# Photoinduced Electron Transfer in Supramolecular Systems for Artificial Photosynthesis

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## I. Introduction

The importance and complexity of electron-transfer reactions in Nature have lead many researchers to look for ways to study the fundamental chemistry of these processes in simplified model systems. A significant part of this effort has been devoted to the study of photoinduced charge separation reactions as a means of capturing and storing solar energy. A long-term goal of this research is to develop an understanding of photoinitiated-electron-transfer reactions that is sufficiently advanced to enable one to design laboratory systems for the conversion of solar energy into chemical potential. A vital part of this research is the design and synthesis of complex molecular systems which are comprised of electron donors and acceptors that mimic the charge separation function of photosynthetic proteins. These complex molecules are usually referred to as supramolecular systems.[1]

Synthetic models have been prepared in which the dependencies of electron-transfer rate constants on donor–acceptor distance and orientation, free energy of reaction, and electronic coupling have been studied. The degree of success with which these models have been able to isolate these factors varies widely. At this time a relatively small number of model systems possess sufficient structural constraints to control both the distance and orientation between a donor and an acceptor. However, this situation is constantly improving, and the thrust of recent work is to produce supramolecular systems with increasingly better characterized structures. Molecules for which the donor–acceptor distances and orientations are accurately known provide a useful vehicle for understanding mechanisms of electron transfer.
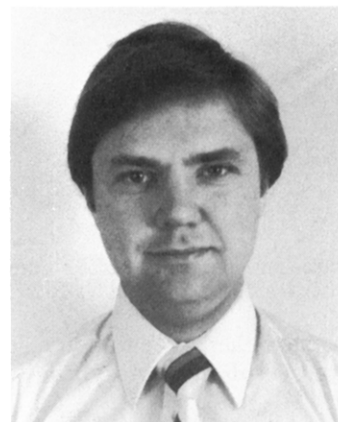
Michael R. Wasielewski was born in Chicago, IL, in 1949. He entered the College of the University of Chicago as an undergraduate in 1967, majored in chemistry, and graduated Phi Beta Kappa in 1971. He began graduate studies in chemistry at the University of Chicago in 1971 under the direction of Prof. Leon M. Stock, where he received an M.S. in 1972, followed by a Ph.D. in 1975. He spent 1975 performing postdoctoral research with Prof. Ronald Breslow at Columbia University. He then joined the scientific staff of the Chemistry Division at the Argonne National Laboratory, where he is currently a Senior Chemist and a principal investigator of artificial photosynthesis and molecular electronics research programs. Wasielewski's research interests focus on photochemistry, photochemical electron transfer reactions, the properties of radical ion pairs, ultrafast optical and magnetic resonance techniques, molecule-based optoelectronics, and the biophysics of proteins involved in the primary processes of photosynthesis. Wasielewski recently received the University of Chicago Award for Distinguished Performance at the Argonne National Laboratory.

The purpose of this review is to discuss work in this field that has appeared since 1987. The review will focus primarily on supramolecular systems that utilize porphyrins in their electron-transport schemes. In addition, some reference will be made to work being done with small-ring aromatic donors and acceptors. The very exciting and productive work being done on the use of photoactive transition metal complexes in supramolecular systems will not be covered. Several extensive reviews exist that discuss work performed in each of these subfields in the decade prior to 1987 during which the foundations for much current thinking in this field were laid.[1-4]

## II. The Photosynthetic Apparatus

To clarify the key features of photosynthetic systems that are relevant to the design of supramolecular systems for the capture and storage of solar energy, this section will be devoted to a short summary of recent
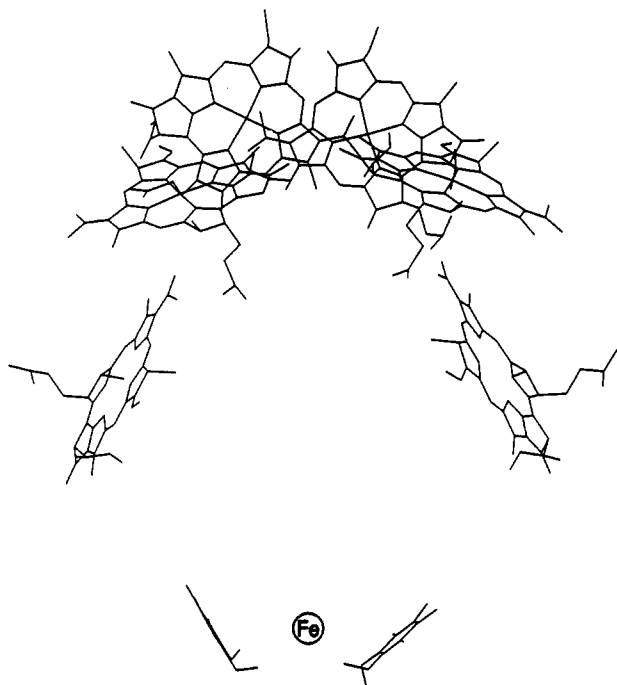
**Figure 1.** Structure and placement of the chromophores within the reaction center from *Rb. sphaeroides* R-26 [ref 9].

work on the primary charge separation reactions of both bacterial and green plant photosynthesis.

## A. Bacterial Photosynthesis

Charge separation in photosynthetic organisms occurs in membrane-bound pigment protein complexes known as reaction centers. The reaction center proteins from a number of purple bacteria have been isolated in pure form over the past 20 years.[5] A wide variety of physical techniques, most notably fast transient optical spectroscopy[6] and magnetic resonance,[7] have been used to determine both the thermodynamics and kinetics of photoinduced electron transfer within these proteins.

A great deal of speculation as to the precise placement of the various chromophores within the reaction center relative to one another and to the protein structure was laid to rest in 1984 with the crystallization and subsequent X-ray diffraction analysis of the structure of the reaction-center protein from *Rp. viridis*.[8] In the intervening years the structure of the reaction center from *Rb. sphaeroides* has also appeared.[9,10] The structures of both reaction centers are very similar. Since the vast majority of physical data has been obtained on the protein from *Rb. sphaeroides*, the structure of this protein is of particular interest. Figure 1 shows the chromophore placement within the *Rb. sphaeroides* reaction center. The chromophores are arranged within the protein along a $C_2$ symmetry element. Two of the BChl *a* molecules are closely associated spatially and electronically to form the primary donor P865. Another pair of BChl *a* molecules are placed in edge-to-edge positions relative to P865. These molecules in turn are adjacent to a pair of BPh *a* molecules, which in turn are next to the quinones.

Although many important details of the electron-transfer reactions occurring within bacterial reaction centers remain to be resolved, several fundamental features concerning rates and energetics of these reactions have been characterized. The primary electron

donor of bacterial reaction centers consists of a pair of BChl molecules that are strongly coupled electronically.[11] This coupling and the interaction of the dimer with the surrounding protein results in a red shift of the lowest energy transition in the optical absorption spectrum of the dimer by about 1300 cm$^{-1}$. Thus, excitation of any of the macrocyclic chromophores within the reaction-center protein results in energy transfer to the dimer in <150 fs.[12] Excitation of the dimer results in unity quantum yield electron transfer from the dimer to BPh$_L$ in 2.8 ps.[12-14] Only the chromophores on the L side of the protein are photochemically active. The reasons for this are subtle and remain a focus of current research.

Some transient absorption experiments suggest that reduction of BPh$_L$ proceeds smoothly without the appearance of a distinct intermediate reduced state on BChl$_L$, while more recent reports suggest that reduction of BChl$_L$ does indeed occur,[15,16] but that the rapid kinetics of the subsequent electron transfer from BChl$_L^-$ to BPh$_L$ precludes a significant buildup of the BChl$_L^-$ intermediate. In theory, it is possible that both mechanisms function simultaneously.[17] If the quinones within the reaction center are either reduced or removed prior to excitation, the BChl$_2^+$–BPh$_L^-$ state possesses a 12-ns lifetime.[18] Charge recombination within BChl$_2^+$–BPh$_L^-$ gives a significant yield of the triplet state of BChl$_2$.[19] This triplet state results from singlet–triplet mixing within the BChl$_2^+$–BPh$_L^-$ radical pair. This radical pair state has been characterized as one in which the electron–electron exchange coupling between the radicals is quite weak, about 0.001 cm$^{-1}$.[20] Thus, very rapid photoinduced charge separation produces an intermediate in which the back electron transfer is sufficiently slow to insure a high quantum yield of charge separation.

Electron transfer from BPh$_L$ to $Q_A$ occurs in about 200 ps to yield the BChl$_2^+$–$Q_A^-$ radical pair which, in the absence of $Q_B$, lives for about 100 ms before charge recombination occurs.[18] Thus, in only two or possibly three sequential electron-transfer events the reaction-center protein has separated charge across 35 Å with a high quantum yield to give a long-lived intermediate. When $Q_B$ is present, electron transfer from $Q_A$ to $Q_B$ occurs in about 0.1 ms to yield a stable, reduced species which ultimately stores the energy that is used to drive the subsequent biochemical reactions.

## B. Green Plant Photosynthesis

The primary charge separation apparatus within green plants is more complex than that found in photosynthetic bacteria. In addition, the reaction-center proteins within chloroplast membranes are more tightly bound both to the membrane and to antenna proteins which funnel light energy into the reaction center. At this time our knowledge of the detailed electron-transfer processes that separate charge within green plants is limited primarily by the lack of sufficiently pure reaction-center preparations.

Green plants contain two different reaction centers, so-called photosystem I, PS I, and photosystem II, PS II. PS I provides the reducing potential necessary to run the carbon fixation biochemistry within the plant, while PS II provides the oxidizing equivalents necessary to split water into protons and oxygen. The primary

photochemistry of PS I is known to involve a primary donor called P700 which may be a Chl dimer.[21] Excitation of P700 results in reduction of a Chl-like electron acceptor called $A_0$ in about 10 ps.[22] The electron then moves from $A_0^-$ to a secondary acceptor $A_1$ in 40 ps.[23] EPR measurements suggest that $A_1$ may be a menaquinone.[24] When the Fe-S clusters which function as subsequent electron acceptors in PS I are reduced prior to excitation, the lifetime of the $P700^+$-$A_1^-$ radical pair is on the order of 1 ms. Very little is known about the structure of these acceptors.

Our knowledge of the PS II reaction center has improved substantially over the past several years. A purified protein complex consisting of the $D_1$, $D_2$, and cytochrome b-559 polypeptides has been isolated and shown to be the reaction center of PS II.[25] Recent work has characterized both the electron-transfer kinetics and magnetic resonance properties of radicals produced within this protein complex following excitation.[26,27] The primary electron donor of PS II, P680, which most likely consists of a pair of Chl $a$ molecules that are weakly electronically coupled, transfers an electron to Pheo $a$ in 3 ps.[28] This electron transfer occurs without producing intermediate reduction products on the accessory Chl $a$ molecules that live longer than 1 ps in the protein complex. The resultant $P680^+$-Pheo $a^-$ radical pair lives for 35 ns before charge recombination occurs to give a substantial yield of the triplet state of P680.[26] The reaction-center complex does not bind quinones well, so that at this time the kinetics of electron transfer to a quinone acceptor are uncertain. However, in more intact PS II preparations, Holzwarth et al.[29] have measured a 500-ps lifetime for the reduction of the primary quinone acceptor by Pheo $a^-$ in the reaction center. Thus, in PS II the electron donor-acceptor molecules and their electron-transfer kinetics appear to be analogous to those found in purple photosynthetic bacteria. As mentioned above, the oxidizing potential generated in PS II is used to oxidize water to oxygen through the catalysis of a Mn-containing protein which is bound to the RC. The nature of this catalysis is uncertain and remains under active investigation.

## III. Electron-Transfer Theory

In the following section a brief discussion of electron-transfer theory is presented. The purpose of this short exposition is to provide the basis for a discussion regarding the features of theory that are addressed by current supramolecular systems for photoinduced charge separation.

### A. Classical Theory of Electron Transfer

Using absolute reaction rate theory, Marcus gives the rate constant, $k$, of electron transfer in terms of a free energy of activation $\Delta G^*$ for the reaction:[30-34]

$$k = \rho(r)Z \exp(-\Delta G^*/RT) \quad (1)$$

where $\rho(r)$ is the probability for the electron transfer to occur normalized to the number of times the molecule acquires the correct nuclear configuration to pass through the intersection of the potential energy surfaces of the reactants and products and $Z$ is either the collision frequency in a bimolecular reaction or the vibrational frequency in a monomolecular (intramolecu-

lar) reaction. At large values of $r$, the value of $\rho$ is assumed to depend exponentially on $r$. When the molecular vibrations of the donor and acceptor required for the molecules to reach the transition state are assumed to be harmonic oscillators, the free energy of activation takes on the well-known quadratic dependence on the $\Delta G^0$ of the reaction:

$$\Delta G^* = (\lambda + \Delta G^0)^2/4\lambda \quad (2)$$

where $\lambda$ is the total energy of nuclear reorganization required for the system to reach the intersection. One of the key features of eq 2 is that it predicts that the rate of an electron-transfer reaction will slow down when the free energy of reaction becomes very large. This is the so-called "inverted region". The total reorganization energy $\lambda$ is usually divided into contributions from oscillators within the molecules, $\lambda_i$, and solvent oscillators, $\lambda_s$.[31] The value of $\lambda_i$ may be calculated from the force constants for all the molecular vibrations in both the reactant and product, while $\lambda_s$ can be determined by application of the dielectric continuum model of a solvent. The simplest application of this model assumes that the donor and acceptor are spherical with radii $a_1$ and $a_2$, lying a center-to-center distance $r$ apart. If $\epsilon_{op}$ and $\epsilon_s$ are the optical and static dielectric constants of the medium, respectively, Marcus has shown that

$$\lambda_s = (\Delta e)^2 (1/2a_1 + 1/2a_2 - 1/r)(1/\epsilon_{op} - 1/\epsilon_s) \quad (3)$$

Equation 3 predicts that the rate of the electron transfer will depend strongly on the distance between the donor and acceptor in the intermediate distance regime, as well as the dielectric properties of the medium.

Hush has developed a similar treatment of electron transfer.[35,36] In the Hush model electron density is gradually transferred from the donor to the acceptor at the same time that the nuclear motion occurs. However, the predicted dependence of electron-transfer rate on free energy is the same as that given above.

### B. Quantum Mechanical Theory of Electron Transfer

Quantum mechanical treatments of electron transfer begin with the golden rule formulation for the probability of a transition between two states, which is derived from the original treatment of Landau and Zener.[37,38] Thus, the rate of electron transfer is expressed as a function of the degree of electronic coupling $V^2_{DA}$ between the donor and the acceptor:

$$k = (2\pi/\hbar)V^2_{DA}(FC) \quad (4)$$

where FC is the Franck-Condon factor, i.e., the sum of products of overlap integrals of the vibrational and solvent wave functions of the reactants with those of the products. These Franck-Condon factors are weighted for the Boltzmann population of the vibrational energy levels. The vibrations are usually treated quantum mechanically, while the treatment of the solvent remains classical, thus the theory is designated semiclassical. In the high-temperature limit, Marcus[30] has shown that this treatment yields the following expression, which involves the electronic coupling matrix element $V^2_{DA}$, the free energy of reaction $\Delta G^0$, and the

total nuclear reorganization energy $\lambda = \lambda_i + \lambda_s$:

$$k = (2\pi/\hbar)V^2_{DA}[1/(4\pi\lambda RT)^{1/2}]\exp[-(\Delta G^0 + \lambda)^2/4\lambda RT] \quad (5)$$

The distance dependence of an electron-transfer reaction can be divided into the distance dependence of the electronic coupling matrix element $V^2_{DA}$ and that of $\lambda$. When the internal molecular vibrational frequencies of the donor and acceptor are not influenced by the distance between them, the distance dependence of $\lambda$ is limited to that involving the solvent, $\lambda_s$ as given by eq 3. In covalently-linked donor–acceptor molecules the vibrational frequencies of the donor and acceptor themselves may be influenced by changes in the structure of the intervening molecular spacer.

Kakitani and Mataga[39-41] have published a number of recent papers describing an alternative theory that imposes some structure on the solvent. They take into account the possibility that the vibrational frequency associated with solvent molecules coordinated to the reactants in the neutral state may be considerably smaller than that in the charged state. They derive separate energy-gap laws for charge-separation, charge-shift, and charge-recombination reactions. In the case of a neutral initial state, charge-separation rate constants increase steadily until they reach a plateau. The rates remain high for large negative free energies of reaction. For charge-shift and charge-recombination reactions that rates begin to slow as the free energy of reaction becomes increasingly negative, with the charge-recombination reactions exhibiting the steepest inverted region.

The preceding discussion points out that the rates of electron-transfer reactions can be strongly influenced by the nature of the medium intervening between the donor and the acceptor. A broad definition of the medium includes the bonds of the spacer molecules joining covalently-linked donors and acceptors. The $\sigma$ and $\pi$ bonds of the spacer moiety will determine the dependence of $V^2_{DA}$ on distance.[42] This dependence will also be modulated by an additional dependence on donor–acceptor orientation.[43,44]

The electronic coupling matrix element $V^2_{DA}$ is an exceptionally difficult quantity to calculate accurately. This results from the fact that at long distances the electronic wave functions of D and A are very sensitive to the asymptotic properties of the basis functions used to construct the wave functions. What seem like relatively small inaccuracies in the wave functions at distances close to the donor and acceptor become magnified at long distances.

At long distances it is assumed that the amplitudes of the wave functions are decreasing exponentially, and thus, the magnitude of $V^2_{DA}$ is also decreasing exponentially as a function of distance. Detailed molecular orbital calculations by Larsson,[45-47] Beratan and Hopfield,[48] and most recently by Closs and Morokuma[44] bear out this point. These calculations show that the overall distance dependence of $V^2_{DA}$ remains exponential and is modulated by the geometry of the intervening molecular spacer group. Thus, one can write

$$V^2_{DA} = (V^0_{DA})^2 \exp[-\alpha(r - r_0)] \quad (6)$$

where $(V^0_{DA})^2$ is the electronic coupling element at the contact distance $r_0$ for the donor and acceptor. The

orientation dependence of the electronic coupling is included in $(V^0_{DA})^2$.

A complete quantum mechanical description of electron transfer must include not only the internal vibrations of the nuclei in the donors and acceptors, but additionally those of the surrounding medium. The complexity of the problem increases substantially. The theoretical approaches to this problem originate with the 1950 paper of Huang and Rhys[49] which describes the effect of electron–phonon coupling on the band shapes of electronic transitions. This theory was employed and elaborated by Levich and Dogonadze to describe electron transfer reactions.[50] In order to make the problem tractable Hopfield, Jortner, and Van Duyne and Fischer independently showed that the large number of vibrational modes of both the donor–acceptor system and the solvent are often reduced to two principal vibrations, a high-frequency mode involving the donor and/or acceptor and a low-frequency mode which is most often, but not exclusively, associated with the solvent.[51-54] The relative contribution of high- vs low-frequency vibrational modes to the electron-transfer rate are reflected principally in the temperature dependence of the electron-transfer rate constant.

Empirically, the dependence of electron-transfer rate constant on donor–acceptor distance in a specific solvent takes on the form given by eq 7:

$$k(r) = k_0 \exp[-\alpha(r - r_0)] \quad (7)$$

where $r$ is the donor–acceptor distance, $r_0$ is the distance, usually van der Waals contact, at which the largest rate occurs, and $\alpha$ is a constant. The largest rate $k_0$ is usually thought to be close to the frequency of a single molecular vibration, $10^{13}$ s$^{-1}$. The value of $\alpha$ usually varies between 1–2 Å$^{-1}$ and is one of the principal pieces of information that can be derived from systematic studies of the distance dependence of electron transfer rates.

Electrons need not transfer from a donor to an acceptor via the direct overlap of their respective electronic wave functions. As mentioned in the discussion above, the molecules that reside between the donor and the acceptor may influence the rate of donor–acceptor electron transfer by means of mixing their electronic states with those of the donor and acceptor. In the case where the donor and acceptor are covalently-linked, this consideration becomes especially important. Several virtual states of the spacer molecule may contribute to the overall electronic configuration of the donor–spacer–acceptor system. The degree to which each of these virtual states contributes to the overall electronic structure of the system is determined by the magnitude of the electron-exchange interaction involving these configurations. These concepts originate with the work of Kramers[55] and have come to be known as "superexchange". Exchange interactions between radical centers within radical pairs separated by saturated bonds were addressed as early as 1950 by Anderson.[56] McConnell has used a theoretical treatment involving superexchange to explain the rates of electron transfer from aromatic radical anions to a second neutral aromatic molecule in which both species are linked by a saturated hydrocarbon chain.[57] Kuznetzov and Ulstrup[58] have considered the effect of bridging molecule states which lie both higher and lower than the initial and final donor–acceptor states on the electron-transfer

rate. They find that the preexponential factor in the rate expression for electron transfer will decrease by a power law as the energy gap between the higher energy bridge states and that of the initial state increases. This is due to the appearance of energy-gap denominators in their rate expressions. For example, these denominators will increase as the number of saturated (high-energy bridging states) bonds between $\pi$ donors and acceptors increase. Recent calculations by Larsson[45-47] and by Beratan and Hopfield[48] have shown that the participation of high-energy intermediate states of the bridging molecules dominate the electron-transfer matrix elements for a variety of systems containing either completely-saturated or partially-saturated bridges. Larsson has shown that electron transfer via superexchange may be important in electron transfer through peptides.[46] More recently, Marcus,[59,60] Bixon et al.,[17,61,62] and Friesner[63] have discussed at length the possible role of superexchange in determining the rate of charge separation in photosynthetic reaction centers. Friesner[63] has summarized many of these issues.

The magnitude of the superexchange contribution to the total donor–acceptor electronic coupling will be proportional to both donor–acceptor orbital overlap and the overlap of orbitals of the spacer with those on the donor and the acceptor and inversely proportional to the energy gap between the initial donor–acceptor state and the virtual state involving the spacer. The terms "through-space" and "through-bond" interactions are often employed in the literature. A through-space interaction is defined as a term contributing to $V^2_{DA}$ involving only direct overlap of the wave functions of the donor with those of the acceptor. Indirect through-bond interactions between the donor and the acceptor are defined as terms contributing to $V^2_{DA}$ which involve participation of the wave functions of the spacer molecules between the donor and the acceptor. These spacers may be the covalent linkage or the solvent. Thus, the term "through-bond interaction" is synonymous with superexchange.

## IV. Supramolecular Systems for Photoinduced Charge Separation

Simple covalently-linked donor–acceptor systems have been employed to study the dependence of electron-transfer rates on free energy of reaction, donor–acceptor distance and orientation, and solvent. In general, molecules that possess more well-defined structural relationships between the donor and acceptor yield more subtle insights into electron-transfer reactions.

The collaborative efforts of Paddon-Row, Warman, and Verhoeven have continued to yield important insights into photoinduced electron transfer across rigid hydrocarbon bridges of varying length. Smit et al.[64] have presented microwave conductivity measurements on the charge recombination reaction in the ion pairs produced within compounds 1a–d in saturated hydrocarbon solvents. Two recombination pathways are observed: a direct transition to ground state, which is temperature and solvent independent, and an indirect route via thermal activation back to the locally excited state of the dimethoxynaphthalene donor. This pathway proves to be dependent on the polarizability of the solvent.



1a



1b



1c



1d
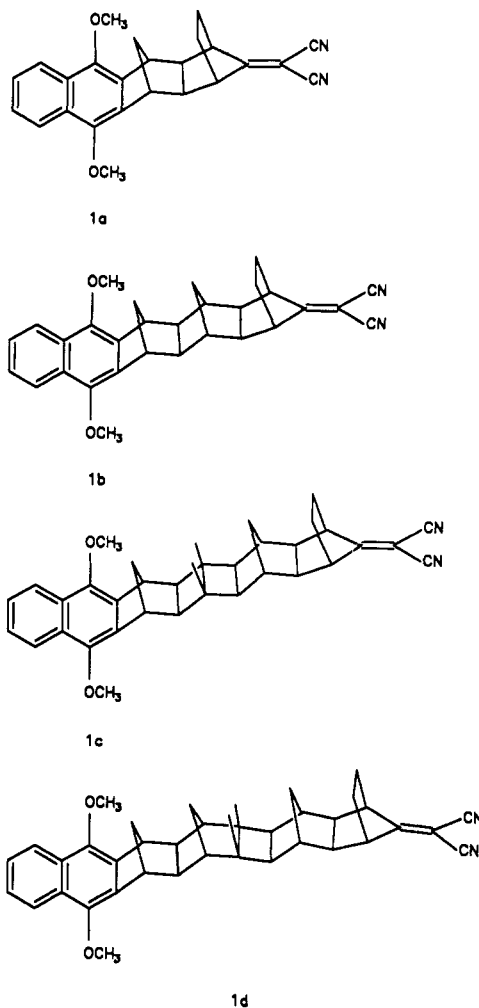
Oliver et al.[65] showed that electron-transfer rates through the hydrocarbon bridge in molecules that are structurally related to 1a–d depends strongly on the cis or trans nature of the carbon–carbon $\sigma$ skeleton. Molecules 1b and 1c can be compared with their isomers 2a and 2b, respectively. The electron-transfer rate constants in the molecules containing all trans



2a



2b
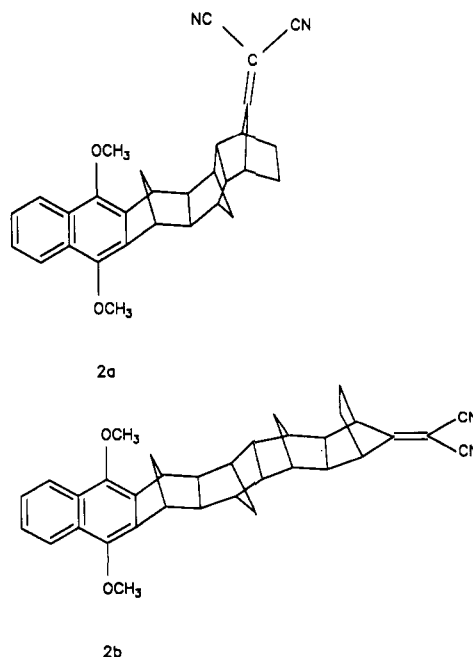
bonds between the donor and acceptor are about 1 order of magnitude faster than those in which an s-cis kink is introduced into the spacer structure. The synthesis and X-ray crystal structures of **2a** and **2b** have been reported subsequently.[71] The electron-transfer rates follow the all-trans rule for maximum through-bond interaction that have been recognized for many years in the magnetic resonance field. The transmission of spin information via saturated carbon frameworks has been examined in great detail for many years. The pioneering work of Karplus[66] showed that nuclear-nuclear spin-spin couplings depend strongly on the distance and orientation of the C–C and C–H bonds in a saturated carbon framework. Similarly, a great deal of effort has gone into characterizing the electron-nuclear coupling parameters (hyperfine splittings) that derive from the interaction of the unpaired electron spin at a radical center in an organic molecule with protons separated from the radical center by several saturated bonds.[67-70]

Penfield et al.[72] and Oevering et al.[73] have studied the electronic absorption and emission spectra of several donor-acceptor compounds including compounds **1a-d** and homologues with longer spacers. They find that sufficient electronic interaction occurs across bridges with a length up to six $\sigma$ bonds to cause detectable perturbations of the electronic absorption spectra. In shorter spacer homologues this leads to the appearance of intramolecular charge-transfer absorptions. Charge-transfer emission bands are also observed. Using these spectra they find that the electronic matrix element for charge recombination to ground state is 850 $cm^{-1}$ for a 3-bond separation and 17.6 $cm^{-1}$ for a 10-bond separation. Also, the rate of recombination is proportional to $V^2_{DA}$ as predicted by eq 4.

Verhoeven's group has also examined a series of rod-shaped fluorescent donor-acceptor molecules of the type shown in **3**.[74] These molecules contain an anilino group as the donor and substituted ethylene groups as acceptors. The emissive properties of these molecules show that the electronic coupling between the donor and the acceptor is sufficient to promote high quantum yield charge separation following excitation. The charge-transfer state displays very strong fluorescence. The fluorescence maximum is very sensitive to solvent polarity.

Warman et al.[75] have summarized these investigations of the distance dependence of charge recombination reactions in a variety of solvents for compounds **1a-d**, **2a-b**, and homologues with longer spacers using the time-resolved microwave conductivity method. They find that $\alpha$ in eq 7 is 0.88 for these compounds. In addition, they find that recombination to ground state proceeds via the two pathways discussed above. Moreover, they find that the energy of the charge-separated state is sensitive to changes in solvent. This occurs because all the solvents that they examined possess low static dielectric constants. Since both the energy of the charge-separated state and the solvent reorganization energy depend on $1/\epsilon_{op} - 1/\epsilon_s$, and since $\epsilon_{op} \approx \epsilon_s$ in the solvents examined, the rate constants show significant solvent variations.
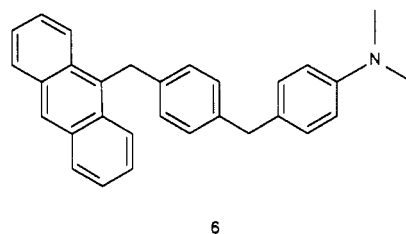
In an interesting and unusual extension of charge-separation chemistry involving saturated hydrocarbon spacer groups Schuddeboom et al.[76] have measured the

molecular hyperpolarizability, $\beta$, of molecules **3–5** using second-harmonic generation. The values of $\beta$ are sim-



ilar to those obtained for more conventional $\pi$-conjugated molecules such as p-nitroaniline. The authors conclude that the nonnegligible value of $\beta$ is evidence of significant electronic interaction between the donor and acceptor through the saturated bonds. Since the donor and acceptor within these molecules are not conjugated, the transition dipole moment makes a small contribution to $\beta$. This decrease in $\beta$ is made up for by the large difference between the ground- and excited-state dipole moment that exists in these molecules.
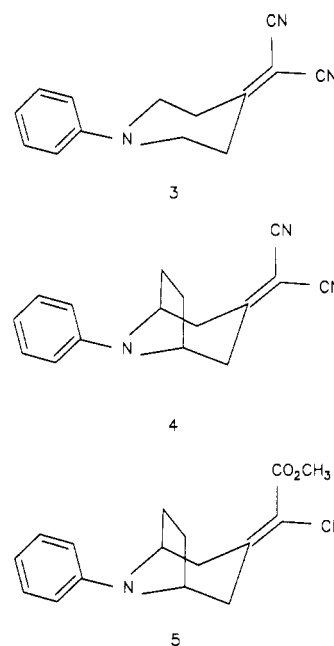
Heitele et al.[77] have presented solvent and temperature dependence data on the compound **6**. This de-



tailed study also considers how the free energy of the charge-separated state depends on solvent. It is concluded that solvents of moderate polarity, such as n-butyl acetate result in an adjustment of the free energy such that the photoinduced-electron-transfer rate remains fast and the back-electron-transfer rate slows.

The collaborative efforts of Miller and Closs have continued to produce key insights into the mechanism of electron-transfer reactions. Although their recent studies involve only charge-shift reactions and not photoinduced-charge-separation reactions, it is nevertheless appropriate to discuss their results in the context of electron transfer involving aromatic donors and acceptors. Closs et al.[78] have summarized their rate vs free-energy work on donor-steroid spacer-acceptor molecules of structural type **7**. Also included in this paper are their results on the distance dependence of electron transfer from the biphenyl radical anion to naphthalene across both decalin, **8**, and cyclohexane,
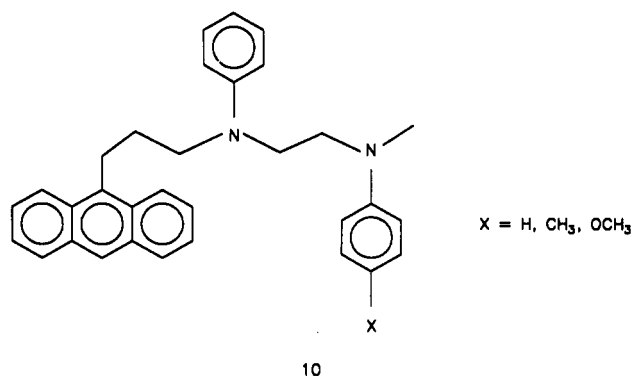
7

8

9

X = H, CH₃, OCH₃

10

11
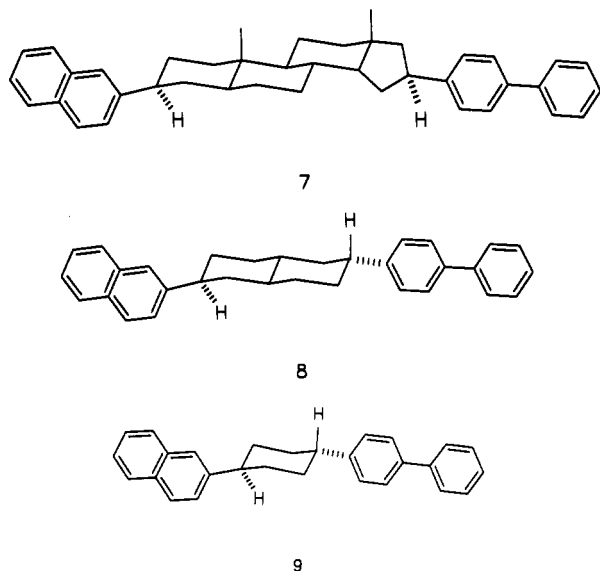
**9, spacers.** They found that the rate vs distance data were clearly interpretable only when the axial–axial, axial–equatorial, and equatorial–equatorial isomers of the cyclohexanes and decalins were considered separately. This data shows that donor–acceptor orientation modulates the apparent distance dependence of electron-transfer reactions to a significant degree. Once again an $\alpha$ value of about 1.1 was obtained for these systems. Miller[79] and Closs and Miller[80] presented two other summaries of these results.

Johnson et al.[81] showed that hole transfer from the biphenylyl cation radical to naphthalene across the same spacers depicted in 7–9 yields almost exactly the same distance dependence as electron transfer. In this case $\alpha$ is also 1.1. The authors conclude that the somewhat unexpected agreement between $\alpha$ determined for both hole and electron transfer is due to equal contributions of $\sigma^*$ orbitals of the spacer transmitting the electronic coupling for electron transfer, while the filled $\sigma$ orbitals of the spacer transmit the coupling for hole transfer. A question remains as to the generality of this result.

Liang et al.[82] have investigated the temperature dependence of the electron-transfer rate from biphenylyl radical anion to naphthalene in structure 7. They found that the rate as a function of temperature could be accounted for by considering the temperature dependencies of $\Delta G^0$ for the reaction and of the solvent reorganization energy $\lambda_s$. Liang et al.[83] extended this work into the inverted region by investigating electron transfer from biphenylyl radical anion to benzoquinone and 2-chlorobenzoquinone using the steroid spacer shown in 7. In both cases the rate constants are almost independent of temperature over a −94 to 100 °C range. The temperature independence provides evidence for the contribution of high frequency vibrational modes to the quantum mechanical picture of electron transfer. These results cannot be explained with classical theory.

Yang et al.[84] have shown that rates and yields of intramolecular exciplex formation and electron transfer in polychromophoric arylamines may be modified dramatically by varying the nature of the aryl or the amino group as well as the nature and length of the chain between the two groups. In trichromophoric system 10 containing one aryl and two amino groups, photoin-

duced electron transfer may be effected between the aryl group and one of the amino groups in fairly nonpolar solvents. The authors attribute this to an exciplex-induced electron-transfer event. Formation of the initial exciplex between the anthracene moiety and the proximate aryl amine results in polarization of the solvent surrounding the entire molecule. Electron transfer between the anthracene and the terminal aryl amine is then facilitated in this more "polar" solvent. Thus, these molecules show that local changes in the polarity of the environment surrounding an electron donor–acceptor pair can have a dramatic effect on electron-transfer rate, even though the bulk solvent polarity is rather low.

Wasielewski et al.[85] have reported the preparation and photochemistry of 2-($N$,$N$-dimethylamino)-5,14-ethanopentacene (11). This molecule possesses an-

thracene and $N$,$N$-dimethylaniline chromophores rigidly positioned across a bicyclo(2.2.2)octadiene spacer. The fluorescence spectra of 11 exhibit solvent polarity dependent red shifts of their emission maxima similar to those observed for the anthracene–$N$,$N$-dimethylaniline exciplex. However, the cage structure of 11 prevents large amplitude motions of the anthracene relative to the $N$,$N$-dimethylaniline before and after excitation. The quantum yield of the broad, red-shifted fluorescence decreases as the solvent polarity increases. The analysis of this shift suggests that the emitting species exhibits the dipole moment of an ion pair. Transient absorption measurements show that electron transfer from the $N$,$N$-dimethylaniline to the lowest excited singlet state of anthracene occurs in solvents with polarity as low as toluene. The exciplex-like luminescence possesses a lifetime that is the same as the recombination time of the anthracene anion–$N$,$N$-dimethylaniline cation pair. Excited 11 thus possesses a duality of properties commonly attributed to both an exciplex and a radical ion pair.
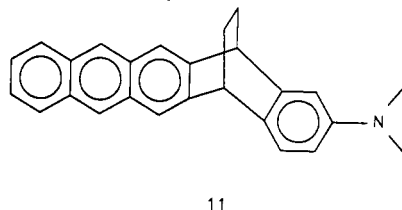
Rettig et al.[86] have also observed charge recombination luminescence from a set of rigid naphthalene–$N$,$N$-dimethylaniline donor–acceptor molecules. The fluorescence spectra of 12 and 13 display strong solvatochromism. The authors conclude that since the coulomb attraction term is somewhat smaller in the

12                                        13
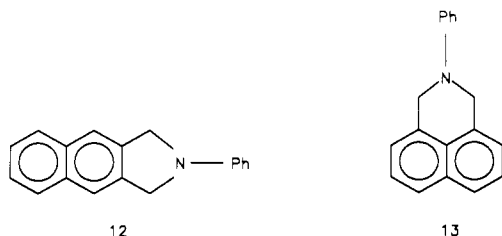
ion-pair produced within 12, the charge-transfer-state energy of 12 is larger than that for 13. The situation is reversed in polar solvents due to increasing solvation arising from the larger mean distance of charge separation in 12. The authors compare the solvatochromic shifts of 12 and 13 with those for the aniline–naphthalene exciplex and conclude that the average distance between the donor and acceptor in polar intermolecular exciplexes is considerably larger than is commonly assumed.

In general, research on photoinduced electron transfer involving macrocyclic electron donors, such as porphyrins and chlorophylls, divides into three categories. First, a number of experiments investigate electron transfer between macrocycles. Since the primary charge separation in photosynthesis occurs between chlorophylls, fundamental questions arise as to the necessity of using donors and acceptors that strongly delocalize the charges once electron transfer has occurred. Second, a larger category of experiments seeks to understand the distance, free energy, solvent, and structural dependencies of both photoinduced-electron-transfer reactions and the subsequent charge-recombination processes. Third, a great deal of work has been done to develop supramolecular systems that mimic the stepwise nature of photosynthetic charge separation. An initial photoinduced charge separation is followed by a sequence of dark electron-transfer steps that proceed at rates sufficiently fast to compete with the series of back-electron-transfer processes. The goal is to achieve a long-lived charge separation with a relatively high quantum yield at the expense of the initial photon energy. While this strategy is relatively simple, the fulfillment of these requirements is often difficult.

McLendon's group has presented data on molecule 14.[87] In 14 the free base porphyrin is isolated from the Fe(III)-containing porphyrin by a phenyl bridge. They



14
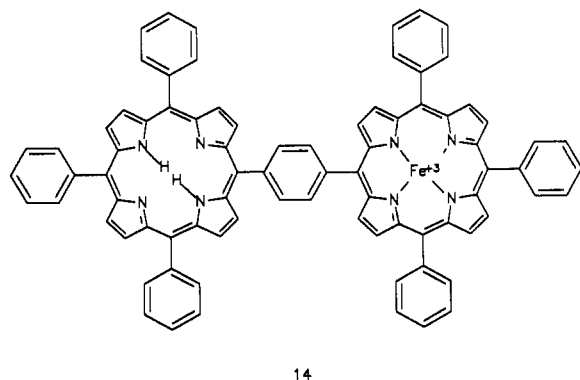
assume that the phenyl bridge spends most of its time perpendicular to the planes of the porphyrins. Electron transfer from the lowest excited singlet state of the free base porphyrin to the Fe(III) in the metalloporphyrin takes place with a rate constant of $2 \times 10^{10}$ s$^{-1}$. Assuming that the 6-Å edge-to-edge distance between the

edges of the porphyrin macrocyclic $\pi$ systems is the relevant distance, McLendon estimates that the magnitude of the electronic coupling is 2.5 cm$^{-1}$. The magnitude of this coupling is not anomalously large, which the authors suggest as evidence that participation of the $\pi$ system of the phenyl spacer in the electron-transfer reaction is weak.

This work has been extended to include a variety of spacers between the two porphyrins that force the macrocycles to adopt preferential orientations of their $\pi$ planes relative to one another.[88] McLendon observes that the minimum rate of electron transfer does not occur when the rings are perpendicular but occurs more closely to the 45° geometry. These results agree with a recent calculation of Cave et al.[89] using the symmetry elements exhibited by porphyrins.

Osuka and Maruyama have reported the preparation of a fixed-distance diporphyrin in which a spirocyclic linkage is used to position the porphyrins in a staggered conformation relative to one another, 15.[90] A single



15
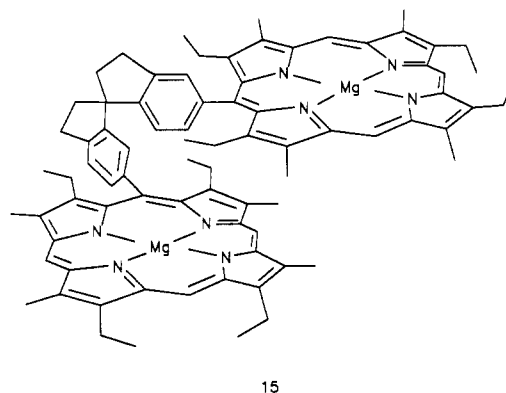
pyrrole ring of one porphyrin overlaps with that of the other porphyrin. The authors utilize this geometry in order to mimic the weak overlap found between the BChl$_2$ primary donor in bacterial reaction-center proteins. The authors report that the Zn$_2$ and Mg$_2$ derivatives display split Soret bands which are indicative of excited-state electronic interaction between the macrocycles. However, they also state that the fluorescence quantum yields of these dimers are not significantly different from those of the corresponding porphyrin monomers. This shows that there are no charge-transfer states formed upon excitation of these molecules. Perhaps future work on these dimers will include studies of monometalated species which might be expected to undergo electron transfer based on energetic considerations.

Johnson et al.[91] have synthesized and studied a fixed-distance symmetric $\Delta^{2,2'}$-bipyrochlorophyllide-$a$ molecule. The molecule, 16, consists of two methyl pyrochlorophyllide-$a$ moieties which share a common vinyl group at the 2-position of each macrocycle. The



16
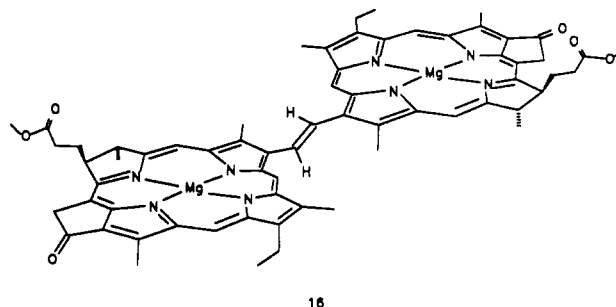
two chlorophylls are trans to one another across the vinyl linkage. The dihedral angle between the plane of each macrocycle and the vinyl linkage is about 50°. The $Q_y$ absorption band of this dimer occurs at 689 nm and is essentially independent of solvent. The band is red-shifted by about 27 nm relative to that of methyl pyrochlorophyllide-$a$. The fluorescence maximum of 16 occurs at 722 nm. This is a red shift of 49 nm relative to methyl pyrochlorophyllide-$a$. The CD spectrum of 16 shows strong, nonconservative bands in the red region. The fluorescence quantum yield, fluorescence lifetimes, and picosecond transient absorbance kinetics all exhibit a very strong dependence on solvent polarity. Possible mechanisms for the polarity dependent increase of the nonradiative decay rate of 16 are considered. The authors favor a mechanism in which mixing low-lying CT states of the dimer into the locally excited state results in enhanced rates of internal conversion.

In further studies of this dimeric chlorophyll Johnson et al.[92] examined the temperature-dependent absorption and emission spectra and line-narrowed fluorescence excitation spectra. The data show that the dimer exists in two conformations A and B and that excited-state relaxation from A into B onsets near the glass transition temperature ($T_g$). Molecular modeling suggests that the two conformations are related by "bicycling" of the two single bonds joined to the vinyl group linkage. At sufficiently low temperature, the solvent dynamics limit the rate of conformational relaxation. For a solvent of sufficiently high polarity (DMF), the excited state of conformation B is shown to access a new radiationless decay channel for $T > T_g$. A CT state is once again suggested to be important for this decay. The model provides a qualitative explanation for the frequency domain, transient absorption, and emission results.

Wasielewski et al.[93] have reported the synthesis and properties of a series of fixed-distance chlorophyll–porphyrin molecules. These molecules consist of a methyl pyrochlorophyllide $a$ moiety which is directly bonded at its 2-position to the 5-position of a 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-($p$-tolyl)-porphyrin. Steric hindrance between adjacent substituents rigidly positions the $\pi$ systems of both macrocycles perpendicular to one another. The macrocycles were selectively metalated with zinc to give the four possible derivatives, 17, 18, 19, and 20. The lowest
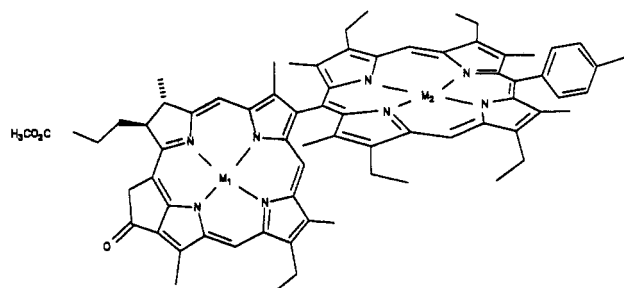


17: $M_1 = M_2 = 2H$,    18: $M_1 = Zn$, $M_2 = 2H$

19: $M_1 = 2H$, $M_2 = Zn$,    20: $M_1 = M_2 = Zn$

excited singlet states of 17 and 18, which are localized on the chlorins exhibit lifetimes and fluorescence quantum yields that are solvent polarity independent and do not differ significantly from those of chlorophyll itself. Compounds 19 and 20, however, display lowest excited singlet state lifetimes and fluorescence quantum

yields that are strongly solvent polarity dependent. Since the fluorescence quantum yield of 20 is proportional to its fluorescence lifetime, nonradiative decay is strongly enhanced for 20 in polar media. However, picosecond transient absorption measurements show no evidence for a distinct ion-pair intermediate. This is consistent with the fact that the energy levels of hypothetical charge separated states within 20, estimated from redox potentials, lie above that of $S_1$, and are therefore virtual states. On the other hand, picosecond transient absorption measurements on 19 show clear evidence of ion-pair formation in butyronitrile in 4 ps. The ion-pair recombines in 43 ps. Compound 19 is the only molecule in the series for which redox potentials in polar solvents predict that an ion-pair state, chlorin$^-$–Zn-porphyrin$^+$, lies below $S_1$ and is therefore a real ion-pair state. Thus, the influence of both virtual and real charge transfer states on donor–acceptor photophysics can be directly observed in similar molecules.

A somewhat different category of dimers can be produced by self-assembly using porphyrins with charges at their periphery. Self-assembly occurs in media that possess a large mole fraction of water and is driven primarily by electrostatics. Hugerat et al.[94] have described both transient absorption and EPR results on one such dimer produced from zinc *meso*-tetrakis(4-trimethylanilinium)porphyrin tetrachloride and copper *meso*-tetrakis($p$-sulfonatophenyl)porphyrin, sodium salt. Varying the central metal results in changes in redox potential for each macrocycle that comprises the dimer. This dimer exhibits biphasic absorption transient decays with lifetimes of about 150 ns and 30 $\mu$s in fluid solution. In addition, in a glass at 77 K this dimer also exhibits an EPR signal that decays biphasically. The long-lived transient is attributed to the triplet state of the zinc porphyrin, while the short-lived signal is assigned to a radical ion pair.

Vergeldt et al.[95] recently examined another series of porphyrin dimers held in a sandwich configuration by electrostatics. An ultrafast, nonexponential absorption increase is observed that is attributed to solvent-controlled, intradimer charge separation. The rise time of the absorption increase is 300 ± 100 fs and agrees reasonably well with the 200-fs longitudinal relaxation time of water. The charge separation is apparently energy gap independent. However, the subsequent much slower charge recombination reaction is energy gap dependent.

Cowan et al.[96] have compared the photochemistry of a stacked dimer with an acceptor cofacial to it and an edge-to-face dimer with an edge-to-face acceptor, 21a,b. Electron transfer to the pyromellitimide occurs about 1000x slower within the edge-to-face system than to the acceptor in the stacked system. The authors argue that the geometry change is crucial. The number of saturated atoms in the linkage between the porphyrin and the pyromellitimide in the edge-to-face system is 9, whereas that in the stacked system is 7. Although through-bond electron-transfer rates should change by about a factor of 100 for the additional two methylene groups, it is not likely that the electron-transfer rate constants approaching $10^{10}$ s$^{-1}$ reported by these workers could be sustained by even the seven methylene-containing linkage. It is more likely that this is a case of direct donor–acceptor overlap.
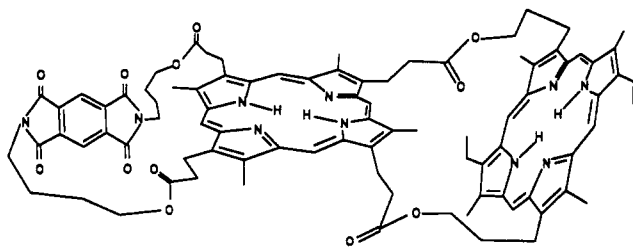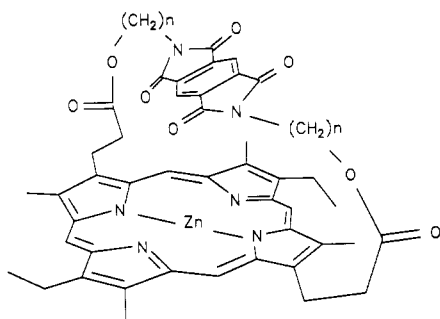
21a
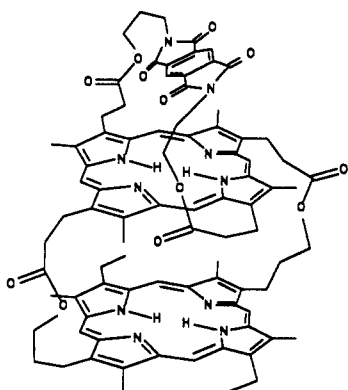


21b

Harrison et al.[97] have presented an extensive study of electron transfer in a series of porphyrin–pyromellitimide sandwich donor–acceptor systems, **22**.



22

These molecules were strapped together with two tethers of varying lengths. The free base, Zn, and Mg derivatives of the porphyrin were studied. Rate constants for both charge separation and ion-pair recombination were measured as a function of solvent polarity and temperature. The rate vs free-energy dependence of the data follows the predictions of semiclassical electron-transfer theory. The total reorganization energy of the electron-transfer reaction is about 0.8 eV. Although the covalent linkages between the donor and acceptor are flexible in these molecules, the average distance between the donor and acceptor increases as the length of the hydrocarbon chain increases. While the authors observe the expected decrease in electron-transfer rate as the distance increases, the trend is solvent dependent, thus precluding an accurate estimate of $\alpha$ for these molecules. Perhaps, one of the most interesting observations by these authors is the dramatic decrease in the rate of photoinduced charge separation in **22**, $n = 3$, as the temperature is lowered through the glass transition of the solvent. The rate vs temperature dependence is approximately sigmoidal with a slow decrease in rate occurring while the temperature is lowered when the solvent is fluid, a rapid

change to a low rate at the glass transition, and a leveling off of the rate vs temperature profile as the temperature is lowered further in the low temperature glass. The authors conclude that restriction of solvent reorientation within the low temperature glass limits the rate of photoinduced electron transfer. Further work on the problem of charge separation in low-temperature glasses will be discussed below.

Osuka et al.[98] have observed a similar distance and/or conformational effect on electron-transfer rate in a conformationally restricted porphyrin–quinone molecule prepared by a photochemical coupling route, **23a,b**.
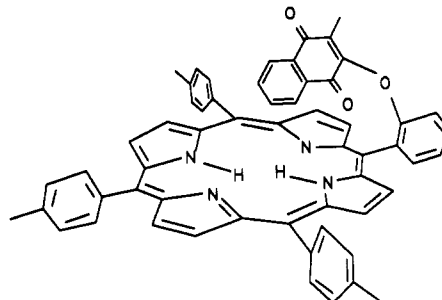


23a
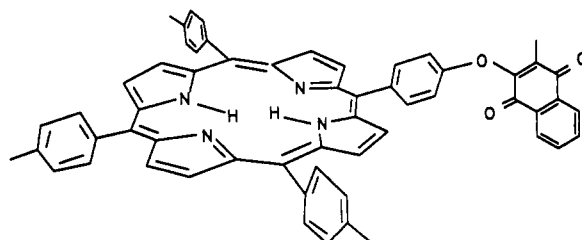


23b

The authors find that the fluorescence emission from the porphyrin is more highly quenched for the ortho-substituted derivatives than for the para-substituted ones. A notable exception is observed for the 3-substituted naphthoquinones. Steric interactions between the 3-substituents on the naphthoquinone and the porphyrin prevent the naphthoquinone from lying cofacially across the porphyrin. For these molecules, the fluorescence quantum yields are higher for the ortho substituents than for the para substituents. The authors attribute this effect to the greater distance between the donor and acceptor in the 3-substituted naphtho derivatives. An alternative explanation is that the orientation of the bonds linking the donor and acceptor are twisted away from the optimum w-planar arrangement in the sterically-hindered molecules. This makes electron transfer through the bonds less efficient for these molecules.

Osuka et al.[99] have summarized the synthesis and fluorescence properties of several quinone-linked and quinone-capped porphyrins. Since saturated linkages several bonds in length are placed between the porphyrins and the quinones, these authors attribute the fluorescence quenching that they observe to a through-space interaction. This is a reasonable conclusion based on the fact that the rates of electron transfer from porphyrins to quinones through saturated bonds drop off by about 1 order of magnitude for each saturated atom. Thus, once four or five saturated atoms link the porphyrin with the quinone, electron transfer through the bonds proceeding from the lowest excited

singlet state of the porphyrin cannot compete kinetically with decay of the porphyrin excited singlet state.

The role of the intervening medium that lies between a donor and an acceptor is beginning to be studied both theoretically and experimentally. In the bacterial photosynthetic reaction center a bacteriochlorophyll molecule lies between the dimeric bacteriochlorophyll donor and the bacteriopheophytin acceptor. It is thought that mixing low-lying ionic states of the intermediate bacteriochlorophyll with those of the donor and acceptor lead to a greatly increased rate of electron transfer via superexchange. In general, molecules possessing low-lying $\pi$ molecular orbitals can contribute strongly to a superexchange mechanism for electron transfer. It is possible that aromatic amino acids, such as tyrosine, phenylalanine, and tryptophan, which lie between an electron donor and an acceptor in proteins, can facilitate electron transfer reactions. However, there are few experimental tests of superexchange in donor–acceptor molecules, especially those involving excited-state electron transfers. The problem lies in producing a series of rigid donor–acceptor molecules in which the effects of changing the orbital energies of the intervening spacer molecule are not convolved with changes in conformation.

One approach to this problem is to produce a series of fixed-distance, rigidly-linked molecules possessing several porphyrins. Sessler and Johnson have published[100] the preparation and characterization of porphyrin–quinone molecules 24 that are hybrids of those
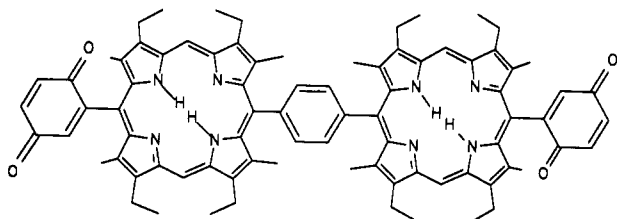


24

reported originally by Dalton and Milgrom[101] and those reported by Tabushi[102] and McLendon.[87,88] As was the case for the monomeric porphyrin–quinone system prepared earlier by Dalton and Milgrom, addition of the quinone directly bonded to the porphyrin meso position results in reduction of the fluorescence quantum yield from 0.1 to be less than $10^{-5}$.

Sessler et al.[103,104] have expanded on this theme and have developed an interesting set of supramolecular donor–acceptor molecules that are designed to mimic the multichromophoric electron-transfer events of photosynthesis, 25a–d. The synthetic and structural properties of these molecules are described in these papers. The molecules are designed to investigate whether porphyrin molecules can act as bridging molecules in superexchange-mediated electron transfer. The photophysics of these molecules are described in a paper by Rodriguez et al.[105] The two porphyrins that comprise these triads are electronically very similar. The only way to distinguish between them is to selectively metalate one of the macrocycles. Reference 105 reports on the photophysics of 25a–d in which the porphyrin either proximal or distal to the quinone is metalated. Selective excitation of one of the macrocycles proves to be a problem with these molecules. Nevertheless, excitation of 25a at 582 nm with 350-fs
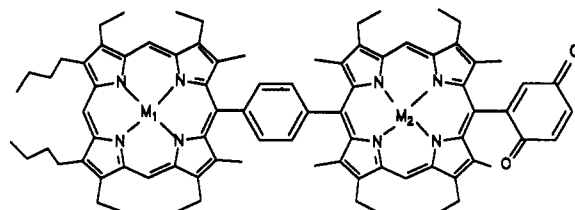


25a: $M_1$ = 2H, $M_2$ = Zn;  25b: $M_1$ = Zn, $M_2$ = 2H
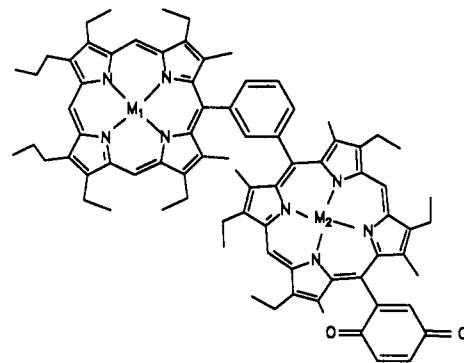


25c: $M_1$ = 2H, $M_2$ = Zn;  25d: $M_1$ = Zn, $M_2$ = 2H

flashes results in observation of two processes. First, a fast charge separation–recombination occurs between the zinc porphyrin and the quinone. Second, a slower 55–75-ps process attributable to deactivation of the free-base excited state to ground state by the presence of the quinone occurs. The time constant for this process is weakly temperature dependent and independent of solvent. This result is interpreted as superexchange-mediated electron transfer from free-base to quinone. Excitation of the distal metalated isomers, 25b and 25d results in behavior that is attributed to electron transfer from free base to the quinone followed by charge recombination that occurs in less than 15 ps.

In another approach to studying superexchange Wasielewski et al.[106] have studied molecules 26-syn, 26-anti, 27-syn, and 27-anti. These molecules utilize
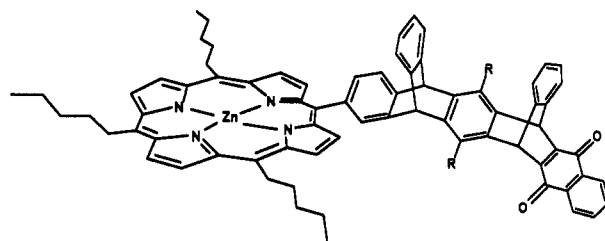


26–syn: R = H,  27–syn: R = OCH₃
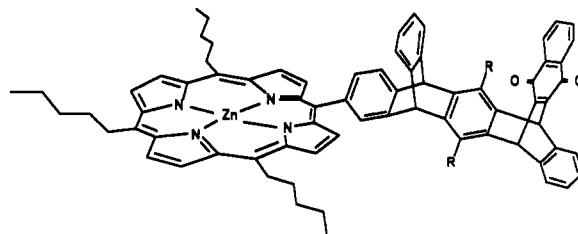


26–anti: R = H,  27–anti: R = OCH₃

a polycyclic hydrocarbon spacer to maintain a fixed distance and restricted orientation between the porphyrin donor and the quinone acceptor. This spacer belongs to a general class of hydrocarbons that have

been named "iptycenes" by Hart.[107] In particular, the hydrocarbon spacer used in **26** and **27** is a "pentiptycene" because it contains five aromatic rings. There are several advantages to using this ring system as a spacer. First, it is closely related to triptycene, a spacer that has been studied extensively.[108,109] Second, the presence of two positional isomers, in which the porphyrin and quinone are either syn or anti relative to one another, affords the opportunity to study the orientation dependence of photoinduced-electron-transfer reactions at a fixed distance. Third, the presence of a central benzene ring, rigidly fixed between the two triptycene moieties, allows one to use substituents on the remaining free positions of this ring to alter the energy of the HOMO and LUMO of this intervening spacer fragment. This alters the relative contribution of ionic states of the spacer to a superexchange description of electron transfer.

The central benzene ring of the spacer is unsubstituted in **26** and possesses p-dimethoxy substituents in **27**. The naphthoquinone is oriented either syn or anti to the porphyrin across the spacer. The rate constants for the syn isomers are uniformly a factor of about 2 slower than those of the anti isomers. The charge separation reaction rates for **26** and **27** are similar, while the ion-pair recombination reactions are about 3–4× faster in **27** than in **26**. The conformational effect is attributed to better overlap of the spacer wave functions in the anti vs the syn conformation, while the increase in recombination rate for **27** over **26** is attributed to a superexchange interaction involving an electronic configuration of the spacer in which the dimethoxybenzene cation contributes.

Following the appearance of Sessler's initial reports on structures such as **24** and **25**, Osuka and Maruyama have published extensive work on multiple-porphyrin supermolecules.

Osuka and Maruyama[110] have utilized a series of disubstituted naphthalenes as spacers between two porphyrins, **28**, to rigidly fix the orientation of the two
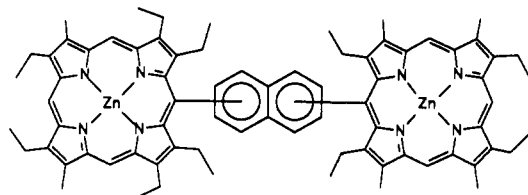


28: 1,3; 1,4; 1,5; 1,6; 1,7; 1,8; 2,6; 2,7 naphthalene isomers

porphyrin macrocycles relative to one another. They observed exciton splitting in the porphyrin Soret band

that could be described by a classical dipole–dipole interaction between the transition moments of the porphyrins. They also observed slight red shifts in the $Q_y$ bands of the porphyrins and quenching of the fluorescence in dimers in which the two porphyrin macrocycles possess significant π overlap. This observation led these workers to develop an extensive series of electron-transfer models based on this structural theme. Osuka, Maruyama, and their co-workers have greatly expanded the number and variety of models based on 5,15-diarylated octaalkylporphyrins. Nagata et al.[111] have summarized the synthetic and optical properties of a number of trimeric and pentameric porphyrin arrays. Both extended and stacked arrays such as trimers **29a,b** (Chart I) are described. Once again, in concert with standard exciton theory, the extended series shows an ever-increasing splitting of red and blue Soret components, from 930 cm$^{-1}$ for a dimer to 1450 cm$^{-1}$ for the pentamer. In addition, the stacked series shows only the blue exciton component shifted from the monomer origin by 250 cm$^{-1}$ in the dimer and 560 cm$^{-1}$ in the pentamer.

Osuka et al.[112] have used the information derived above to develop models of photosynthetic reaction center pigments consisting of 2, 3, and 4 porphyrins with an individual benzoquinone attached to the terminal porphyrin, **30a–d** (Chart II). Two porphyrins are stacked to act like the special pair dimer in photosynthetic systems. Fluorescence quenching in each molecule relative to the monomer porphyrin was about 90%, suggesting an additional nonradiative path to ground state. These molecules were examined by picosecond transient optical spectroscopy.[113] The authors showed that rapid electron transfer occurs between the porphyrin and quinone that are adjacent to one another. This electron transfer may be followed by a second dark electron transfer from the dimeric porphyrin to the central porphyrin, although evidence for this reaction is not particularly strong. In fact, the use of electronically similar porphyrins within these molecules makes the identification of hypothetical charge-transfer intermediates very difficult. Moreover, in **30b–d** the porphyrin dimer may not be significantly easier to oxidize than the porphyrin that lies between the dimer and the quinone. Thus, the free energy of the secondary, dark electron-transfer reaction may be quite small. In the molecules with the phenylated spacers the ion-pair lifetimes are only 20, 50, and 70 ps, whereas the lifetime for the molecule with the biphenyl spacer is 500 ps. Apparently additional electronic decoupling between the porphyrins is necessary in these systems to
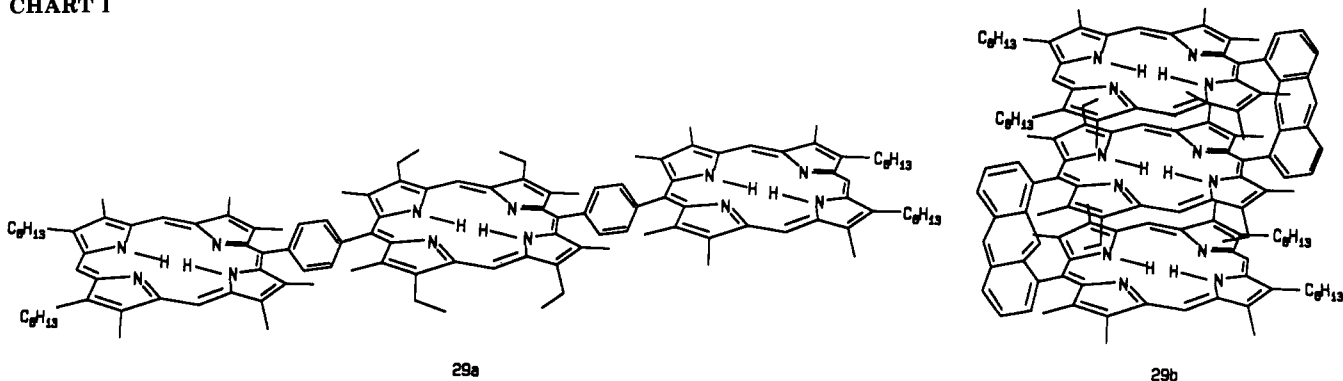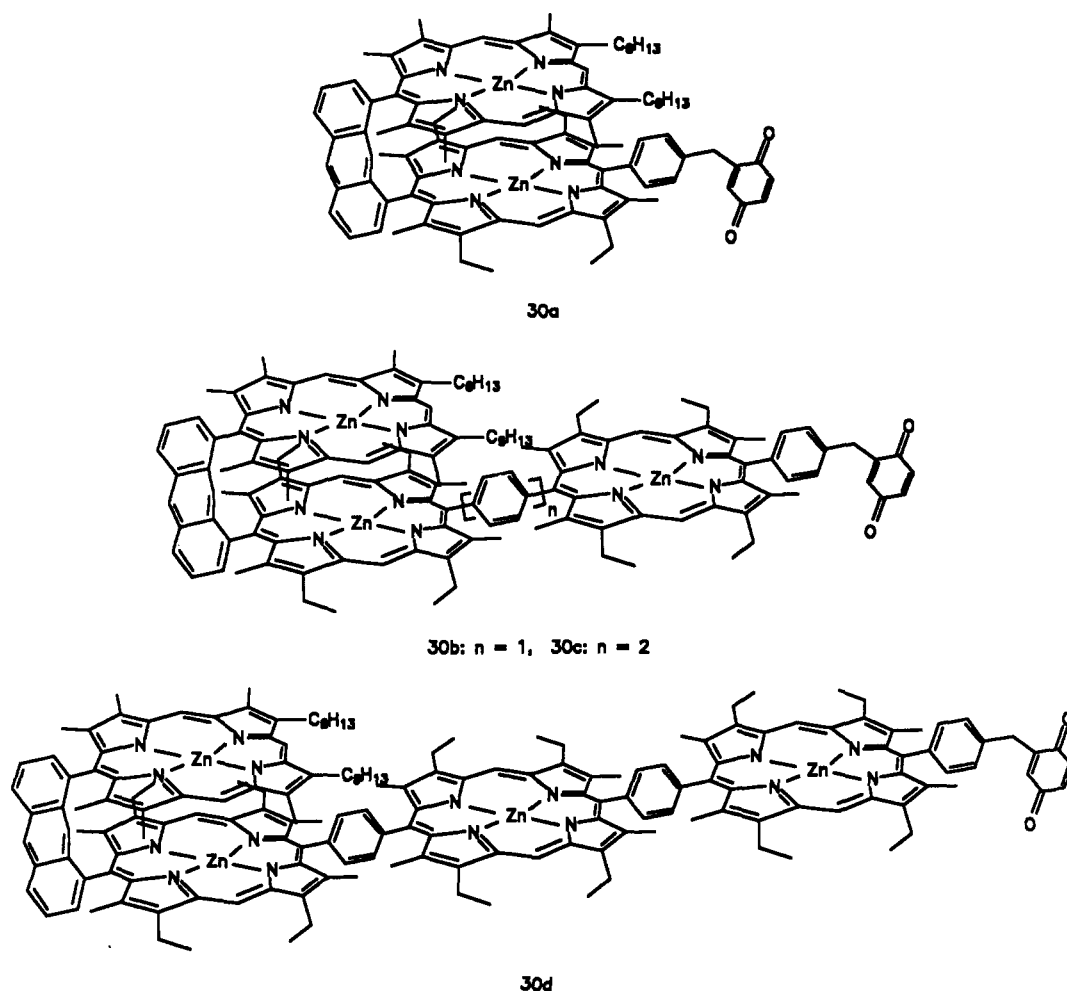
CHART I



29a



29b

**CHART II**



30a



30b: n = 1,  30c: n = 2



30d

extend the lifetime of the ion-pair state.

The assignment of transient absorption spectra to the various oxidized and reduced species in a donor–acceptor model is often complicated by broad, indistinct spectra and by similarities between the spectra of the excited states and the ionic states. For example, the optical spectra of octaalkylated metalloporphyrin cation radicals, such as zinc octaethylporphyrin, show a fairly well-defined band at 670 nm that is not present in the lowest excited singlet or triplet states of the porphyrin. However, in meso-substituted metalloporphyrins, such as zinc tetraphenylporphyrin, this band shifts to 650 nm, broadens, and is less distinct. Thus, it is useful to choose specific donors or acceptors in electron-transfer studies that provide unequivocal optical evidence for charge separation. Although this point may seem obvious, the number of systems in the literature that do not fulfill this criterion is surprisingly large.

Osuka et al.[114] have prepared the same series of porphyrins discussed in ref 112, replacing the benzoquinone acceptor with a pyromellitimide acceptor. The pyromellitimide radical anion possesses a distinct, narrow optical transition at 715 nm that is diagnostic for charge separation. For the simple porphyrin–pyromellitimide donor–acceptor pair **31a** (Chart III) in THF the forward electron transfer occurs with a rate constant of $1.7 \times 10^{10}$ s$^{-1}$, while the ion pair recombines with a rate constant of $9.3 \times 10^{9}$ s$^{-1}$. The free energy of reaction is about 0.5 eV. The authors observed

two-step electron transfer in **31b** (Chart III). In this molecule strong interaction between the two sandwiched porphyrins results in lowering of their S$_1$ energy by 0.19 eV and their oxidation potential by 0.17 eV. The pyromellitimide radical anion absorption decays biexponentially with lifetimes of 70 ps and 2.5 $\mu$s. Molecule **31b** is a significant design improvement over **30c**, and successfully addresses the problems outlined above.

Osuka et al.[115] have attached carotenoids to the 5- and 15-diaryl positions within an octaalkylporphyrin, **32a–c** (Chart IV). The attachment provides a fairly rigid linkage between the polyene and the porphyrin. In the free-base derivatives energy transfer occurs from the lowest excited singlet state of the carotenoid to that of the porphyrin. The rates of energy transfer in **32a–c** were estimated from fluorescence excitation spectra to be $4 \times 10^{10}$, $9 \times 10^{9}$, and $3 \times 10^{10}$ s$^{-1}$, respectively.

Osuka et al.[116] combined the carotenoporphyrins with a pyromellitimide acceptor to produce a molecular triad **33** (Chart V) that exhibits photoinduced electron transfer from the lowest excited singlet state of the carotenoid, Car, to the pyromellitimide, Pym. Excitation of the porphyrin free base results in formation of the Car$^+$ and Pym$^-$ within 40 ps following the laser flash. The resultant charge separation lasts 15 ns. It is not clear from the data whether the porphyrin donates an electron first to Pym, followed by oxidation of Car, or whether there is energy transfer from the
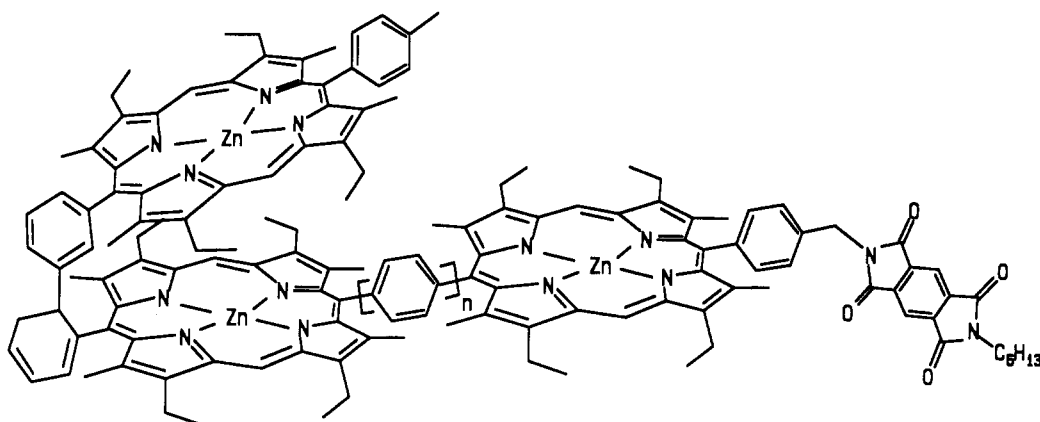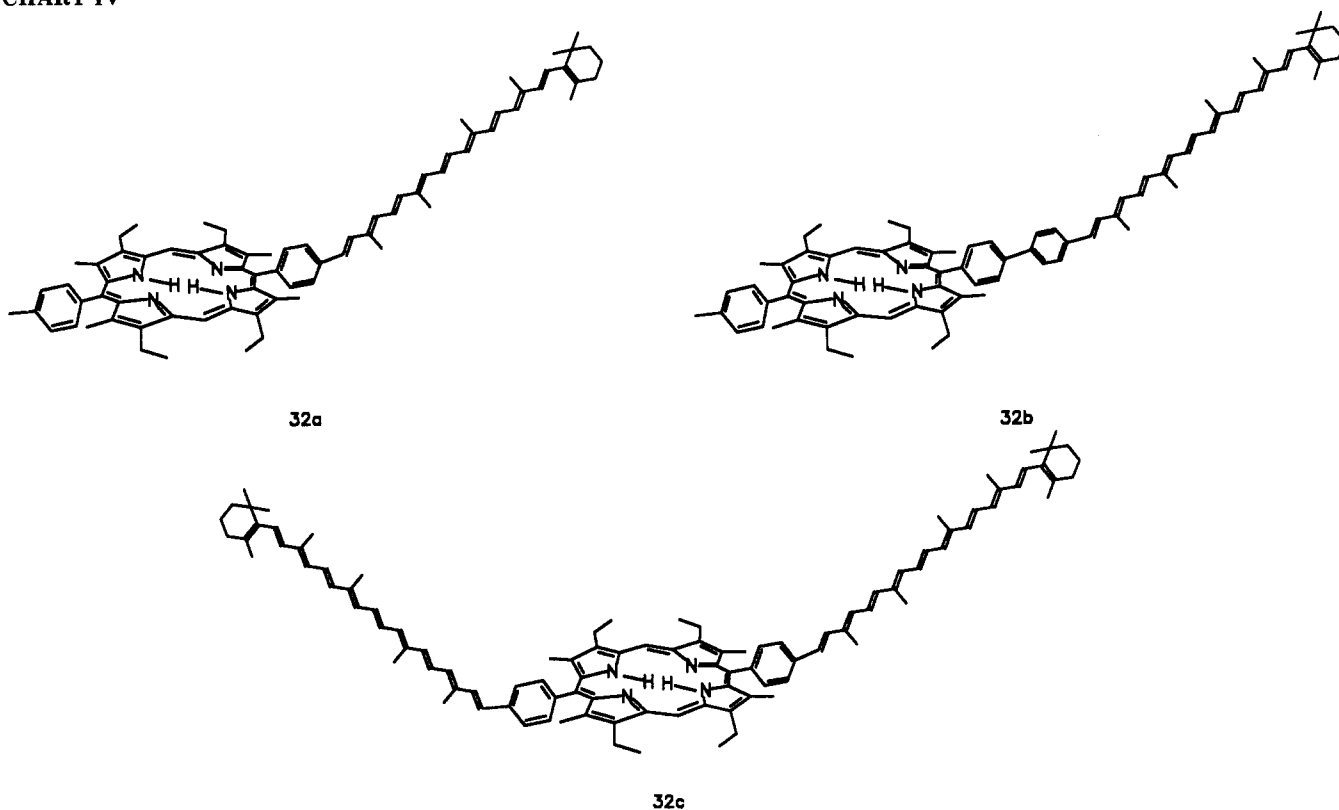
CHART III



31a



31b:  n = 2

CHART IV



32a



32b



32c
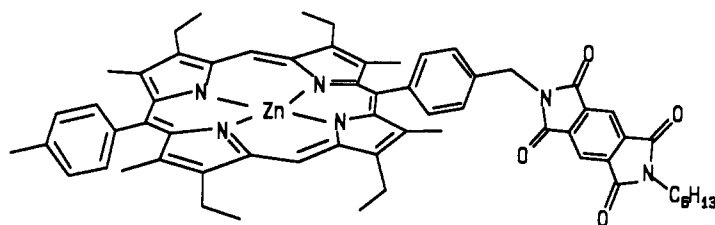
porphyrin to Car, followed by electron transfer to Pym using the porphyrin as a virtual intermediate. Comparing these results with those in ref 115, it is probable that the lowest excited singlet state of the free-base porphyrin and Car are nearly degenerate. Excitation of either chromophore results in distribution of the excitation between the chromophores. The corresponding zinc porphyrin does not produce a long-lived

charge separation because the zinc porphyrin is easier to oxidize than the carotenoid.

Joran et al.[117] have studied the influence of reaction exothermicity on the rates of electron transfer in derivatives based on structure 34. Several substituted quinones were employed. Rate constants of electron transfer were determined by monitoring the decrease in fluorescence lifetime of the porphyrin in the presence

**CHART V**



33
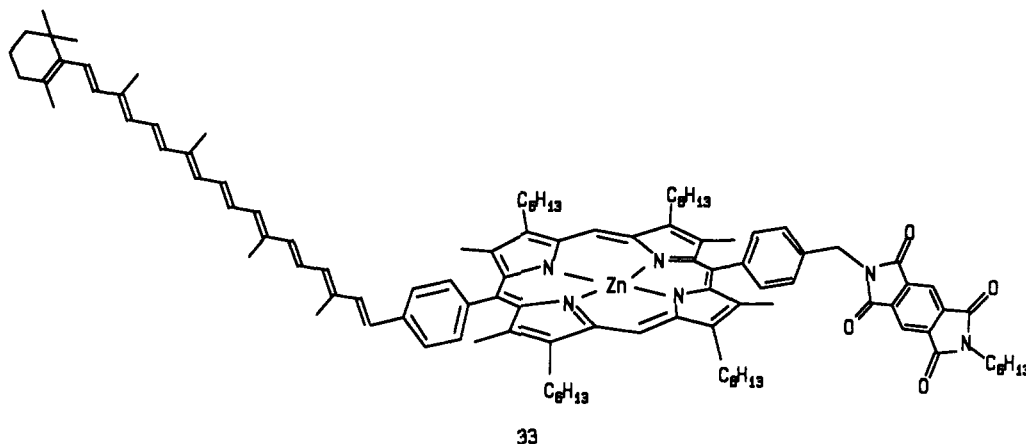
of the electron acceptor. Weak polarity effects were observed with only about a factor of 6 change in rate from benzene to acetonitrile. Classical and semiclassical expressions for the electron-transfer rate constants adequately describe the change in rate with $\Delta G^0$ at a fixed 10 Å distance.



34
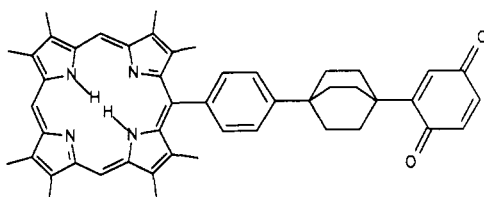
Lindsey and Mauzerall[118,119] have presented thorough studies of the porphyrin–quinone sandwich molecule **35**. These workers suggest that this molecule exists as



R = CH$_2$——⟨ ⟩——OCH$_2$CH$_2$

35
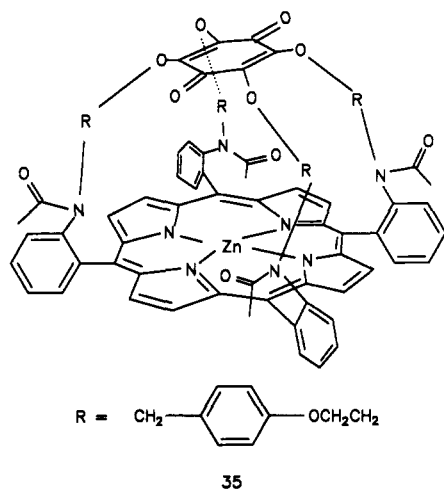
two slowly equilibrating conformers differing in interplanar porphyrin–quinone distance. The close conformer, PQ$_a$, shows a 4-fold change in rate of quenching of fluorescence in 21 solvents of widely varying properties. Rate constants were measured from 80–300 K. The activation energies in several solvents are small, 1–2 kJ/mol. The quenching rates for the more distant conformer PQ$_b$ vary over a greater range (10-fold) in these solvents with activation energies of about 4 kJ/mol. The activation energies of both the forward and reverse electron-transfer reactions from the triplet state are about 7 kJ/mol. The rates show very little change when the solvent makes the transition to the glassy

state. This is unusual in view of the work of Harrison et al.[97] The authors suggest that their data are most consistent with nonadiabatic electron tunneling.

Although the porphyrin–quinone distance in Dervan's bicyclo(2.2.2)octyl derivative and Lindsey and Mauzerall's cofacial porphyrin are similar, the donor–acceptor geometries are different, as are the free energies of reaction. Since the cofacial geometry might be expected to increase the electron-transfer rate because of an increased direct interaction between the donor and acceptor, the weaker driving force for the forward electron transfer in the cofacial molecule would offset this rate increase.



36a



36b
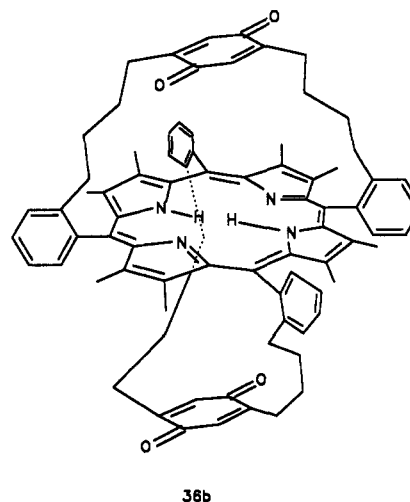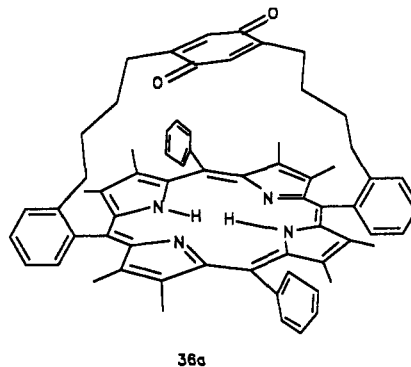
Mauzerall et al.[120] have studied two porphyrin–quinone molecules **36a,b** in which either one or two benzoquinone molecules are stacked atop the porphyrin.

The fluorescence of both molecules is quenched and exhibits only weak solvent dependence. Variations in quenching behavior of the monoquinone vs the diquinone molecules are attributed to the orbital symmetry properties of the system.

Wasielewski et al.[109] have recently studied a series of fixed distance chlorophyll–quinone donor–acceptor molecules, **37a–d**. The donor consists of either methyl



**37a: M = 2H, 37b: M = Mg**

**37c: M = 2H, 37d: M = Mg**
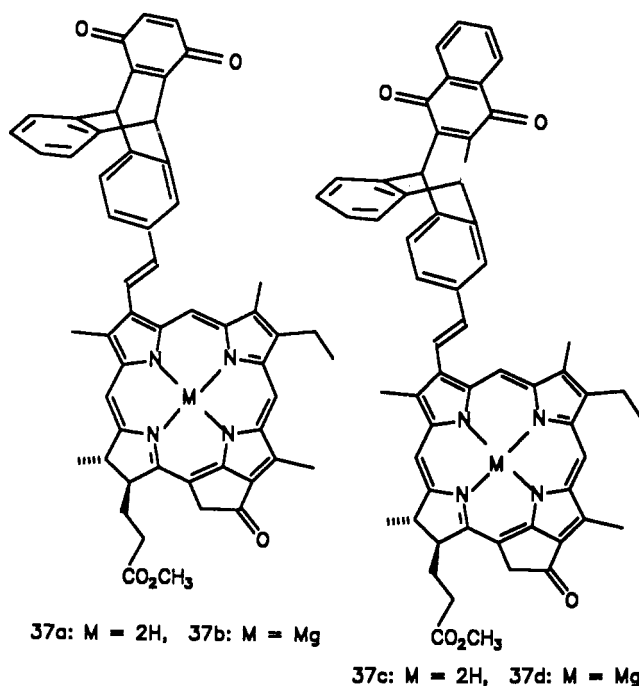
pyropheophorbide *a* or methyl pyrochlorophyllide *a*, while the acceptor is either benzoquinone or naphthoquinone. The acceptors are fused to a triptycene spacer group, which in turn is attached to the donors at their vinyl groups. Picosecond transient absorption measurements have been used to show that electron transfer from the lowest excited singlet state of the donor to the acceptor is the mechanism of fluorescence quenching in these molecules. The charge separation rate constants increase to values as high as $3 \times 10^{11}$ s$^{-1}$ as the free energy of charge separation increases, while the radical pair recombination rate constants decrease from the same maximum value as the free energy of recombination increases. The total reorganization energies, $\lambda$, for both reactions are 0.9 eV.

Sakata et al.[121] have prepared a porphyrin–quinone molecule, **38**, that possesses a long alkyl tail designed to facilitate the association of this molecule with bovine serum albumin. The authors report that the porphyrin quinone molecule associates well with BSA and shows substantial fluorescence quenching upon association with the protein, presumably because electron transfer from the excited porphyrin to the quinone occurs.



**38**
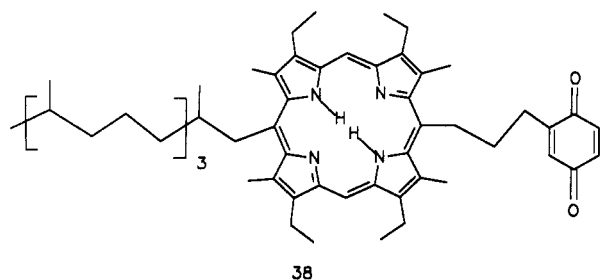
Sakata et al.[122] have recently presented two model systems, **39a,b**, which illustrate very nicely the role that donor–acceptor orientation plays in determining electron transfer rates. They found that **39a** undergoes



**39a**



**39b**
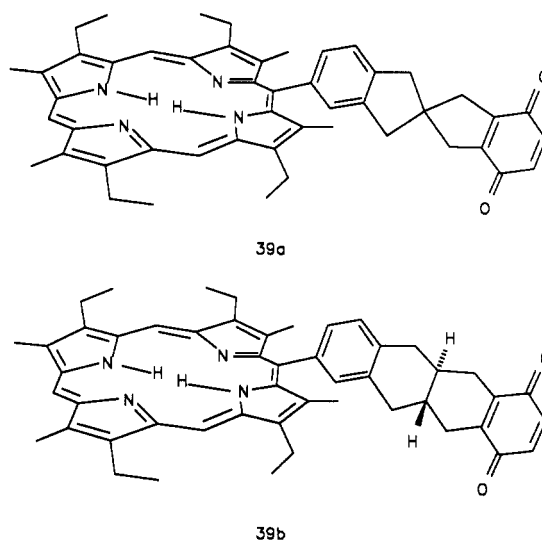
charge separation with a $3.3 \times 10^8$ s$^{-1}$ rate constant, while **39b** does so with a $6.5 \times 10^7$ rate constant. In both molecules the number of saturated carbon atoms and the donor–acceptor distances are the same. Sakata et al.[123] have recently extended this work to include two isomers of compounds **39a** and **39b**. Once again, the quinones are held in a rigid configuration relative to the porphyrin. Electron-transfer rates from the lowest excited singlet state of the porphyrin to the quinone in **40a** and **40b** are $3.5 \times 10^9$ and $4.0 \times 10^8$ s$^{-1}$, in THF respectively. This set of molecules is interesting because the rate constant for **40b**, the molecule with all trans bonding is slower by 1 order of magnitude than that for



**40a**



**40b**
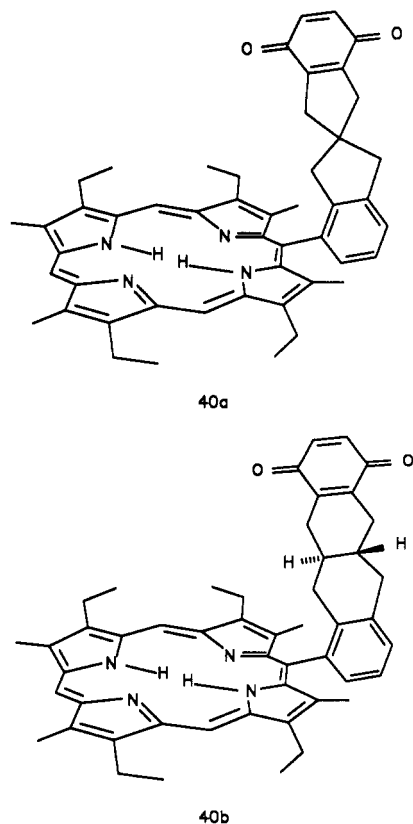
**40a.** The authors suggest that the large orientation effect may be evidence for a dominant through-space orbital interaction.

Knapp et al.[124] have presented data on a related series of molecules that use spirocyclobutane linkages to fix both the distance and the orientation between a porphyrin and quinone molecule, **41**. They measured the
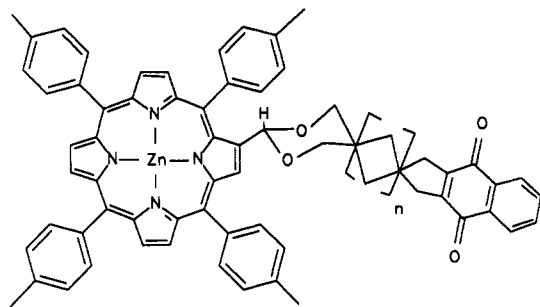


41: n = 0, 1, 2, 3

rate of photoinduced electron transfer as a function of the distance between the donor and acceptor using picosecond transient absorption spectroscopy. The rates of charge separation yield $\alpha$ values of about 1.03–1.15 Å$^{-1}$, dependent on solvent, whereas the charge recombination rates yield $\alpha = 0.97$ Å$^{-1}$. These values are comparable to those reported for other donor–hydrocarbon spacer–acceptor systems.[81–83]

Antolovich et al.[125] have used the norbornyl-based hydrocarbon spacer groups that they employed previously for dimethoxynaphthalene donors and dicyanoethylene acceptors to fix both the distance and orientation between a porphyrin and a quinone, **42a,b**. The
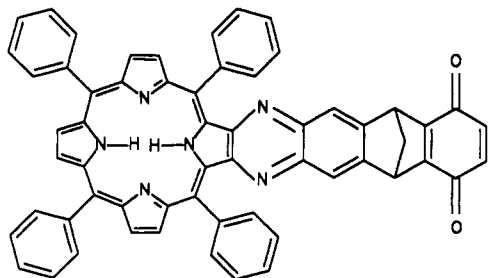


42a
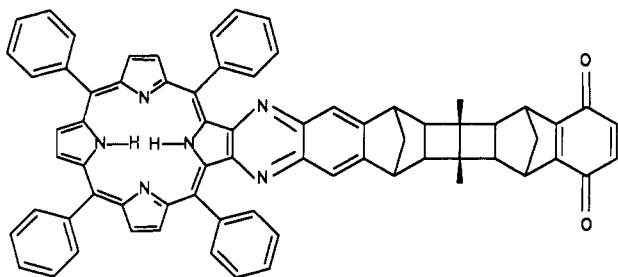


42b

spacers have two and six saturated bonds between the donor and acceptor. In **42a** the charge separation rate constant is about $2.5 \times 10^{10}$ s$^{-1}$ in solvents of moderate to high polarity. The rate constant decreases by about 200× in low dielectric constant solvents. Dioxane is exceptional in that the rate constant remains high. The charge separation rate constant for **42b** in high polarity solvents is about 200× smaller than that for **42a** in the same solvents. Ion-pair recombination rates were

measured in dioxane/benzene mixtures for **42b**. These recombination times are about 2–4 ns. The rates remain moderately rapid across the longer bridge. It may well be that the degree of strain present in such bridges increases the $\pi$ character in the bonds and thus increases the donor–spacer and acceptor–spacer electronic coupling.

Cormier et al.[126] have presented data on a porphyrin–anthraquinone molecule in which the anthraquinone is directly bonded to the meso position of the porphyrin, **43**. The absorption spectrum of the por-
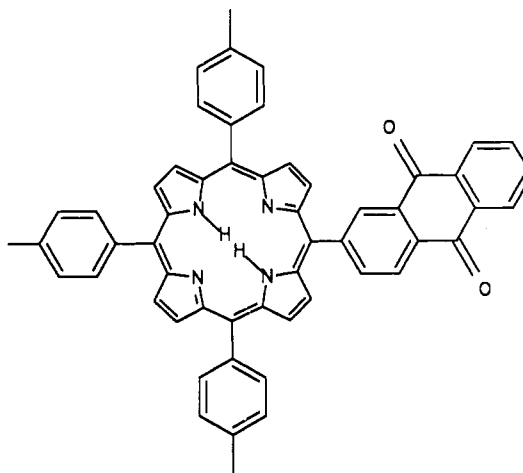


43

phyrin is perturbed by the strong electronic coupling with the quinone. Solvent polarity dependent quenching of the porphyrin fluorescence occurs in a manner similar to many other porphyrin–quinone molecules. While the free energy for the charge separation process is only marginally negative, the high rates of electron transfer can be attributed to the strong electronic coupling between the porphyrin excited state and the quinone.

Shafirovich et al.[127–129] have published a series of papers that deal with multistep photoinduced electron transfer in systems that use photoexcited porphyrin donors and viologen and/or quinone acceptors. The porphyrin–viologen diad **44** (Chart VI) displays interesting magnetic field effects following electron transfer from the porphyrin excited triplet state to viologen. Formation of the radical ion pair within a magnetic field increases its lifetime by a factor of 11. The magnetic field value at which this kinetic effect reaches half saturation varies between 150–300 G. This is precisely the behavior that is expected if electron transfer from the porphyrin triplet state to the viologen yields a spin-correlated triplet radical pair. These workers have examined the fluorescence decay properties of this molecule[128] and have concluded that the molecule exists primarily in two conformations, one in which the porphyrin and viologen are folded and one in which they are extended. These difficulties in conformational assignment and the ensuing difficulties that arise in kinetic interpretation invariably arise when flexible linkages are employed between the donor and acceptor. These same workers have added a benzoquinone secondary electron acceptor to the porphyrin–viologen described above, **45**[129] (Chart VI). They observe complicated kinetics that may indicate formation of a long-lived P$^+$–Q$^-$ species.
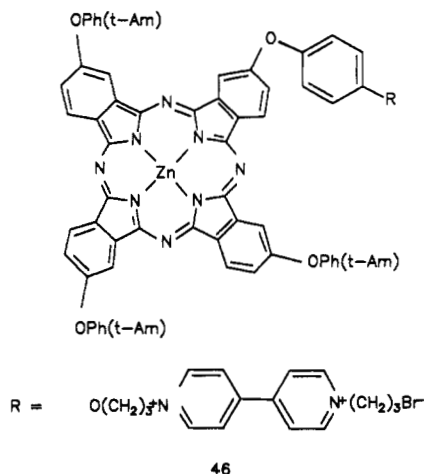
CHART VI
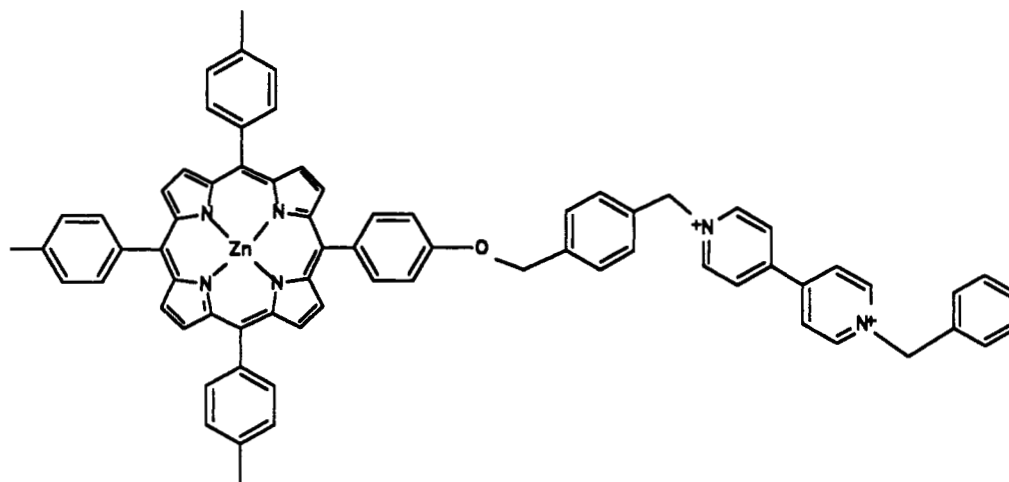
**44**
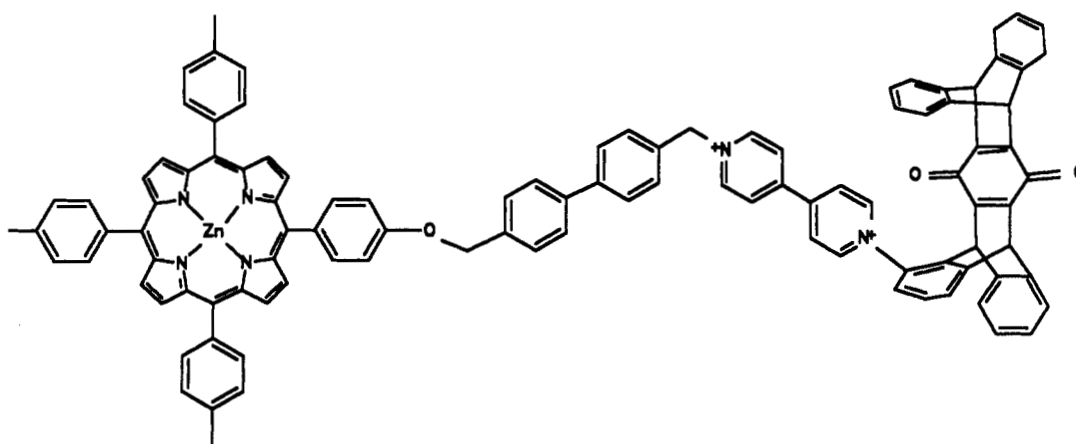
**45**

Liu et al.[130] have utilized a soluble phthalocyanine derivative to produce an analogous phthalocyanine-viologen-linked donor–acceptor molecule, **46**. These

OPh(t–Am)

R = O(CH$_2$)$_3$N⁺(CH$_2$)$_3$Br⁻

**46**

workers report indications of both singlet and triplet electron transfer. In the former case, fluorescence quenching is observed and evidence for both static and dynamic quenching is presented. This indicates that conformational heterogeneity similar to that indicated by Levin et al.[129] is also present in these systems. On a microsecond time scale there is evidence of formation of ZnPc⁺-V⁺ ion pair.

Li et al.[131] have extended this approach to produce

a porphyrin–phthalocyanine–quinone triad molecule, **47**. In this case the ZnPc is easier to oxidize than is

OPh–Q

**47**
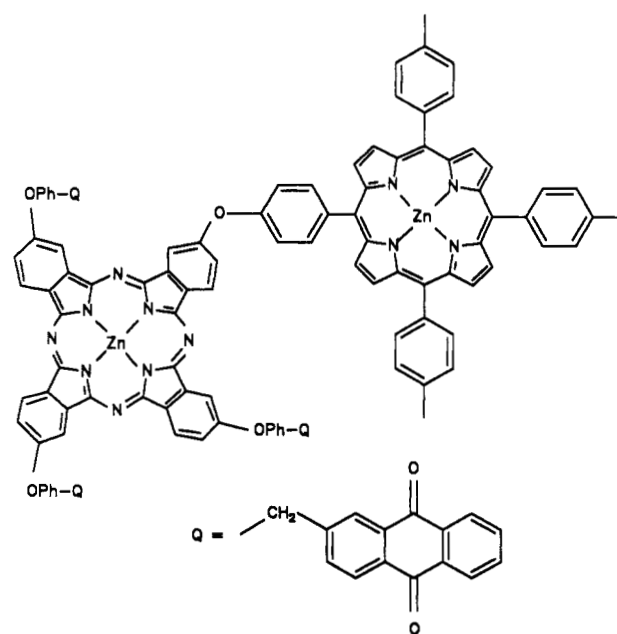
the ZnTPP by about 0.17 V. Thus, the porphyrin functions only as an antenna molecule. These workers suggest that the porphyrin is oxidized. However,

spectroscopic data to support this claim is lacking. Additional fluorescence quenching in the triad molecule may be due to enhanced nonradiative decay influenced by electronic coupling between the two macrocycles.

Saito et al.[132] have observed large magnetic field effects on the lifetime of the triplet radical pair state in a series of porphyrin–viologen molecules bound together with hydrocarbon chains of varying length, **48**. The



**48**
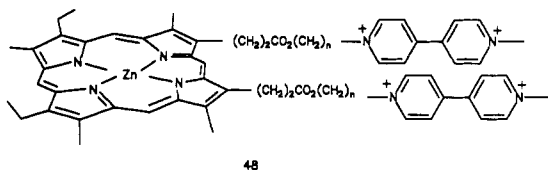
largest effect occurs for the molecules in which $n = 11$. For this system the lifetime of the radical pair increases by a factor of 3 for application of a 500-G magnetic field. This observation is similar to that made by Levin et al.[127]

Batteas et al.[133] have examined a free-base TPP–tetraviologen molecule, **49**, in which the viologen mol-



R = OCH₂CH₂CH₂N⁺⟨⟩⟨⟩N⁺CH₃

**49**
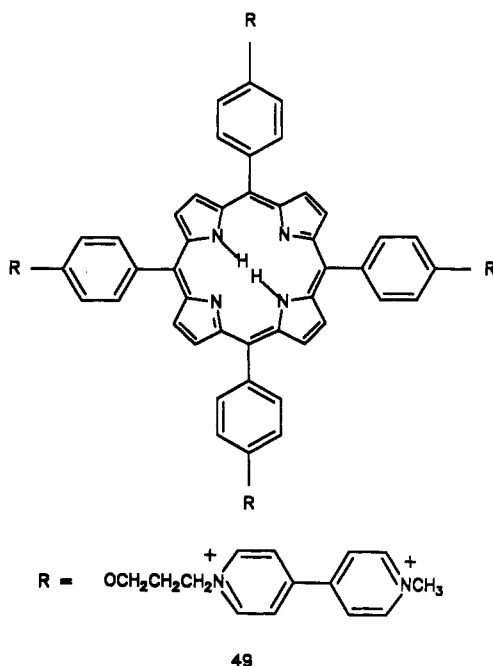
ecules are attached to the porphyrin via a 1,3-propan-oxy-4-phenyl chain. In DMSO rapid charge separation occurs from the lowest excited singlet state of the porphyrin. The charge separated products last remarkably long for a single-step donor–acceptor molecule, about 6.4 $\mu$s. The mechanism behind the formation for this long-lived product is discussed in terms of the dynamics of the multiple viologen sites.

Gust and Moore[134] have extensively explored the use of carotenoids as secondary donors to promote long-lived charge separation in supramolecular systems. They have developed a variety of systems in the past several years that expand upon this theme. Gust and Moore have studied the distance dependence of the electron-transfer reaction from porphyrin to quinone using triads with 1–4 CH₂ groups between the quinone and the porphyrin, **50**[135] (Chart VII). They have also examined the corresponding compounds lacking the carotenoid. They observe $\alpha = 0.58$ Å⁻¹, if they exclude the data from the compound with the single CH₂ group.

This value of $\alpha$ is quite low. The deviation of the one CH₂ molecule from the linear dependence is probably due to a dramatic change in *average* orientation of the quinone relative to the porphyrin, enforced by the single CH₂ group. They explain this effect by noting that, during the lifetime of the excited singlet state, compounds with more than one CH₂ group are able to adopt a variety of conformations. They conclude that their value of $\alpha$ is a lower limit because the NMR data yield distances that are ones corresponding to the most extended conformation of the molecules.

Moore et al.[136] have described the incorporation of modified triads into lipid bilayers. The hydrophilic character of the porphyrin was increased by substituting pyridines for two of the phenyl groups on the porphyrin, **51** (Chart VIII). These triads demonstrate photodriven transport of charge across the membrane. Since the triad is incorporated into the BLM with an equal distribution of donor and acceptor moieties on either side of the membrane, the system was asymmetrized using donors and acceptors on either side of the membrane that would react spontaneously if allowed to come into contact. The triad photocatalyzes charge transport across the membrane.

Momenteau et al.[137] have also presented caroteno-porphyrin–quinone triad molecules based on basket handle porphyrins, **52**. They obtain steady photocurrents when these molecules are illuminated in bilayer lipid membranes. This behavior is presented as evidence of intramolecular charge separation.

Gust et al.[138–140] have discussed extensively their molecules which utilize three sequential electron transfer steps in order to stabilize a charge separation. The molecular tetrad, **53** (Chart IX) consists of a polyene, a porphyrin, and two quinones. The quinone with the more negative redox potential was attached directly to the porphyrin, while the quinone with the less negative redox potential was at the terminus. This arrangement is designed to promote sequential electron transfer from the naphthoquinone to the benzoquinone. The initial charge separated species is formed within 15 ps following excitation of the porphyrin and lies about 1.6 eV above the ground state. The final charge-separated species is formed with a quantum yield of 0.23 at room temperature and lies about 1.1 eV above the ground state. The rates and yields of the intermediate electron-transfer processes remain unknown.

These workers have also described[140] a carotenoid-porphyrin–porphyrin–quinone, **54** (Chart IX). Excitation of the porphyrins in this molecule yields the Car⁺–Q⁻ state that lives for 2.9 $\mu$s in anisole solvent and is produced with a 0.25 quantum yield. Since these workers presented data on the fluorescence decay of the porphyrins and the lifetime of the final state, i.e. only the first and last reaction, some ambiguities remain as to the role of the various ionic porphyrin intermediates in the sequence leading to the final charge separation.

In the carotene–porphyrin–quinone triads and car-otene–porphyrin–diquinone molecules the carotene cation radical can be easily observed. However, it is very difficult to observe the quinone anion. To remedy this situation Hasharoni et al.[141] have used Fourier transform EPR spectroscopy to monitor the transient radicals produced following excitation of tetrad **53**. In
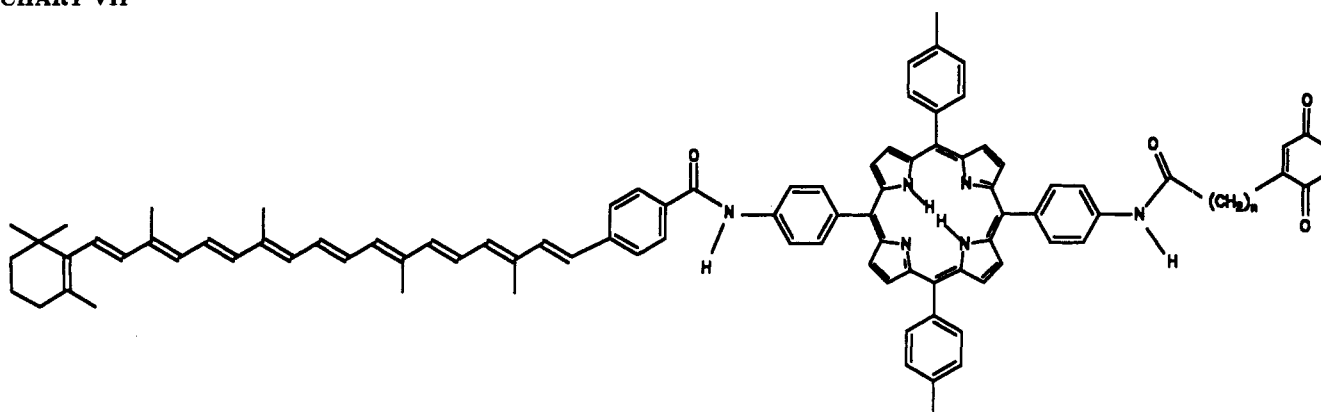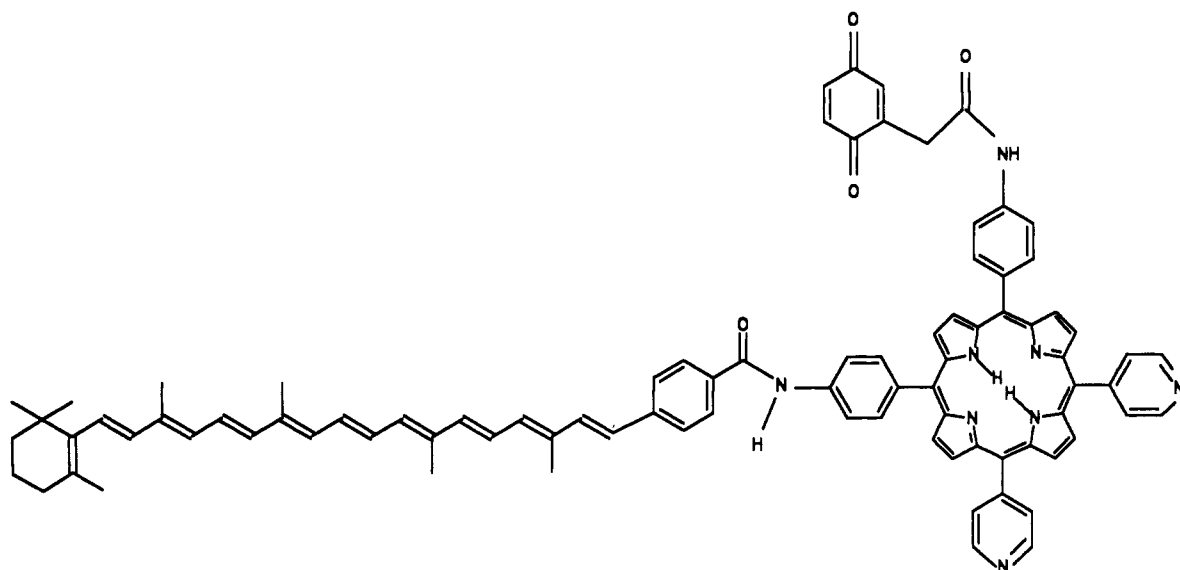
**CHART VII**



**50: n = 1 - 4**

**CHART VIII**



51



52

this case both the terminal quinone radical anion and the carotene cation are observed. The lifetime of the resultant ion-pair matches that found optically. In addition, it was found that the radicals were spin polarized in the fluid medium. Hasharoni et al.[142] have also presented an in-depth account of the spectral distortions that may occur in data obtained by EPR
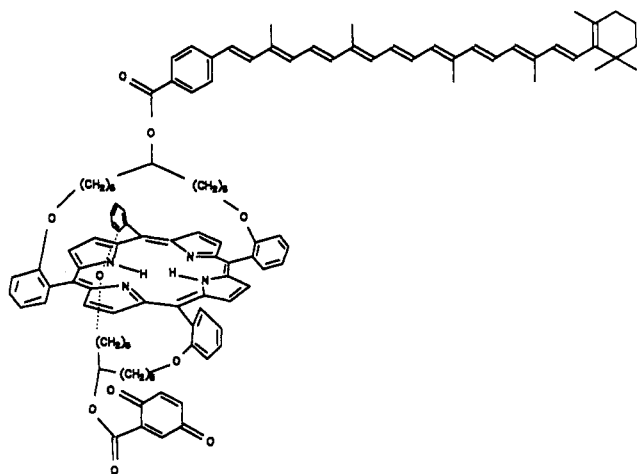
with high time resolution. They discuss the limits under which the data can be interpreted.

Gust et al.[143] have recently presented results on a new triad system that completely lacks a quinone acceptor, 55 (Chart IX). They use two porphyrins and a carotenoid. In this case the redox properties of the diporphyrin pair are made asymmetric by substitution of perfluorophenyl groups on the terminal porphyrin. Electron transfer occurs from the lowest excited singlet state of the central ZnTPP derivative to the terminal free-base fluorinated porphyrin. This reaction occurs with a rate constant of $3.5 \times 10^9$ s$^{-1}$ and a 0.68 quantum yield. The oxidation of the carotenoid by the ZnTPP$^+$ yields a final state C$^+$–ZnTPP–TPP$_f^-$ that lives for 250 ns with 0.32 yield.

Gust et al.[144] have extended their multistep electron-transfer models to include a carotene–Zn porphyrin–porphyrin–naphthoquinone–benzoquinone pentad, 56 (Chart IX). The strategy is once again to maximize quantum yield of ion pair formation and lifetime of the ion pair. In this molecule a 55-$\mu$s lifetime with an 83% quantum yield is achieved. If the Zn atom is removed, the lifetime of the final ion pair lengthens to 340 $\mu$s, while the quantum yield drops to 15%. Once again little or nothing is known about rates of the multitude of intermediate electron-transfer reactions within the

**CHART IX**



53

54

55

56
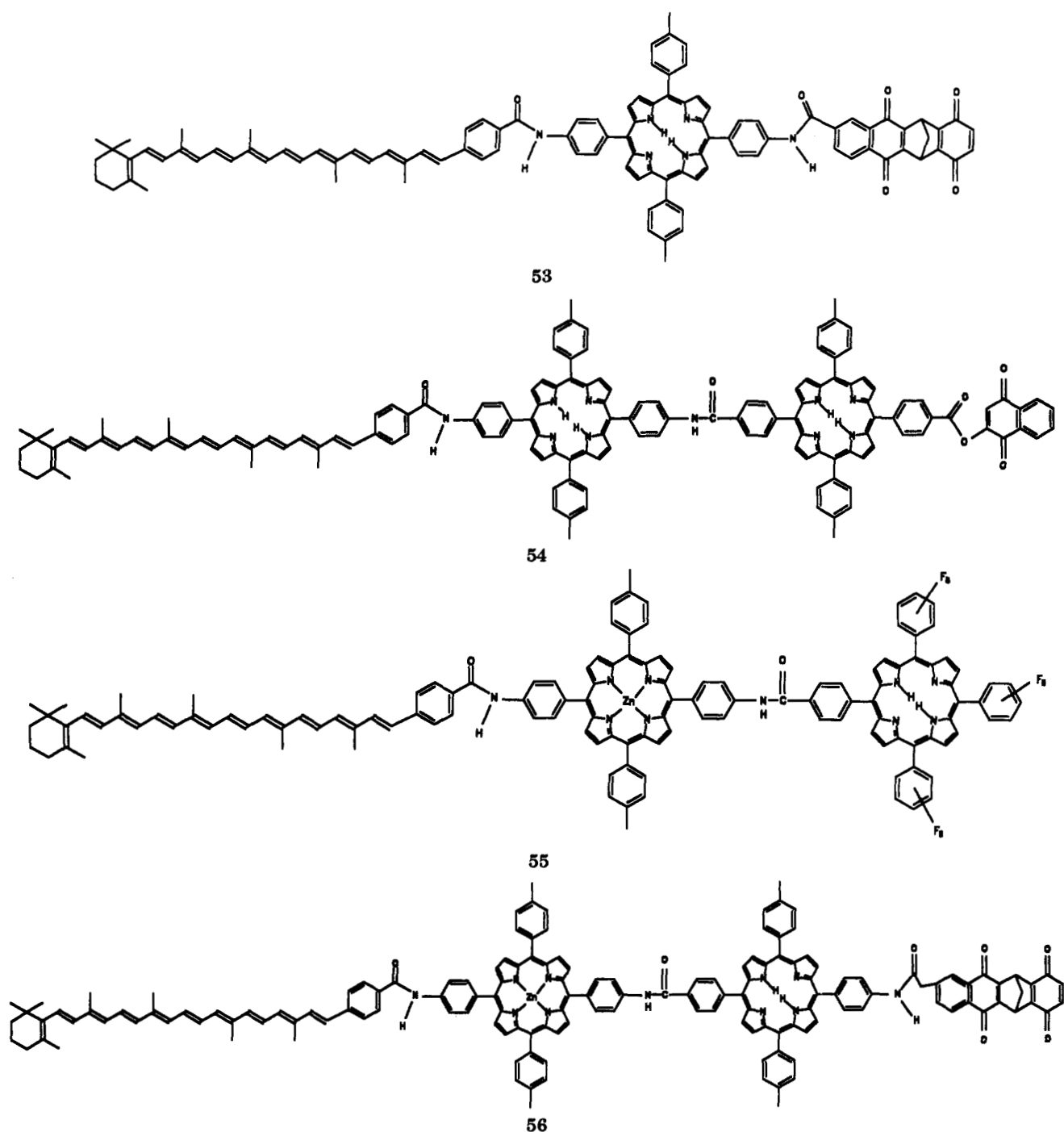
pathways that lead to the final carotene cation–benzo-quinone anion ion pair.

The temperature dependence of photoinduced electron transfer has been addressed by a number of workers using porphyrin–quinone donor–acceptor molecules. As mentioned in the previous discussion Harrison et al.[97] presented an extensive study of the temperature dependence of electron transfer in **22**. They find that the quantum yield of electron transfer changes dramatically as the molecule is cooled below the glass transition of the solvent. Other workers have observed somewhat different behavior. Joran et al.[117] have suggested that the rate of photoinduced electron transfer within **34** is nearly temperature independent. It is interesting to note that the rate of electron transfer

within **34** is comparable to the decay rate of the porphyrin lowest excited singlet state. Lindsey and Mauzerall also observed temperature independence of the rate constant for electron transfer within **35**. Once again the rate constant for electron transfer from the singlet state of the porphyrin is roughly comparable to that of singlet state decay. In contrast to these cases Sessler et al.[103–105] have observed that electron transfer proceeds very well in low-temperature glasses in molecules such as **25**. In Sessler's molecules the free energy of reaction for electron transfer is significant and the rate constants are fast.

In contrast to photosynthesis, which exhibits a quantum yield of primary charge separation near unity at cryogenic temperatures, most photosynthetic model

systems based on chlorophyll or porphyrin electron donors exhibit significantly reduced efficiencies of light-initiated, singlet state electron transfer whenever they are dissolved in rigid glass media. This reduction may occur because solvent dipoles reorient around an ion pair in a polar liquid, decreasing the energy of the ion pair, while solvent dipoles cannot reorient around an ion pair produced within a frozen solvent, and thus, provide little stabilization of the ion pair. As a result, the energy level of the ion pair is much higher in the rigid glass than in the liquid. In fact, the ion-pair-state energy may be so high that it lies above the energy of the excited state, in which case photoinduced electron transfer cannot occur. Balanced against this effect is the influence of the strength of the electronic coupling, $V^2_{DA}$, on the electron transfer rate. Two cases can be identified. First, if the incipient ion pair receives little or no stabilization from the solvent, which is usually the case in low polarity, viscous, or solid media, and if the ion-pair energy level is above that of $S_1$ for the donor-acceptor molecule, electron transfer will be very slow relative to excited-state decay. Second, if the solvent does not stabilize the ion pair, and if the ion-pair energy remains below that of $S_1$, the rate constant for electron transfer may be increased by increasing $V^2_{DA}$ between the donor and acceptor. In the limit the electronic coupling may be increased until the electron-transfer process is adiabatic and eq 5 no longer adequately describes the dependence of its rate on free energy of reaction.

Wasielewski et al.[145] have investigated the regime in which $V^2_{DA}$ is sufficiently small to assume that the photoinduced-electron-transfer reaction is nonadiabatic. They prepared two fixed-distance donor–acceptor molecules in which Zn *meso*-triphenylporphine or Zn *meso*-tripentylporphine donors are linked to a high electron affinity tetracyanonaphthoquinodimethane acceptor via a triptycene spacer, 57a and 57b. At 10 K in MTHF the lowest excited singlet states of the porphyrins in both compounds are oxidized by the acceptor with >99% efficiency to form radical ion pairs. The radical ion pair of 57b recombines to ground state with $\tau$ = 280 ps, while that of 57a recombines to yield the triplet state of the Zn porphyrin with $\tau$ = 520 ps. Picosecond transient absorption spectra and EPR spectroscopy of 57a at 10 K confirm the formation of
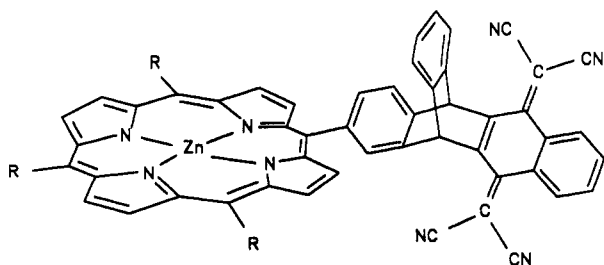


57a: R = phenyl,  57b: R = n–pentyl

the excited Zn porphyrin triplet state product following radical ion pair recombination in 57a. Using these data and the free energies of the charge separation reactions, which were obtained by electrochemical measurements at 294 K, Wasielewski et al. estimate that the radical ion pairs of 57a and 57b in the solid matrix at 10 K are destabilized by about 0.9 eV relative to their energy in fluid polar solvent at 294 K.

Gaines et al.[146] have extended this work and have obtained a more complete and quantitative picture of the dependence of charge separation rate on free energy of reaction in a rigid glass by measuring electron-transfer rate data on 14 porphyrin–triptycene–acceptor molecules, 58 (Chart X), which possess sufficiently large, negative free energies for charge separation to allow electron transfer to compete with excited singlet state decay in glassy 2-methyltetrahydrofuran (MTHF) at 77 K. Electron-transfer rate constants, $k_{cs}$, were determined using picosecond transient absorption and emission techniques along with fluorescence quenching measurements. Since ion-pair recombination in porphyrin–acceptor molecules is nonradiative, the free energy of charge separation, $\Delta G_{cs}$, in the rigid glass is difficult to obtain. On the other hand, in polar liquids the free energies of charge separation in these molecules, $\Delta G'_{cs}$, can be estimated using the one-electron oxidation and reduction potentials of the donor and acceptor, respectively, and the coulomb stabilization of the ion pair. These workers determined $\Delta G'_{cs}$ for the 14 compounds. Thus, the dependence of $k_{cs}$ on $-\Delta G'_{cs}$ can be determined experimentally with no corrections applied. Although this data can be used as a predictive tool, $\Delta G'_{cs}$ obtained from polar solution data differs significantly from $\Delta G_{cs}$ in the rigid glass. Fortunately, the precise relationship between these two free energy scales can be determined. When $\Delta G_{cs} \approx 0$, thermal repopulation of the lowest excited singlet state from the ion-pair state in three of these molecules yields biphasic fluorescence decays. These data can be analyzed to yield $\Delta G_{cs}$ directly. Assuming a linear free energy relationship the $\Delta G'_{cs}$ energy scale can be calibrated to yield $\Delta G_{cs}$ in the rigid glass using these data. Thus, the energies of the ion-pair states in these molecules are destabilized by 0.80 ± 0.05 eV relative to their energies in polar liquids. The measured value of this destabilization energy agrees remarkably well with predictions based on the dielectric continuum model of the solvent.

How do these results relate to the observations of Harrison,[97] Joran et al.,[117] Lindsey and Mauzerall,[118,119] and Sessler et al.?[103–105] In molecule 22 the donor and acceptor are linked by several saturated bonds. The change in rate constant observed as a function of cooling the solvent is similar to that observed by Wasielewski et al.[145] and Gaines et al.[146] Thus, the major term contributing to $V^2_{DA}$ may be a through-bond interaction that results in an electron-transfer rate that is controlled mainly by solvent motions. Molecules 34 and 35 should also fall into this regime as has been suggested by Joran et al.[117] and Lindsey and Mauzerall.[118,119] Yet, their data on 34 and 35, respectively, show evidence of charge separation at low temperatures. This observation is difficult to explain in terms of restricted solvent motion alone and deserves careful consideration in any model proposed to account for the temperature dependence of photoinduced charge separation. Finally, the results of Sessler et al.[103–105] on 25 may provide evidence for the intermediary regime, where increased coupling balances the effects of restricted solvent motion leading to rapid, high quantum yield charge separation in low-temperature glasses. Since this interesting balance can be used to tailor the electron-transfer rate constant of a supramolecular system to its environment, molecules that display this behavior need to be studied in more detail.

**CHART X. Compound 58**

DONORS:



A: M = 2H, B: M = Zn

C: M = 2H, D: M = Zn

ACCEPTORS:



A

D

G

B

E

H

C

F
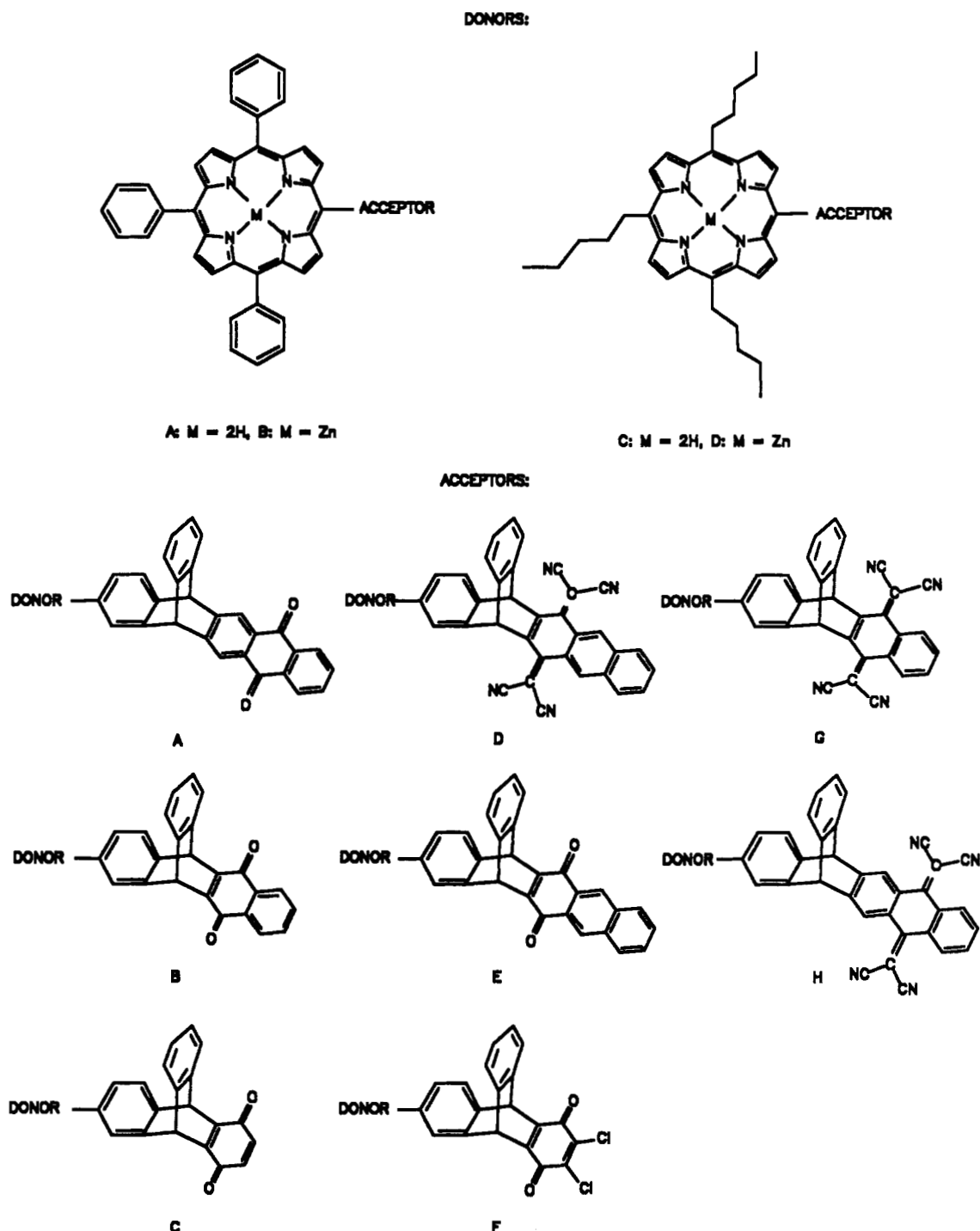
Wasielewski et al.[147] have used the information gathered by Gaines et al.[146] to design a supramolecular triad to separate charge efficiently in the solid state, **59**.



58
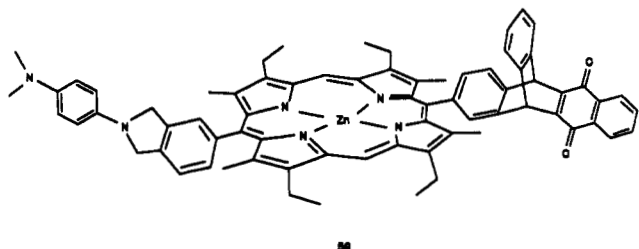
Photoinduced, multistep charge separation in bacterial photosynthetic reaction centers proceeds from the lowest excited singlet state of the dimeric bacterio-chlorophyll electron donor in two steps to yield a weakly interacting dimer cation–quinone anion radical pair, $P^+$–$Q_A^-$, separated by 28 Å. The chromophores within the reaction center are positioned at precise distances and orientations to insure that the electronic coupling between $P^+$ and $Q_A^-$ is sufficiently weak to allow $P^+$–$Q_A^-$ to live for about 100 ms. At long distances the elec-tron–electron exchange interaction, $2J$, between radicals within a charge-separated ion pair is sufficiently weak that differences in local magnetic fields surrounding each radical result in S–$T_0$ mixing of the radical pair spin sublevels. This mixing produces a non-Boltzmann population of the spin sublevels of the radical pair and may result in the appearance of spin-polarized EPR

spectra. Such spectra have been reported extensively for both bacterial and green plant reaction centers,[148,149] but have not been observed previously in rigid model systems. Compound **60**, TAPD–ZP–NQ, undergoes

**60**

**61**
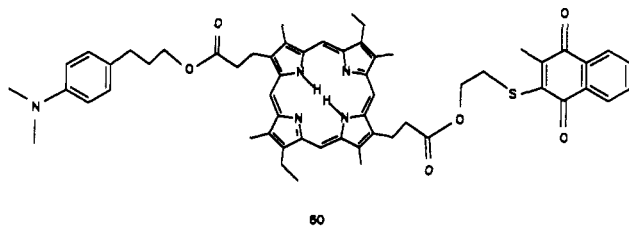
two-step, sequential charge separation at 5 K to yield a radical ion pair, TAPD$^+$–ZP–NQ$^-$, which possesses an overall 23-Å center-to-center distance, a 4-ms lifetime, and exhibits a spin-polarized EPR spectrum. The observed spectrum is best described as a pair of partially overlapping antiphase doublets as is expected for the correlated radical pair model.[150] This mechanism gives rise to a polarization pattern similar to that observed for **59** and for P$^+$–Q$_A^-$ in bacterial reaction centers. These results show that it is now possible to study charge separation over fixed distances and orientations using magnetic resonance as well as optical studies. These studies should provide a direct measure of the electronic coupling between an electron donor–acceptor pair as a function of structure and environment and may lead to a better understanding of electron transfer in photosynthesis.

Angerhofer et al.[151] have applied Fourier transform EPR to study the time course of the development of spin polarization within **59**. These workers observe a radical-pair signal that displays the same polarization that was observed in the light-modulated experiment described in ref 147. More importantly, these workers observed transient oscillations with a period of about 600 ns, which they suggest may be due to quantum beats. The frequency of quantum beats in radical pairs may arise from both spin–spin coupling and from the g-factor difference between the two radicals.[152]

Borovkov et al.[153] have recently produced a triad molecule consisting of flexibly bound N,N-dimethylaniline, mesoporphyrin II, and naphthoquinone, **60**. Both the free-base and zinc complex were studied. Rate constants for photoinduced electron transfer from the lowest excited singlet states of the porphyrins to the quinone were determined by picosecond fluorescence spectroscopy to be 1.5 × 10$^9$ and >5 × 10$^{10}$ s$^{-1}$, respectively. These workers do not provide data that would suggest that the secondary dark oxidation of N,N-dimethylaniline by the porphyrin cation occurs. Indeed, given the fact that there are three saturated bonds between the secondary donor and the porphyrin cation, it is unlikely that the rates of secondary electron transfer are sufficiently fast to compete with charge recombination in the initial porphyrin–quinone ion pair.

Rempel et al.[154] have presented results on a semirigid triad molecule consisting of two porphyrins and a benzoquinone, **61**. Since the lowest excited singlet states of the two linked porphyrins are isoenergetic, these workers observe a single electron transfer event from the porphyrins to the quinone upon excitation. This electron-transfer reaction is complicated by energy transfer between the two porphyrins.
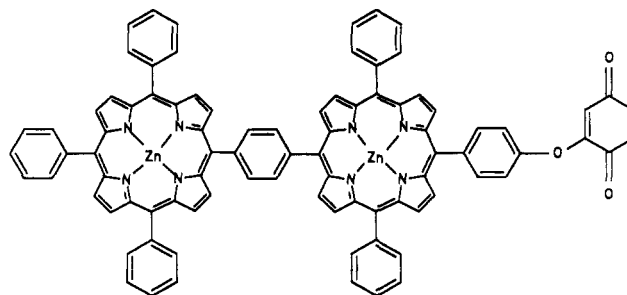
Lendzian and von Maltzan[155] have described a simple ZnTPP molecule that is linked via an ether bridge to benzoquinone, **62**. Excitation of this molecule in frozen
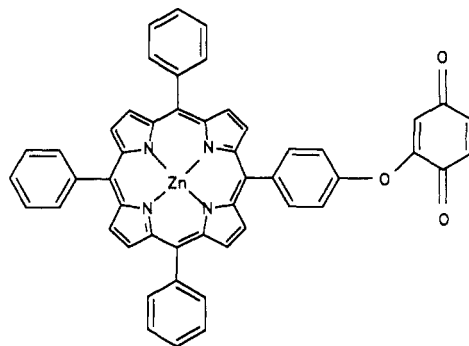
**62**

solution at 140 K results in formation of $^{3*}$ZnTPP. The authors suggest from EPR measurements that the triplet state is oxidized by the quinone leading to the formation of a triplet radical pair. Their time-resolved EPR spectra suggest that the triplet state precedes the formation of radicals. However, an inconsistency arises when one considers that the energy level of the radical pair state in frozen media is certainly well above that of the triplet.[146] In fact, these authors see no evidence of singlet state quenching by the quinone at low temperatures. This suggests that the energy level of the ion-pair state may even be above that of the lowest excited singlet state of ZnTPP. Thus, the mechanism of ion pair formation in **62** at low temperatures remains a puzzle.

Lendzian et al.[156] have described a set of ZnTPP compounds in which a meso position of the porphyrin is attached to the 1-position of a cyclohexane, while a benzoquinone is attached to the 4-position of the cyclohexane in both cis and trans stereochemistry, **63a,b**. Once again time-resolved EPR experiments were used to probe the lowest excited triplet state of the ZnTPP and the ZnTPP$^+$–BQ$^-$ radical pair produced in highly viscous ethanol at 150 K. Analysis of the radical pair signals suggests that the dipolar splitting in the trans radical pair is 2.65 G, while that of the cis radical pair is 3.75 G. This result is consistent with the larger radical–radical distance in the trans compound. The use of a viscous fluid permits enough solvent motion to permit solvation of the initially formed triplet ion pair on the microsecond time scale of its lifetime.

Aoyama et al.[157] have presented an interesting set of results based on a self-assembling system consisting of a rigid dihydroxy-substituted 5,15-diaryloctaalkylporphyrin, **64**. In chloroform this porphyrin self-as-
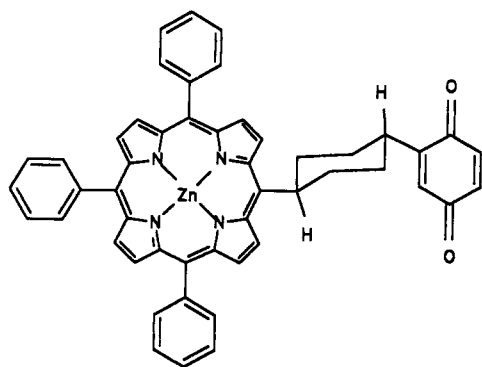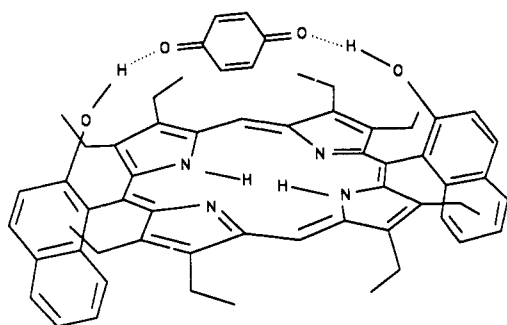
**63a**
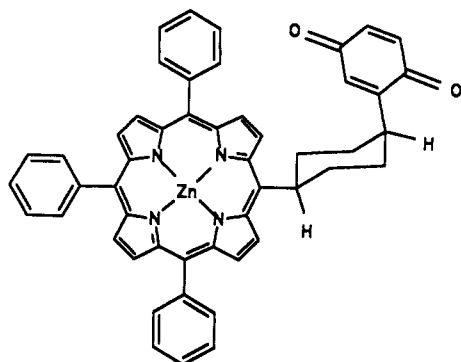


**63b**

sociates with quinones via two hydrogen-bonding interactions to the carbonyl groups of the quinone. Binding constants are reasonably high, typically about 100 M$^{-1}$. The ability of the quinones to quench the fluorescence of the porphyrin was found to depend on



**64**

their binding constants and not on their redox properties. This suggests that the close spatial association of the donor and acceptor makes the electronic coupling between them dominate the Franck–Condon term that depends on free energy.

Harriman, Kubo, and Sessler[158] have examined an interesting porphyrin–quinone in which the porphyrin is associated with the quinone by means of hydrogen bonds in a cytosine–guanine pair, **65**. The approach taken in developing this system is a particularly appealing one. It permits one to probe photoinduced electron transfer in a system in which the electronic coupling between the donor and acceptor is transmitted across weak hydrogen bonds such as one might find in photosynthetic proteins. The fluorescence of the Zn porphyrin in **65** is only weakly quenched by the asso-
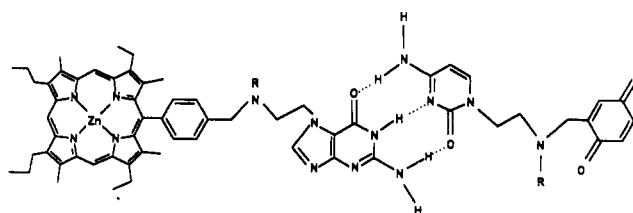


**65**

ciation of the quinone. Given the large number of atoms in the bonded pathway between the porphyrin and quinone, this is not unexpected. While observation of weak fluorescence emission quenching in and of itself does not prove that the quenching mechanism is electron transfer, the bonded pathway between the donor and acceptor could be shortened to increase the degree of quenching. This would also make it easier to use transient absorption techniques to verify the electron-transfer mechanism.

## V. Conclusion

Significant advances in the development of supramolecular systems for photoinduced charge separation and storage continue to be made. As this work progresses more and more workers come to realize that structural control is a necessary criterion for developing systems that will yield clear answers to questions concerning the mechanism of electron transfer. In addition, significant advances are being made to address problems associated with the environment surrounding a supramolecular species. Solvent plays a significant role in determining both the rates and energetics of electron transfer events. This role cannot be ignored in even the most sophisticated structures designed to promote long-lived charge separation. Finally, future designs of supramolecular systems for charge separation will deal with the problem of interfacing these systems to other chemical reactions. The stored oxidizing and reducing potential produced in these systems can be used to explore other chemistry in organized systems. The incorporation of these supramolecular charge separation systems into organized assemblies still lags behind our ability to synthesize them and study their interesting photophysical and electron-transfer properties. Hopefully, future work will remedy this situation.

## VI. Acknowledgment

## VII. References

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