes discussed above. One approach is to use pigments and electron donors and acceptors related to those found in natural photosynthesis (and thus presumably optimal for that system), but to replace the protein with covalent bonds as an organizing precept. Molecular pentads **1** and **2** (Figure 1) exemplify the success of this approach.[7] At the heart of these molecules are two covalently linked synthetic porphyrin moieties (P-P). One of these models for chlorophyll is attached to a carotenoid polyene (C), whereas the other is linked to a rigid diquinone (Q-Q). As discussed later in this paper, excitation of such a pentad is followed by photoinitiated electron transfer steps which ultimately give a $C^{\bullet+}-P-P-Q-Q^{\bullet-}$ charge-separated state. Depending upon the structure of the pentad and the conditions, these states are formed with quantum yields of up to 0.83, have lifetimes approaching 0.5 ms, and store about one-half of the energy of the excited singlet state. Related photosynthesis mimics display singlet–singlet energy transfer from carotenoid polyenes to porphyrins and among porphyrin chromophores, and rapid quenching of porphyrin triplet states by attached carotenoids. How have the structures of these and other successful artificial reaction centers evolved, and what will be the next steps in their development? We will address these

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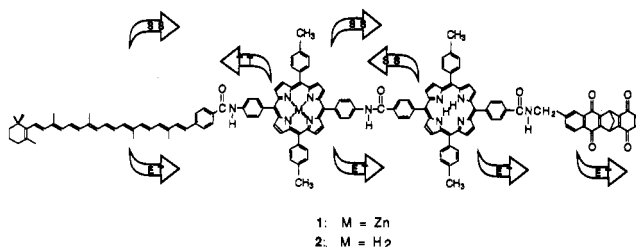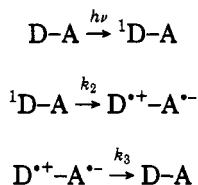
1: M = Zn
2: M = H₂

Figure 1. Molecular pentads which mimic photosynthetic energy and electron transfer. The arrows represent electron transfer (ET), singlet–singlet energy transfer (SS), and triplet–triplet energy transfer (TT) between adjacent moieties, as detected in the pentads or appropriate model systems. These three transfer processes are important in photosynthetic energy conversion, antenna function, and photoprotection from singlet oxygen damage, respectively.

questions from the point of view of photoinitiated electron transfer, and then we will briefly consider singlet and triplet energy transfer.

Photoinitiated Electron Transfer

Design Principles. Let us begin with the design of the simplest artificial reaction center of the type discussed above. It will consist of a visible-light-absorbing pigment which can act, for example, as an excited singlet state electron donor (D), and a covalently attached acceptor (A). Illumination of this dyad molecule will lead to the sequence of electron-transfer events shown in Scheme I.

Scheme I

$$D\text{–}A \xrightarrow{h\nu} {}^1D\text{–}A$$

$$^1D\text{–}A \xrightarrow{k_2} D^{\bullet+}\text{–}A^{\bullet-}$$

$$D^{\bullet+}\text{–}A^{\bullet-} \xrightarrow{k_3} D\text{–}A$$

The excited singlet state of the donor transfers an electron to the acceptor in step 2 to yield a charge-separated state, which returns to the ground state by charge recombination (step 3).

How do we select the donor and acceptor, and how do we choose the linkage? A starting point for answering these questions is eq 1, a simple form of the theory for nonadiabatic electron transfer originated by Marcus and elaborated by Marcus and many others.[8-11]

$$k_{ET} = (\pi/\hbar^2\lambda k_B T)^{1/2}\,|V|^2 \times$$

$$\exp[-[(\Delta G^\circ + \lambda)^2/4\lambda k_B T]] \quad (1)$$

The electron-transfer rate constant k_{ET} is given by the product of a preexponential term including the matrix element V, which describes the electronic coupling between the state of the system prior to electron transfer and the final state, and an exponential term. The magnitude of the exponential term depends upon the free energy change for the reaction, ΔG°, and the reorganization energy, λ. In the exponential, the terms containing ΔG° and λ are analogous to the classical

activation energy. The reorganization energy is associated with changes in both the internal structure of the moieties in question and the organization of the surrounding medium on going from the initial to the final state.

The time scale for step 2 in Scheme I is set by the nature of photochemical reactions; in order to maximize the quantum yield, k_{ET} must be rapid relative to the other pathways which lead to decay of the excited state. Energy storage will be optimal if the free energy change for the reaction is near 0. Equation 1 suggests ways to achieve these goals. For a given value of λ (ca. 1 eV in many organic systems in the usual solvents), one should minimize the thermodynamic driving force and maximize the electronic coupling. This coupling is mediated by direct, through-space overlap of the relevant orbitals of the donors and acceptor, which, to a first approximation, falls off exponentially with donor–acceptor separation, or by through-bond superexchange terms which involve the highest occupied and lowest unoccupied molecular orbitals of the linkage.[9-12] In general, both types of coupling will increase in strength as the number of bonds joining the donor and acceptor moieties decreases.

Molecular Dyads. A large number of covalently linked porphyrin–quinone dyads which sucessfully meet these design criteria have been prepared and studied by many workers.[13,14] Excitation of the porphyrin to its first excited singlet state is followed by electron transfer to the quinone to yield $P^{\bullet+}$–$Q^{\bullet-}$. The quantum yields of well-designed dyads can be essentially unity. A great deal concerning the basic parameters governing photoinitiated electron transfer has been gleaned from such studies. However, from the point of view of artificial photosynthesis, these dyads suffer from a serious constraint. The very electronic coupling factors that lead to a high quantum yield for photoinitiated electron transfer also favor another electron-transfer reaction: charge recombination to yield the ground state. Thus, when step 2 in Scheme I is rapid, step 3 also tends to be rapid, and the photogenerated charge-separated state recombines before it can be harnessed to do useful work. Typically, $P^{\bullet+}$–$Q^{\bullet-}$ states have lifetimes of hundreds of picoseconds or less.

Evidently, the design of a successful artificial reaction center requires more than a simple application of eq 1. The photoinitiated electron transfer reaction must be fast, but charge recombination should be slow. We look to natural photosynthesis for a solution to this conundrum. The preponderance of evidence suggests that the reaction center inhibits rapid recombination by isolating the charges at large separations, e.g., across the thickness of a lipid bilayer membrane. Low quantum yields for formation of such charge-separated states are avoided via a series of short-range, and therefore fast and efficient, electron transfers rather than a single, long-range step.[4-6]

Molecular Triads: Sequential Multistep Electron Transfer. Some years ago, we initiated an investigation of this multistep electron transfer strategy

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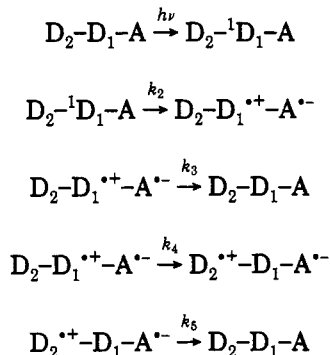
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as applied to artificial reaction centers. The simplest system for such a study is a triad molecule consisting of three covalently linked donor–acceptor species. For example, a secondary electron donor could be linked to the primary donor in the dyads described above. Excitation of D_1 in such a D_2–D_1–A triad could be followed by the series of electron transfers shown in Scheme II.

Scheme II

$$D_2\text{--}D_1\text{--}A \xrightarrow{h\nu} D_2\text{--}{}^1D_1\text{--}A$$

$$D_2\text{--}{}^1D_1\text{--}A \xrightarrow{k_2} D_2\text{--}D_1{}^{\bullet+}\text{--}A^{\bullet-}$$

$$D_2\text{--}D_1{}^{\bullet+}\text{--}A^{\bullet-} \xrightarrow{k_3} D_2\text{--}D_1\text{--}A$$

$$D_2\text{--}D_1{}^{\bullet+}\text{--}A^{\bullet-} \xrightarrow{k_4} D_2{}^{\bullet+}\text{--}D_1\text{--}A^{\bullet-}$$

$$D_2{}^{\bullet+}\text{--}D_1\text{--}A^{\bullet-} \xrightarrow{k_5} D_2\text{--}D_1\text{--}A$$

As with the dyad, photoinitiated electron transfer will be followed by rapid charge recombination of D_2–$D_1{}^{\bullet+}$–$A^{\bullet-}$ (step 3). However, competing with charge recombination will be a second forward electron transfer step, 4, which moves the positive charge to the secondary donor. The final $D_2{}^{\bullet+}$–D_1–$A^{\bullet-}$ state has the positive and negative charges well separated, and thus k_5 should be significantly smaller than k_3. A relatively long-lived charge-separated state might result.

In practice, this strategy works well. Triad **3**, consisting of a porphyrin bearing a quinone electron acceptor and a carotenoid secondary donor, was the first successful photosynthetic model of this type.[15–17]
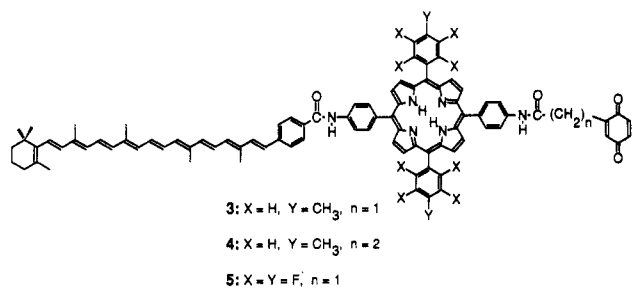
Its photochemistry is outlined in Figure 2. Excitation of a dichloromethane solution of **3** with a laser pulse at 590 or 650 nm, where the porphyrin moiety absorbs, generates the porphyrin first excited singlet state. Time-resolved fluorescence studies show that this state decays with a lifetime of 100 ps. Similar studies with the hydroquinone form of the triad, in which porphyrin-to-quinone electron transfer is precluded, yield a lifetime of 3.4 ns. The quenching observed in the quinone form of the molecule is ascribed to electron transfer via step 2 in Figure 2. The rate constant is 9.7
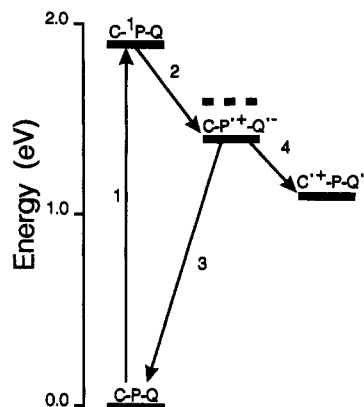

Figure 2. Transient states of carotenoid–porphyrin–quinone (C–P–Q) triad molecule **3**, which demonstrates the sequential multistep electron transfer strategy used by natural reaction centers to achieve long-lived charge separation with a high quantum yield. The dashed line represents a C–P$^{\bullet+}$–Q$^{\bullet-}$ state whose energy has been raised by substitution on the periphery of the porphyrin, as in triad **5**.

$\times 10^9$ s^{-1}, and the quantum yield is essentially unity. The fate of the initial C–P$^{\bullet+}$–Q$^{\bullet-}$ charge-separated state can be determined by transient absorption spectroscopy. Although much of this state decays by charge recombination via step 3, a second electron transfer (step 4) competes to yield a final C$^{\bullet+}$–P–Q$^{\bullet-}$ state, which is easily detected through the strong transient absorption of the carotenoid radical cation in the 960-nm region. In dichloromethane, C$^{\bullet+}$–P–Q$^{\bullet-}$ has a lifetime of about 300 ns. Thus, the lifetime of the final charge-separated state in the triad is at least 3 orders of magnitude longer than in simple P–Q dyads. The final state is still a high-energy species, preserving about 1.1 eV of the 1.9 eV stored in the porphyrin excited state. These energy estimates for charge-separated states are based on electrochemical studies of the triads and models.

Since our initial report of the triad results, the generality of the multistep electron transfer strategy for generation of high-energy charge-separated states in reasonable quantum yield and their temporal stabilization has been amply demonstrated by its application to other systems. For example, Wasielewski and co-workers have reported comparable results with triads consisting of a porphyrin bearing a quinone acceptor and a dimethylaniline-based secondary donor.[18] In the inorganic area, Meyer and co-workers have reported the preparation of a triad-type system based on the ruthenium trisbipyridyl chromophore.[19] Excitation initiated a multistep electron transfer sequence leading to a final charge-separated state with a lifetime of 165 ns. Mallouk and co-workers have reported somewhat related systems in which a dyad consisting of a ruthenium complex covalently linked to an electron acceptor is positioned relative to a secondary acceptor by interactions with a zeolite channel, rather than through covalent bonding.[20] This system also produces a long-lived charge-separated state. A variety of other successful three-part systems for temporal stabilization

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of charge separation have been reported in recent years.[14,21,22]

Improving the Yield. Although triad **3** successfully demonstrated the multistep electron transfer strategy, the overall quantum yield for charge separation was not optimal. For example, in dichloromethane, the $C^{\bullet+}-P-Q^{\bullet-}$ state was formed with a yield of only 4%. Figure 2 reveals that because the photoinitiated electron transfer step occurs with a quantum yield of unity, the low yield of the final state must be due to unfavorable partitioning of the intermediate $C-P^{\bullet+}-Q^{\bullet-}$ species between charge recombination and step 4. Equation 1 suggests ways in which the structure of the triad might be engineered in order to increase the quantum yield. Three approaches are apparent. The electronic coupling between the various moieties could be adjusted, the energetics could be altered, or the reorganization energy could be changed. Strategies involving the tuning of $\Delta G°$ and V are illustrated below.

Increasing the separation (decreasing the coupling) between the porphyrin and quinone moieties of **3** while leaving that between the porphyrin and carotenoid unaltered might be expected to slow steps 2 and 3 in Figure 2, but to leave the rate of step 4 unaffected. This approach would decrease the quantum yield of step 2, but might produce a more-than-compensating increase in the yield of step 4. Triad **4** was prepared in order to exploit this strategy.[23] ^{1}H-NMR investigations of **3**, **4**, and related triads have shown that insertion of a second methylene group in the porphyrin–quinone linkage does indeed increase the separation of these moieties. Excitation of **4** in dichloromethane is followed by photinitiated electron transfer with a rate constant of 8.3×10^8 s^{-1}. The rate has been slowed by a factor of about 10 relative to **3**, and this results in a quantum yield of 0.74 for $C-P^{\bullet+}-Q^{\bullet-}$. Transient absorption studies show that, in spite of this reduction, the final $C^{\bullet+}-P-Q^{\bullet-}$ state for **4** is formed with an overall yield of about 6%, which is a 50% improvement over that for **3**. This increase must be due to a greater efficiency for step 4. Thus, **3** and **4** demonstrate the concept of fine-tuning quantum yields in multistep electron transfer systems via control of the electronic coupling, although the magnitude of the effect is far from satisfying.
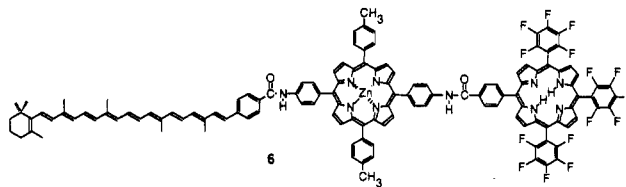
A second strategy for increasing quantum yield is to fine-tune the energy levels of the transient species. As shown in Figure 2, raising the energy of $C-P^{\bullet+}-Q^{\bullet-}$ while leaving the energies of the other states unperturbed will decrease the thermodynamic driving force for step 2 and increase that for steps 3 and 4. This could be advantageous because of a peculiarity of eq 1. As the free energy change becomes more negative, the rate of the reaction will increase until it reaches a maximum when $\lambda = -\Delta G°$. This is the so-called normal region of the relationship. However, as the free energy change continues to become more negative, the electron-transfer rate is predicted to decrease. The existence of this Marcus "inverted" region has been demonstrated in several reactions. Various studies suggest that the reorganization energy λ is near 1 eV for porphyrin–

quinone systems in solvents like dichloromethane.[24-26] Thus, raising the energy of $C-P^{\bullet+}-Q^{\bullet-}$ as discussed above should decrease the rate of step 2 and increase that of step 4, as both reactions occur in the normal region of the Marcus relationship. However, charge recombination by step 3 lies in the inverted region, and increasing the driving force should decrease the reaction rate, if eq 1 applies. The net effect would be a decrease in the efficiency of step 2 which could be more than compensated for by an increase in the efficiency of step 4.

Triad **5** was synthesized in order to investigate this approach.[27] The porphyrin bears two pentafluorophenyl groups which destabilize a positive charge on the porphyrin, and therefore the $C-P^{\bullet+}-Q^{\bullet-}$ state, by about 0.2 eV (Figure 2). Excitation of **5** initiates electron transfer to yield $C-P^{\bullet+}-Q^{\bullet-}$ with a rate constant of 6.1×10^8 s^{-1}. The quantum yield of $C-P^{\bullet+}-Q^{\bullet-}$ is only 0.41. However, the quantum yield of the final $C^{\bullet+}-P-Q^{\bullet-}$ species was found to be 0.30. Thus, although the efficiency of step 2 has decreased relative to that in **3** due to the reduced driving force, the efficiency of step 4 (defined as $k_4/(k_3 + k_4)$) has increased by a factor of 18 to 0.73, and the overall yield of the final charge-separated state has increased by almost a factor of 8.

Taken together, the results for triads **4** and **5** illustrate that in a multiple step device it is necessary at each step to find the proper balance between $\Delta G°$, which controls the activation energy and the amount of energy stored, and V. If V is too large, the overall yield will be limited by reduction of the lifetimes of intermediates, whereas if it is too small, electron transfer cannot compete with decay of other pathways.

Interporphyrin Electron Transfer. One respect in which the C–P–Q triads differ from natural reaction centers is that the photoinitiated electron transfer step involves porphyrin–quinone transfer, whereas in reaction centers, the initial transfer is to a pheophytin (a chlorophyll lacking a central metal atom). Functional triads featuring interporphyrin photoinitiated electron transfer can be prepared if the redox potentials of the porphyrin moieties are adjusted so that there is sufficient driving force. One such molecule is **6**, which consists of a zinc tetraarylporphyrin linked by amide bonds to a carotenoid and a free base porphyrin bearing three pentafluorophenyl groups.[28] Being electron with-

6

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2.0

$C-^1P_{Zn}-P_F$

1

2

3

$C-P_{Zn}-^1P_F$

4

$C-P_{Zn}^{\bullet+}-P_F^{\bullet-}$

6

$C^{\bullet+}-P_{Zn}-P_F^{\bullet-}$

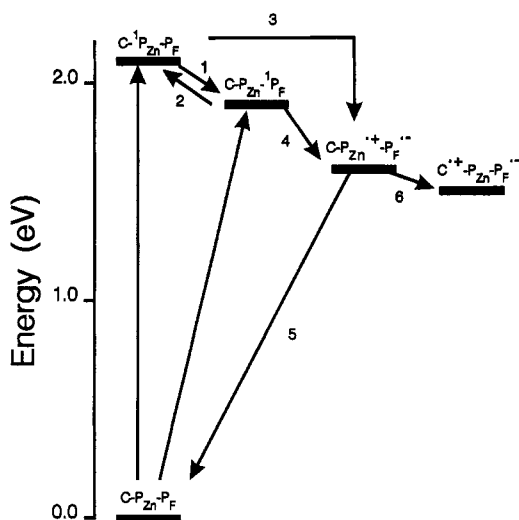Energy (eV)

1.0

5

0.0

$C-P_{Zn}-P_F$

Figure 3. Transient states for carotene–diporphyrin triad 6 and relevant interconversion paths. This triad demonstrates singlet–singlet energy transfer between porphyrin moieties, photoinitiated electron transfer between porphyrins, and a sequential multistep electron transfer scheme which leads to a long-lived charge-separated state.

drawing, these groups stabilize a negative charge on the porphyrin ring, so that the energetics of various potential transient species are as indicated in Figure 3. Energetically, the $C-P_{Zn}-P_F$ molecule is designed so that photoinitiated electron transfer between the porphyrin moieties could ultimately lead to a $C^{\bullet+}-P_{Zn}-P_F^{\bullet-}$ charge-separated state which could have a reasonable lifetime.

Excitation of 6 in dichloromethane with a laser pulse at 590 nm creates two porphyrin excited singlet states, as both moieties absorb. Their fate can be studied with fluorescence techniques. Global analysis of the fluorescence decay profiles at seven wavelengths in the 635–725-nm region yielded two exponential components with lifetimes of 62 ps and 2.9 ns. The short component featured strong emission at 640–650 nm, where most of the fluorescence is due to the zinc porphyrin. Thus, 62 ps is the lifetime of the zinc porphyrin first excited singlet state. This same component has a negative amplitude (*growth* of fluorescence intensity with time) around 710 nm, where most of the emission is due to the free base porphyrin. This growth signals singlet–singlet energy transfer from the zinc porphyrin to the free base, which has a lower-energy excited state. From steady-state fluorescence excitation experiments on the diporphyrin portion of the triad, the quantum yield of energy transfer (0.77) was calculated, yielding a rate constant for step 1 in Figure 3 of 9.4×10^9 s^{-1}.

In addition to singlet–singlet energy transfer, attachment of the free base porphyrin to the zinc porphyrin in 6 introduces a second new pathway for decay of the zinc porphyrin singlet. This is electron transfer to form $C-P_{Zn}^{\bullet+}-P_F^{\bullet-}$ (step 3 in Figure 3). From the above data, the rate constant for this process can be calculated to be 3.5×10^9 s^{-1}, and the quantum yield is 0.22.

As mentioned above, the time-resolved fluorescence data for 6 featured a second decay component with a lifetime of 2.9 ns. This component has the spectrum of the free base porphyrin and, thus, represents the decay of the free base first excited singlet state. The

Scheme III

$$D_2-^1D_1-A_1-A_2 \xrightarrow{k_1} D_2-D_1^{\bullet+}-A_1^{\bullet-}-A_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} \begin{matrix} D_2-D_1^{\bullet+}-A_1-A_2^{\bullet-} & \xrightarrow{k_5} \\ D_2^{\bullet+}-D_1-A_1^{\bullet-}-A_2 & \xrightarrow{k_6} \end{matrix} D_2^{\bullet+}-D_1-A_1-A_2^{\bullet-}$$

$$\downarrow k_2$$

$$D_2-D_1-A_1-A_2$$
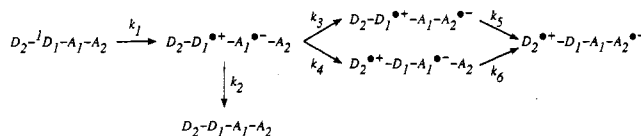
excited singlet lifetime of a model free base porphyrin monomer is 8.5 ns. The quenching arising from attachment of the carotenoporphyrin moiety is due to electron transfer from the zinc porphyrin to yield the same $C-P_{Zn}^{\bullet+}-P_F^{\bullet-}$ species discussed above (step 4 in Figure 3). This transfer occurs with a rate constant of 2.3×10^8 s^{-1} and a quantum yield of 0.67 based upon $C-P_{Zn}-^1P_F$. Because singlet–singlet transfer in 6 is not complete, the overall quantum yield of $C-P_{Zn}^{\bullet+}-P_F^{\bullet-}$ will depend upon the excitation wavelength. At 590 nm, for example, this yield is 0.64.

The energetics of triad 6 suggest that $C-P_{Zn}^{\bullet+}-P_F^{\bullet-}$ might decay by electron transfer from the carotenoid to yield a final $C^{\bullet+}-P_{Zn}-P_F^{\bullet-}$ state (step 6 in Figure 3). Transient absorption studies demonstrate that this indeed occurs. The $C^{\bullet+}-P_{Zn}-P_F^{\bullet-}$ species has a lifetime of 240 ns in dichloromethane and is formed with an overall quantum yield of 0.32 with 590-nm excitation. Thus, step 6 occurs with an efficiency of about 50%.

As the above examples demonstrate, triad devices that achieve high quantum yields of long-lived, energetic charge separation can be designed through application of the multistep electron transfer strategy coupled with basic theories of electron transfer. The success of these tactics suggests that it would be fruitful to investigate other approaches to multistep electron transfer. The implementation of more complex schemes, outlined below, requires more complex molecular systems.

Molecular Tetrads and Pentads: Parallel Multistep Electron Transfer. The multistep electron transfer strategy used by the triads and natural reaction centers is sequential. An initial charge-separated state is produced by photoinitiated electron transfer, and a series of subsequent dark reactions moves the positive and negative charges apart and thus enhances the charge-separation lifetime. Parallel multistep electron transfer schemes are also conceivable (Scheme III). Photoinitiated electron transfer (step 1) generates a primary charge-separated state which can recombine to yield the ground state (step 2). However, two additional transfers operating in parallel (steps 3 and 4) compete with this undesirable process to give two new intermediate charge-separated states. Decay pathways for these (steps 5 and 6) converge on the same final charge-separated species. The advantage of this strategy is that two pathways, neither of which need be completely efficient, work in parallel to compete with an undesired decay route.

We have prepared a variety of complex molecular devices which exploit both parallel and sequential multistep electron transfer tactics.[14,17,21] Only one example, pentad 1, will be discussed.[7] Figure 4 shows the relevant transient species and their possible interconversion routes. The pentad is designed so that photoinitiated electron transfer from the free base porphyrin to the attached naphthoquinone can be followed by a cascade of electron-transfer pathways which converge upon a final $C^{\bullet+}-P_{Zn}-P-Q-Q^{\bullet-}$ charge-separated state. The process begins with excitation of
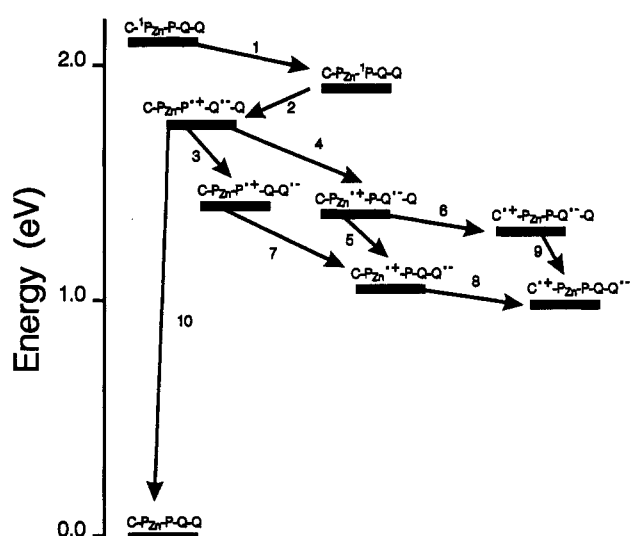
Figure 4. Transient states for pentad 1 (see Figure 1) and relevant interconversion pathways. In addition to singlet–singlet energy transfer, this molecule demonstrates long-lived charge separation in high quantum yield which has been achieved using both sequential and parallel multistep electron transfer strategies.

the free base porphyrin moiety. This can occur via direct absorption of light, or by singlet–singlet energy transfer from the attached zinc porphyrin, as was observed for triad 6. The rate constant for the energy-transfer process (step 1 in Figure 4) is 2.3×10^{10} s^{-1} in chloroform solution, as determined from global analysis of the time-resolved fluorescence behavior of the molecule at 14 wavelengths. The energy-transfer quantum yield is about 90%.

The free base porphyrin first excited singlet state decays in part by electron transfer to the attached naphthoquinone (step 2) to produce C–P$_{Zn}$–P$^{\bullet +}$–Q$^{\bullet -}$–Q. The rate constant is 7.1×10^8 s^{-1}, and the quantum yield is 0.85. This initial charge-separated state can in principle decay to the ground state through charge recombination (step 10). However, two electron-transfer steps operating in parallel compete with recombination. One of these, step 3, involves electron migration from the naphthoquinone radical anion to the attached benzoquinone, which is a better electron acceptor. The other, step 4, is electron donation from the zinc porphyrin to the free base radical cation. This reaction has a reasonable driving force, as the zinc stabilizes the positive charge on the macrocycle. Although the two new intermediates can decay by charge recombination as well, these reactions are expected to be slow compared to step 10 because the charges are farther apart. The two intermediates can in turn undergo electron transfer by steps 5, 6, and 7 to yield yet another two intermediates which both decay to C$^{\bullet +}$–P$_{Zn}$–P–Q–Q$^{\bullet -}$. This ultimate state may be readily detected spectroscopically by observation of the carotenoid radical cation absorption. In chloroform at ambient temperatures, 650-nm excitation yields the final state with an overall quantum yield of 0.83. As this yield is essentially the same as that of the initially formed C–P$_{Zn}$–P$^{\bullet +}$–Q$^{\bullet -}$–Q species, the parallel electron-transfer pathways compete very efficiently with step 10. The lifetime of C$^{\bullet +}$–P$_{Zn}$–P–Q–Q$^{\bullet -}$ is 55 μs.

In dichloromethane solution, the lifetime of C$^{\bullet +}$–P$_{Zn}$–P–Q–Q$^{\bullet -}$ is increased to about 200 μs, and the quantum yield drops to 0.6. Pentad 2, which lacks the

zinc ion but is otherwise similar in structure to 1, yields a C$^{\bullet +}$–P–P–Q–Q$^{\bullet -}$ state upon excitation in dichloromethane which has a lifetime of 340 μs and is formed with a quantum yield of 0.15. Part of the reason for the reduced quantum yield in 2 is that removal of the zinc reduces the thermodynamic driving force for step 4 by about 0.2 eV, and this in turn slows down step 4 so that it competes less effectively with charge recombination.

It was mentioned that the triad structures led to charge-separation lifetimes at least 1000 times longer than those found with simple porphyrin–quinone dyads. The pentad systems extend this lifetime by another 3 orders of magnitude. In terms of energy conversion, one measure of the performance of these devices is the product of the fraction of the excited-state energy conserved in the final charge-separated state and its quantum yield. To put this into perspective, for isolated reaction centers of purple bacteria the product is ca. 0.4, for triad 6 it is 0.2, and for pentad 1 it is 0.5.

Singlet–Singlet Energy Transfer

Antenna function in photosynthesis is important because is allows metabolically "expensive" reaction centers to turn over at optimal rates and permits organisms to harvest light of wavelengths where the extinction coefficients of reaction centers are relatively low. Two of the major antenna pigments are chlorophylls of various types and carotenoid polyenes. Antenna function is likewise desirable in synthetic systems which mimic photosynthesis and has been realized for both types of pigments.

Interchlorophyll energy transfer can readily occur by the Förster dipole–dipole mechanism.[29] This nonradiative transfer is a resonant process resulting from Coulombic coupling of the transition dipoles of the donor and the acceptor. Efficient transfer is facilitated by good spectral overlap of donor emission and acceptor absorption, a high fluorescence quantum yield for the isolated donor chromophore, and a large molar extinction coefficient for the accepting transition. The transfer rate depends upon interchromophore separation to the inverse 6th power and mutual orientation. Because chlorophylls and their porphyrin relatives feature strongly allowed transitions and relatively high fluorescence quantum yields, Förster singlet–singlet energy transfer among such pigments is facile over long distances. This makes antenna function relatively easy to design into biomimetic systems. For example, in both triad 6 and pentad 1 the zinc porphyrin moieties act as reasonably efficient antennas for the free base porphyrin. Elaborate arrays of covalently linked porphyrins which display antenna function have been reported.[30,31]

Carotenoid polyenes, on the other hand, are very poor energy donors in the Förster sense. The intense color of carotenoids such as β-carotene is due to the strongly electric dipole allowed transition to the second excited singlet state, S$_2$. The radiative rate constant for this state is large, but the state is very short-lived (ca. 200 fs), and the fluorescence quantum yield is therefore very low. The lower-lying S$_1$ state has a longer lifetime

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(ca. 10 ps), but is strongly electric dipole forbidden and is not observed in conventional absorption. Its radiative rate constant is very small, and its fluorescence quantum yield is also extremely low.[32] As a consequence, the spatial and mechanistic requirements for efficient singlet–singlet energy transfer from carotenoids to porphyrins or chlorophylls are very stringent, and this imposes strict limitations on molecular design of artificial reaction centers. Results for two model carotenoporphyrin dyads illustrate this point clearly.

Dyad 7 consists of a tetraarylporphyrin bearing a synthetic carotenoid related to β-carotene.[33] The carotenoid is linked to the porphyrin macrocyle via an ester linkage at the para position of a porphyrin *meso*-aryl ring. Carotenoid to porphyrin singlet–singlet
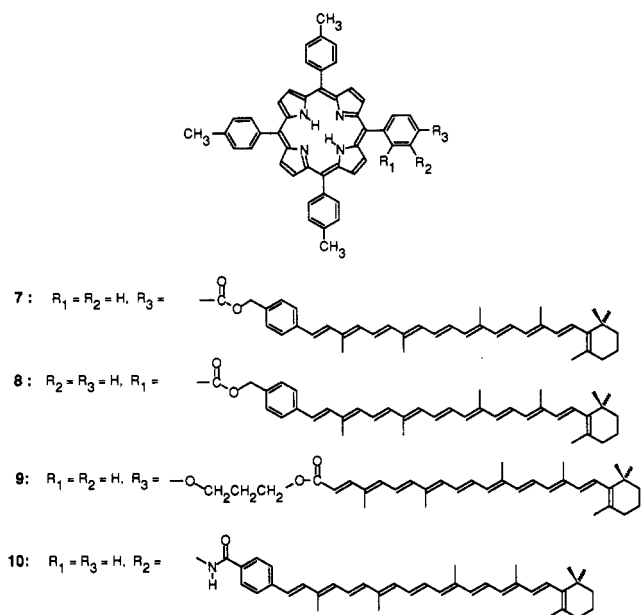
transfer in this molecule may be studied using fluorescence excitation spectroscopy. In this experiment, the porphyrin fluorescence intensity is monitored as a function of the excitation wavelength. If light absorbed by the carotenoid gives rise to porphyrin fluorescence, singlet–singlet transfer must have occurred. Examination of the corrected porphyrin fluorescence excitation spectrum of 7 shows only porphyrin features, and singlet–singlet transfer is insignificant. This is the case even though the π-electron systems of the two chromophores are only a few angstroms apart. As demonstrated by the diporphyrin-containing molecules discussed above, singlet energy transfer between two porphyrin moieties at similar separations is facile.

It seems evident that efficient carotenoid to porphyrin singlet energy transfer requires stronger interactions between the two pigments. Dyad 8 was prepared in order to evaluate this conclusion.[34] The porphyrin and carotenoid moieties are essentially identical to those in 7, but the carotenoid is now attached to the porphyrin at the ortho position of the meso ring. The conformational consequences of this change are apparent from

¹H-NMR investigations. In the para isomer 7, the carotenoid unsaturated chain is extended out, away from the porphyrin macrocycle, whereas in 8 the carotenoid is folded back across the porphyrin with an internuclear spacing of about 4 Å, so that the π-clouds of the two chromophores are in virtual contact. Fluorescence excitation experiments with 8 reveal carotenoid features in the 430–530-nm region. Singlet–singlet transfer is occurring with an efficiency of about 25%.

The close orbital contact required for singlet–singlet transfer in 8 brings into question the applicability of the Förster derivation, which was formulated for interchromophore separations which are large relative to chromophore dimensions, and raises the possibility of singlet–singlet transfer mediated by electron-exchange interactions, which require orbital overlap. We have recently reported several carotenoporphyrins in which the chromophores are joined through partially conjugated amide linkages. In some of these molecules, the singlet–singlet transfer efficiency is about 50%, and electron-exchange interactions involving the linkage bonds appear to play a role in the transfer process.[35]

Triplet–Triplet Energy Transfer

Photoprotection from singlet oxygen damage is an important aspect of natural photosynthesis and a desirable feature of artificial reaction centers. Such protection can be provided by rapid quenching of chlorophyll triplet sensitizers through energy transfer to carotenoids. Unlike singlet–singlet energy transfer, triplet–triplet transfer is "forbidden" by the dipole-dipole mechanism and must occur by an electron-exchange mechanism. As a result, orbital overlap of the donor and acceptor are required. This is illustrated by carotenoporphyrin 9, which features a flexible polymethylene linkage between the two chromophores.[36,37] Triplet–triplet energy transfer in 9 and similar molecules may be studied by monitoring the decay of the transient absorption of the porphyrin triplet state in the 440-nm region and the concomitant rise of the carotenoid triplet absorption at about 550 nm. Excitation of the porphyrin moiety of 9 in a rigid plastic matrix at ambient temperatures or in an organic glass at 77 K is followed by normal intersystem crossing and the appearance of the porphyrin triplet state absorption at 440 nm. This absorption decays normally with a time constant of several milliseconds, and no carotenoid triplet can be detected. The absence of triplet transfer is consistent with the relatively long, insulating methylene spacer group which prevents significant orbital overlap, and thus strong electron-exchange interactions.

In deoxygenated benzene solution at ambient temperatures the situation is altogether different. Immediately after excitation of the molecule with a 25-ns laser pulse, the porphyrin triplet state appears, as signaled by the 440-nm transient absorption. However,

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this absorption decays with an 80-ns lifetime, and a carotenoid triplet–triplet absorption grows in at 540 nm with the same time constant. This absorption is accompanied by carotenoid ground-state bleaching and has a typical carotenoid triplet state lifetime of a few microseconds. Thus, triplet–triplet transfer is occurring with a rate constant of 1.2×10^7 s^{-1}.

The explanation for this dichotomy of behavior is that the most stable conformation(s) of **9** in solution feature the carotenoid extended far from the porphyrin and insulated from it by the polymethylene chain. Thus, in a glass or plastic matrix orbital overlap is poor, and triplet–triplet transfer is not observed. In fluid solution, however, intramolecular motions about the mobile linkage between the chromophores bring the two π-electron systems into momentary contact, and triplet–triplet transfer follows. Thus, the transfer is mediated by intramolecular motions and is in a sense analogous to "collisional" transfer as occurs between nonlinked donors and acceptors.

Triplet transfer in viscous media requires electronic coupling between the porphyrin and carotenoid which is not a function of intramolecular motions. Such coupling can be a design feature of artificial reaction centers. For example, carotenoporphyrin **10** features a carotenoid linked to a porphyrin through the meta position of a *meso*-aryl ring via an amide linkage.[35] In toluene solution at ambient temperatures, the porphyrin triplet state is quenched by energy transfer to the carotenoid with a rate constant of 2.5×10^7 s^{-1}. The triplet–triplet transfer rate is identical when measured in a 2-methyltetrahydrofuran glass at 77 K and is thus independent of intramolecular motions. Studies of triplet–triplet transfer in a series of related carotenoporphyrins has suggested that the electron-exchange interactions leading to transfer are mediated by the π-electrons of the linkage joining the two chromophores. This conclusion is supported by molecular orbital calculations. As might be expected, carotenoporphyrin **8**, which features relatively good spatial overlap between porphyrin and carotenoid orbitals, also demonstrates rapid triplet–triplet transfer which is not dependent on intramolecular motions.

Conclusions

This Account illustrates how the design of molecular mimics of photosynthetic reaction centers requires careful attention to the selection of the spectral and excited-state properties of the chromophores, the redox properties of donors and acceptors, and the nature of the linkages joining the various moieties. The structure of natural reaction centers coupled with fundamental theories of electron and energy transfer provides a framework for the initial design and fine-tuning of the molecular devices. Finally, as emphasized in this Account, a key feature in the mimicry of natural photosynthesis is the exploitation of multistep electron

and energy transfer strategies, which are a function of the supramolecular architecture of the device, rather than simple pairwise interactions of linked donors and acceptors.

Of course, photosynthetic reaction centers are complex entities whose study poses questions and supplies answers in many areas of biology and chemistry. Although the artificial reaction centers discussed above begin to address only a few facets of reaction center structure and function, their availability opens up new avenues for research. Consider, for example, that the polypeptides in a bacterial reaction center not only arrange six cyclic tetrapyrroles, one carotenoid, two quinone molecules, and a ferrous ion in an optimal geometry for energy and photoinitiated electron transfer but also, at the same time, compress these cofactors into a compact, membrane-spanning package. This unit not only recognizes the membrane to the extent necessary to orient itself properly but also provides mechanisms for chemically coupling the charge-separated states to the aqueous phases on either side. Attaining the supramolecular organization necessary to interface an artificial reaction center with biological transmembrane energy transduction processes is a piquant challenge.

Interfacing artificial reaction centers to nonbiological structures is an equally challenging problem. Researchers are beginning to investigate the incorporation of such molecules into ordered assemblies such as liposomes, micelles, polymers, monolayers (which may be deposited on conducting substrates), and self-assembled domains spanning the distance between nanofabricated electrodes. The use of scanning probe techniques to electrically address single molecules which have been optically excited is also being explored. Research in these areas should help define parameters of optoelectronic devices at the molecular level such as their thermodynamic energy conversion efficiency under chemical or electrical load. Indeed, it seems clear that there is no intrinsic barrier to employing the basic principles of photosynthesis in the design of synthetic molecular devices whose versatility and performance could equal or exceed those of their natural progenitors.