The Role of the Electronic Structure of the Porphyrin as Viewed by EPR/ENDOR Methods in the Efficiency of Biomimetic Model Compounds for Photosynthesis

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A project to investigate the parameters that determine the efficiency of biomimetic porphyrin quinone model compounds for photosynthesis is described. It should aid in understanding the origin of the high efficiency of energy conversion in the light-induced charge separation in photosynthesis. Specifically, the contribution of the electronic matrix element to the electron transfer (ET) rates is addressed. Targeting the electronic structure of the ET components, EPR (electron paramagnetic resonance) and ENDOR (electron nuclear double resonance) spectroscopy were performed on the appropriate radical derivatives of the porphyrins and quinones to determine MO coefficients. Together with semiempirical MO methods, these coefficients were used to obtain information on the frontier orbitals of the donor and acceptor moieties, the porphyrins, and quinones of the model compounds. The porphyrin frontier orbitals (HOMO and LUMO) have been implicated in the balance of ET rates for charge separation and charge recombination, which is related to the efficiency. A model is presented to correlate the substitution pattern of the porphyrin with the efficiency of the model compound. In particular, the effect of porphyrin substitution, including the covalent link to an acceptor, and the comparison of porphyrins with chlorins and chlorophylls are addressed. The model allows for a quantification of these effects in some cases. Differences in the frontier orbital structure suggest that the [5,10,15,20 tetraaryl(alkyl)porphyrinato]-metal complexes are sufficiently different from chlorophylls to be nonideal model compounds. These results are related to recent publications, and possible improvements of experimental and theory approaches are addressed.

Introduction

The high efficiency of the energy conversion from sunlight to electrical energy in photosynthesis makes understanding the mechanism of the underlying chemical reactions one of the most fascinating questions from the boundary between chemistry and biochemistry. Here we discuss how biomimetic model compounds, consisting of porphyrins covalently linked to quinones, can aid the understanding of these primary processes. The large number of publications related to model compounds over the last couple of years reflects the scientific interest in this area of research. The present account is directed towards mechanistic aspects that should ultimately allow us to correlate the structure of the model compound with the expected performance. A model is introduced to assess efficiency in relation to chemical constitution, by an analysis of the factors entering electron transfer rates (k_{ET}). Specifically, the relation between the electronic structure, the electronic matrix element V_{DA} and the efficiency of the model compounds is addressed.

In nature, energy conversion occurs in the primary processes of photosynthesis, also called light reactions, which take place in a protein−pigment complex, the reaction

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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center (RC). The RC is a membrane protein containing the electron transfer pigments. The arrangement of these pigments in the RC is shown schematically in Figure 1.[1−4]

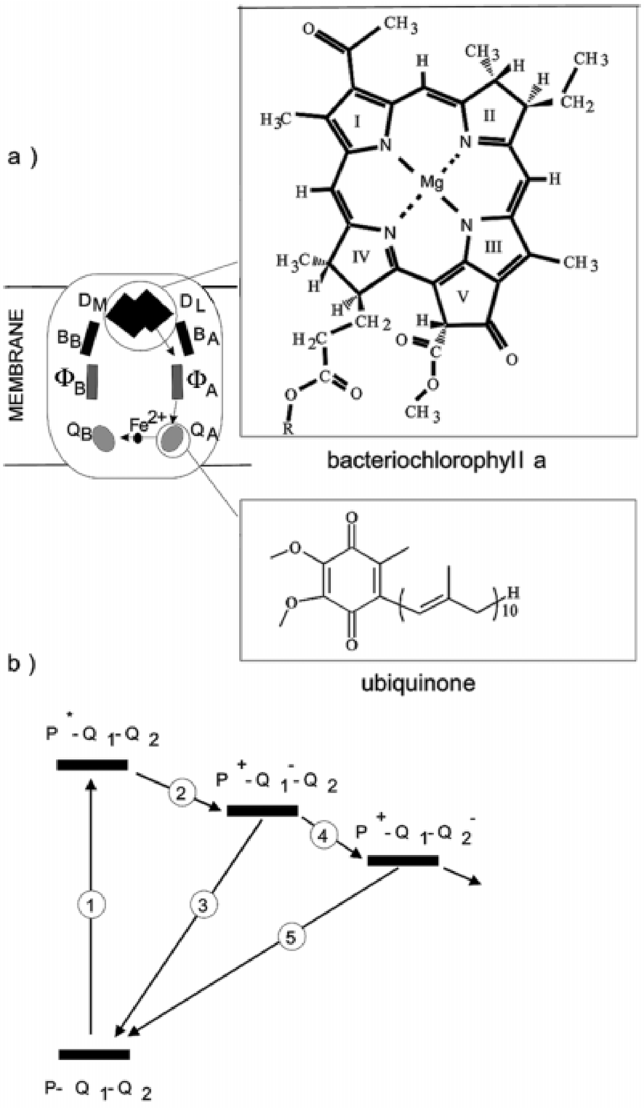

Figure 1. Schematic representation of the bacterial photosynthetic reaction center (a), which contains the cofactors performing light-induced electron transfer (ET) in a membrane-spanning protein; **D**: electron donor, a bacteriochlorophyll dimer; **B**: two monomeric bacteriochlorophylls; **Φ**: bacteriopheophytins; $\mathbf{Q_A}$ and $\mathbf{Q_B}$: primary and secondary ubiquinone-10 acceptors; (b) energy level scheme of light-induced ET; in model compounds **P** is the electron donor, an analogue of **D**, $\mathbf{Q_1}$ and $\mathbf{Q_2}$ successive acceptors, often quinones in model compounds; relevant reactions: light excitation (1), charge separation (2), charge recombination to the ground state (3), further charge separation (4), etc.; reactions 1−3 can be performed by diads ($\mathbf{P\text{-}Q_1}$), reactions 4, 5, etc. require larger aggregates (triads, etc.)

Upon light excitation, the primary electron donor (D), which in many photosynthetic bacteria is a dimer of bacteriochlorophyll (BChl) molecules, is promoted to a singlet excited state (D*). Subsequently, D* transfers an electron onto a chain of electron acceptors, whose redox potentials are adjusted to form an energy cascade (compare Figure 1, b). Within the first three picoseconds (ps) the state $\mathbf{D}^{+\cdot}\mathbf{\Phi}^{-\cdot}$, where **Φ** is the bacteriopheophytin (BPhe *a*) acceptor, is formed, from which the electron is then further transferred to the quinone acceptors (the primary and secondary quinones $\mathbf{Q_A}$ and $\mathbf{Q_B}$ in Figure 1a. The high efficiency of the native system is due to an intricate balance of electron transfer rates, such that forward reactions (e.g. reaction 4 in Figure 1b) are orders of magnitude faster than the wasteful back reactions, namely electron recombination to the ground state (e.g. reaction 3 or 5 in Figure 1).

Biomimetic model compounds are designed to aid the understanding of these processes and the present account describes one aspect of such investigations. The following conventions will be used: By biomimetic we mean, that the components resemble the natural cofactors structurally and with respect to their electronic properties. With respect to **D**, we take this to refer to porphyrins in the more narrow sense, excluding ring isomers like porphycenes, or expanded porphyrins like texaphyrin. By the above criteria, the recently synthesized model compounds with fullerene acceptors (e.g. ref.[5]) are not included in the present account.

Furthermore, model compounds investigated in ordered media, e.g. Langmuir−Blodgett films or liquid crystals have not been included, since in these environments special mechanisms of ET are at work, which are beyond the scope of this microreview.

Thus, biomimetic model compounds are described in which a porphyrin derivative (**P**) plays the role of **D**, and quinones are used as acceptors. ET can occur either from an excited singlet or triplet state of **P**. The model compounds are further classified according to the number of redox-active components as diads (**P-Q**), triads ($\mathbf{P\text{-}Q_1\text{-}Q_2}$), tetrads ($\mathbf{P\text{-}Q_1\text{-}Q_2\text{-}Q_3}$) etc. Depending on the number of components, they can perform reactions 1, 2, and 3 (diads), 1−5 (triads), etc. The necessity to chemically link donor and acceptors in a well-defined conformation to allow meaningful interpretations, was recognized early on.

Understanding the factors that determine k_{ET} in these model compounds is the key to making efficient model compounds. Therefore, we have engaged in a program to systematically investigate these factors through a combination of spectroscopy and theoretical methods. Using EPR (electron paramagnetic resonance) and ENDOR (electron nuclear double resonance) spectroscopy has allowed us to specifically analyze the electronic matrix element V_{DA}, about which much less is known than about the Franck−Condon term (FC), the second term entering k_{ET} (for a review on ET theory, see e.g. ref.[6] and below). The goal was to identify the parameters that allow us to compare and improve the efficiency of model compounds, and to ultimately predict the performance of the model compound using specific aspects of the structure. The latter point will allow for a determination of suitable target structures, thus avoiding the synthesis of model compounds whose performance is not optimal. In the course of this, we have studied the conformation and electronic structure of model compounds such as those shown in Figure 2.

The results of the spectroscopic investigations and semi-empirical molecular orbital (MO) calculations are described in several articles,[7−9] where the conformation and elec-

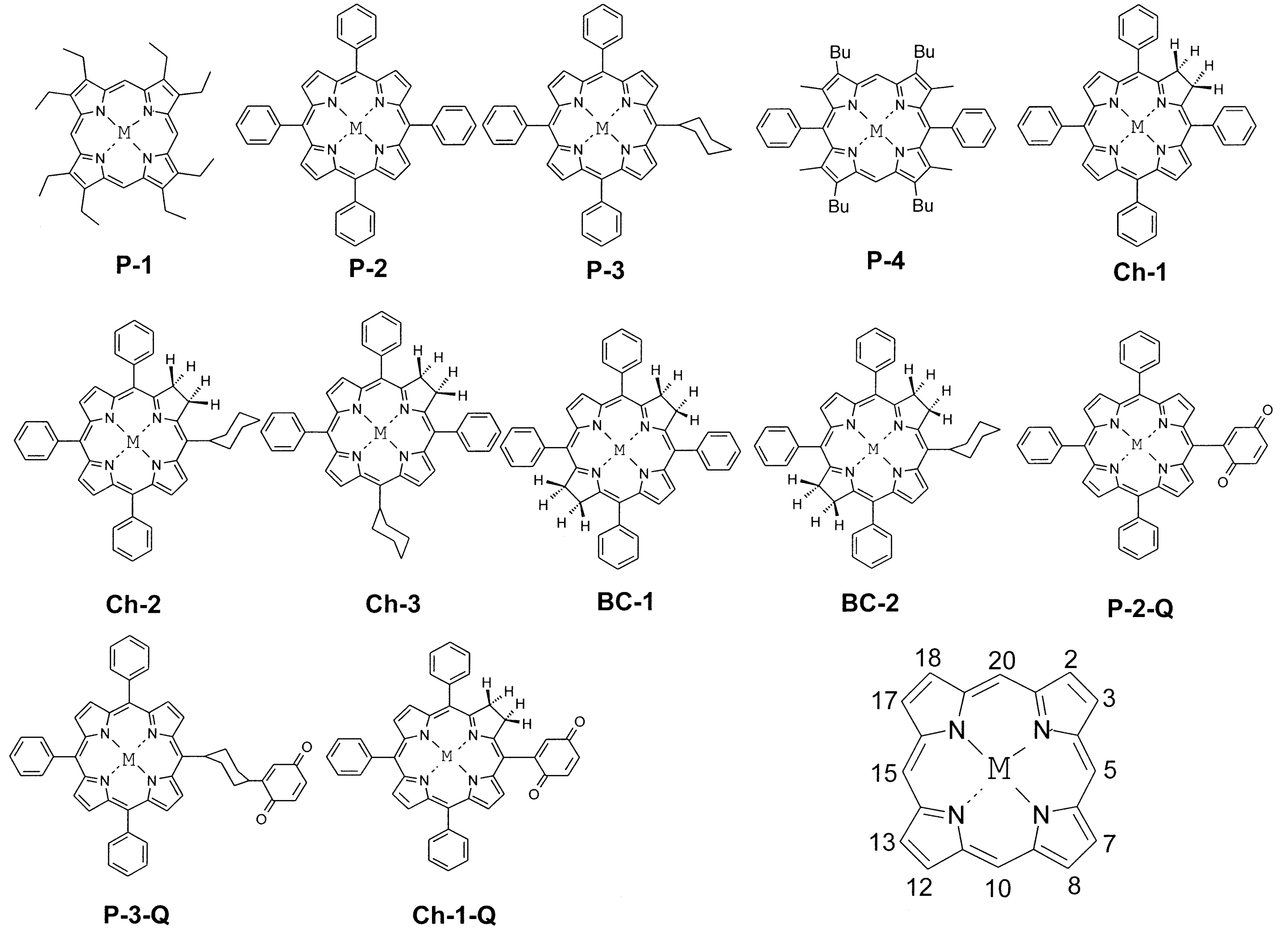

Figure 2. Structures of the porphyrin and chlorin derivatives discussed; **P**: porphyrin; **Ch**: chlorin; **BC**: bacteriochlorin derivative; three examples of linked porphyrin−quinone diads (**P-2-Q**, **P-3-Q**, and **Ch-1-Q**) are also shown; the insert shows the numbering scheme used throughout

tronic structure of porphyrins, chlorins, quinones, and linked donor−acceptor compounds are discussed in detail. Therefore, a brief outline of the methods of measurement and analysis is sufficient in the present context, allowing us to concentrate on the comparison of the properties of the electron donors **P** of different systems and to draw general conclusions that can aid in the design of future model compounds.

As discussed below, the electronic matrix element V_{DA} is partially determined by the electronic structure of **D** and **A**, in particular by the frontier orbitals, i.e. the HOMO (highest occupied MO) and LUMO (lowest unoccupied MO) of the porphyrin donor. Before our investigations started, information on the porphyrin HOMO was available for differently substituted porphyrins, but MO information on the LUMO was particularly sketchy. This had prompted us to focus our experimental endeavors on determining MO coefficients of the LUMO of porphyrins used in model compounds. Additionally, the effect of substituents on the electronic structure of the porphyrin, and thus potentially on ET properties, was not given much attention within the community involved with model compounds. This is in marked contrast to the fact that substituent effects on porphyrin frontier orbitals had been the subject of long term investigations in porphyrin chemistry. In order to bridge that gap, we investigated the frontier orbitals in a series of differently substituted porphyrin and chlorin derivatives (see Figure 2), including the effect of the covalent link used to attach the acceptor. With respect to improving model compounds, it was of interest to determine if particular linking positions should be preferable over others. Last but not least, we wanted to determine whether the difference between porphyrin and chlorin derivatives was sufficiently large to warrant the synthesis of chlorin-, rather than porphyrin-based model compounds.

The series of porphyrin and chlorin derivatives compared in the present account is shown in Figure 2. In these models, the influence of different substitution patterns of the porphyrin (**P-1** to **P-4** [10]), properties of chlorins and bacteriochlorins (**Ch-1** to **Ch-3**, **BC-1**, **BC-2**), and of different bridging units for the attachment of the acceptor are investigated. As the acceptor-linked molecules are diads, the relevant reactions are 1−3 in Figure 1. On this level, the efficiency is determined by the balance of the rate of reactions 2 and 3, i.e. charge separation and charge recombination. In larger units, e.g. triads, the balance between reactions 3 and 4 becomes dominant, which can be addressed in a manner analogous to that described here.

To put the present account into perspective, there are a large number of elegant studies related to the ET rates in biomimetic model compounds and their interpretation with respect to the FC term. Many focus on the effects of the driving force (ΔG) on k_{ET} (see for example ref.[11]), using a theory that has become popular under the name of one of the chief proponents, R. Marcus.[6]

Given the large number of publications in the field, it would be impossible to give a complete overview. Therefore, some illustrative examples are discussed, which are directly relevant to the present investigation or illuminate future developments. These include publications from the group of Moore, Moore, and Gust,[12−14] from Williamson and Bowler,[15] and from Hyslop and Therien.[16] On the theoretical side, ab initio MO calculations of the electronic matrix element V_{DA} by Hayashi and Kato[17] are of particular interest.

In the following sections, a summary of the relevant theoretical background will be given, in order to demonstrate the connection between the electronic structure (in particular the frontier orbitals) and k_{ET}. Experimental ways to determine the frontier orbitals by EPR and related methods are described. The comparison between the properties of the molecules shown in Figure 2 and the way this could aid the choice of target molecules in the synthesis will be discussed. This account will end with a summary of recent experimental and theoretical developments that are considered relevant for the present investigation.

Theoretical Background and Experimental Methods

Electron Transfer Rate and Electronic Matrix Element

The efficiency of light-induced electron transfer (ET) is brought about by a delicate balance of k_{ET} for the different processes. In the following, the theoretical description of k_{ET} is outlined, in order to understand its dependence on molecular parameters.

For weakly coupled donor and acceptor systems, the nonadiabatic approximation for k_{ET} is used. The conditions under which (1) is valid are discussed by Onuchic et al.[18] Briefly, the approximation applies to reactions in which the ET components are not too close in space, a condition that is expected to be fulfilled in the systems of interest here.

$$k_{ET} = \frac{2\pi}{\hbar} V_{DA}^2 FC \tag{1}$$

Here FC is the Franck−Condon weighted density of states. In the formulation according to Marcus theory this parameter depends on the driving force (ΔG) and the reorganization energy (λ), and V_{DA} is the electronic matrix element. Quantum-mechanically, V_{DA} is the splitting between the energy surfaces of compound (**D**−**A**) and product ($\mathbf{D}^{+\cdot}$−$\mathbf{A}^{-\cdot}$) electronic states. For weak electronic coupling (nonadiabatic ET, see refs.[6,17−20]) the molecular orbital overlap approximation can be used, which allows for the visualization of the molecular origin of V_{DA}. According to ref.[21] V_{DA} can be calculated by using

$$V_{DA} = KS_{DA} \tag{2}$$

which can be further broken down into the contribution of individual atomic orbital contributions:

$$V_{DA} = K \sum_{ij} c_i^{D} c_j^{A} S_{ij} \tag{3}$$

Here K is an empirical constant, c_i^{D} and c_j^{A} are the atomic orbital coefficients of the molecular orbitals on **D** and **A** involved in electron transfer, and S_{ij} the overlap integrals of atomic orbitals on atoms of **D** (i) and **A** (j). The magnitude of S_{ij} is determined by the structure, i.e. distance and orientation of **D** and **A**, c_i^{D} and c_j^{A} by the electronic structure. The orbitals relevant for the ET reactions in a diad molecule undergoing light-induced ET are shown in Figure 3.

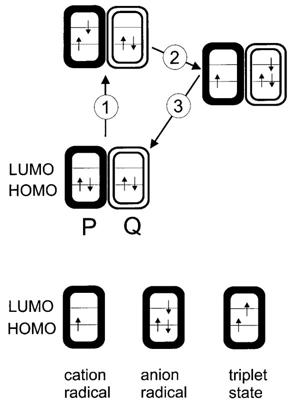

Figure 3. Schematic representation of the frontier orbitals of the donor (**P**) and the acceptor (**Q**) involved in light-induced charge separation; reaction 2: ET from the LUMO of **P** to the LUMO of **Q**; reaction 3: ET from the LUMO of **Q** to the HOMO of **P**; bottom: paramagnetic states of **P**; by EPR the orbital containing the unpaired electron was probed; cation radical: HOMO; anion radical: LUMO; (photo-excited) triplet state: HOMO and LUMO

In the charge separation reaction (CS, reaction 2 in Figure 3) an electron from the LUMO of **P** is transferred to the LUMO of **Q**. In the charge recombination (CR, reaction 3) the electron from the LUMO of **Q** is transferred to the HOMO of **P**. Thus, for reaction 2 the overlap of the porphyrin LUMO with the quinone LUMO is important, whereas the overlap of the latter orbital with the porphyrin HOMO enters reaction 3. Consequently, two different orbitals of **P** participate in these key reactions. If the relevant MO coefficients of these two orbitals differ, the efficiency of the model compound could be affected, as in this case V_{DA} would differ for both reactions (see Figure 4).

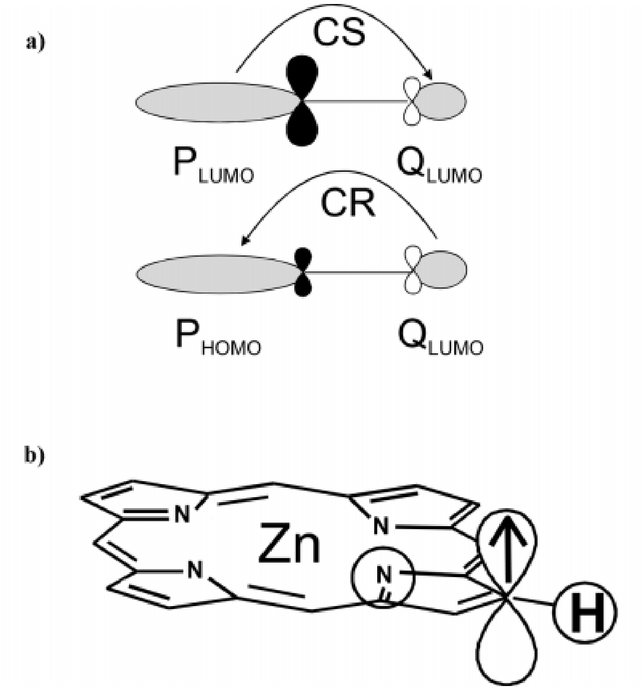

Figure 4. Simplified illustration of orbital control in ET rates of charge separation (CS) vs. charge recombination (CR); arrows: direction of ET; a): a large LUMO coefficient of the donor (**P**) at the linking position with the acceptor enhances the rate of the CS reaction, a small HOMO coefficient slows down the CR reaction; the combination of both is expected to increase the efficiency (see text); b): hyperfine couplings (hfcs) of magnetic nuclei (H or N) close to π electron system reflect the spin density in the p_z orbital

As a quantitative criterion for evaluating the efficiency of a diad model compound, we used the ratio of charge separation vs. recombination rate (k_{CS}/k_{CR}). This ratio should be maximized, as that combines the speedy formation with a long lifetime of the charge-separated state **$P^{+\cdot}$-$Q^{-\cdot}$**.The latter factor is important in coupling the primary reaction product **$P^{+\cdot}$-$Q^{-\cdot}$** to the subsequent ET reactions (reaction 4 in Figure 1), and ultimately to the chemical reactions that are involved in utilizing the redox energy. With respect to V_{DA} this means that the ratio of V_{DA} for the charge separation has to be compared to that of charge recombination $(V_{CS}/V_{CR})^2$. Of the factors entering V_{DA} in (3) we expect that the dominating contribution to the ratio is due to c_i^D, the MO coefficients of the porphyrin. S_{ij} and c_j^A can be considered constant for CS and CR reaction because S_{ij} depends on the geometry rather than the orbitals on **P** and **Q** (for possible limits to this statement see ref.[16]), and the c_j^A coefficients are identical for both reactions. Under the further assumption that V_{DA} is dominated by the MO coefficient at the linking position, i.e. c^D_{HOMO} or c^D_{LUMO} the contribution of V_{DA} to k_{CS}/k_{CR} is given by

$$k_{CS}/k_{CR} = (V_{CS}/V_{CR})^2 = K'(c^D_{LUMO}/c^D_{HOMO})^2 \qquad (4)$$

Figure 4a shows a favorable situation in a cartoon-like representation. In the model compounds of interest here, **D** and **A**, i.e. **P** and **Q**, are linked by a spacer, and there is no doubt that the spacer orbitals contribute to ET between **D** and **A** by providing a pathway for ET. This has been addressed in several theoretical and experimental studies,[16,22] but has to be neglected in the analysis presented here.

Experimental Determination of MO Coefficients

Magnetic resonance methods, in particular EPR and ENDOR spectroscopy on paramagnetic derivatives of porphyrins, have aided significantly towards understanding the electronic structure,[23] since it is relatively straightforward to relate the hyperfine (hf) interaction of electron and nuclear spin measured by these methods to the molecular orbital coefficients. In π radicals, to a first approximation, the (squared) MO coefficients of the orbital occupied by the unpaired electron are measured. [The difference in the definition of the spin densities thus measured and electron densities required in order to utilize (3) is described in ref.[24]] This means that in a cation radical MO coefficients of the HOMO, in an anion radical those of the LUMO are determined (Figure 3; for clarity, orbitals are always labeled according to their occupancy in the neutral ground state of the respective porphyrin or quinone derivative). The isotropic hfcs (a_{iso}) of radicals observed by EPR and ENDOR are due to the Fermi contact interaction, see ref.[25] Empirical formulae for obtaining π spin densities and thereby MO coefficients from measured hf coupling constants are of the McConnell type, and for a proton bound to a carbon atom (see Figure 4b) that is part of the π electron system, the McConnell relation takes on the form[26]

$$a_{iso} = Q_{C-H}\,\rho_{C\pi} \qquad (5)$$

where Q_{C-H} is an empirical constant whose magnitude depends on the type of radical and the nucleus in question, and $\rho_{C\pi}$ is the spin density in the π electron orbital at the carbon nucleus, which, in turn, can be related to c_i^D. Measuring a_{iso} of nuclei at different positions in the π electron system thus gives local information about MO coefficients, as illustrated in Figure 4b. For systems with a larger number of inequivalent nuclei, the resolution of EPR is not sufficient. For such cases, an arsenal of ENDOR, TRIPLE, etc. methods have been developed, and employed successfully.[27,28] An illustration for applying the ENDOR technique is given in Figure 5.

Figure 5 shows ENDOR spectra of the cation radical of **Ch-1** (**Ch-1**$^{+\cdot}$) and the directly linked chlorin quinone **Ch-1-Q**$^{+\cdot}$. The hfc a_{iso} is read off as the separation of two ENDOR lines as shown for a_{iso} of the protons at positions 2 and 3 ($a_{2,3}$). The hfcs of all relevant groups of protons of **Ch-1**$^{+\cdot}$ are resolved, and the large hfc observed for protons at positions 2 and 3 identify the HOMO of the chlorin as a_{1u}, as discussed below. Linking the quinone causes splitting of the ENDOR lines assigned to the protons at positions 2 and 3 (see Figure 5, b). Furthermore, a small hfc can be identified, which is due to a proton at the quinone (a_{Q-3}), revealing some electronic communication between the chlorin donor and the quinone acceptor. In general, the assignment of hfcs to individual protons is one of the chal-

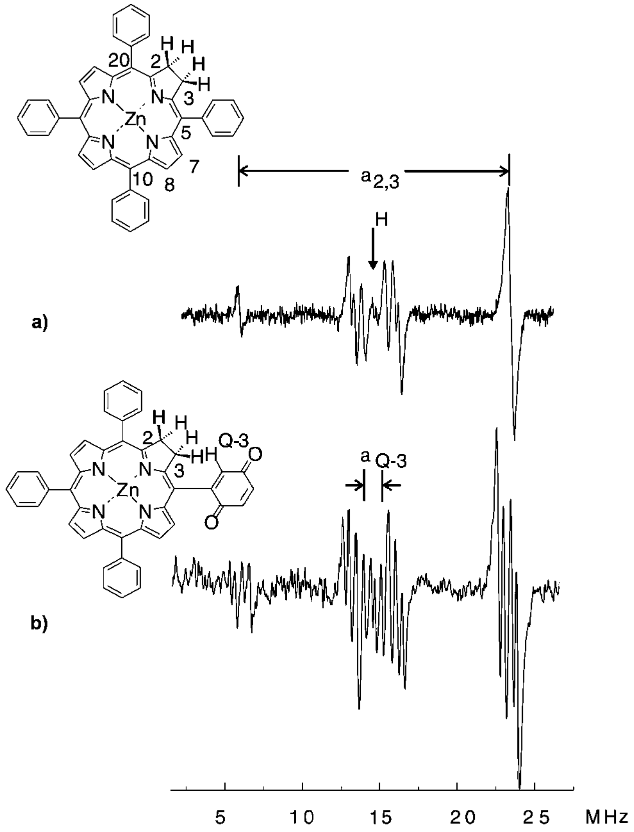

Figure 5. Electron nuclear double resonance (ENDOR) spectra of the chlorin cation radicals **Ch-1**$^{+\cdot}$ (a) and **Ch-1-Q**$^{+\cdot}$ (b) in liquid solution; the unpaired electron is localized on the chlorin fragment; ENDOR lines occur symmetrically about the Larmor frequency of the free proton (ν_H); measurement of isotropic hfc (a_{iso}) is indicated for protons at positions 2 and 3 ($a_{2,3}$); effect of directly linking the quinone acceptor (b), resulting in splitting of lines belonging to $a_{2,3}$ and additional hfc from quinone proton Q-3 (a_{Q-3}); measurement conditions see ref.[9]

lenges in EPR/ENDOR spectroscopy and has been achieved in the present case through a combination of selective deuteration by Fajer et al.[29,30] and semi-empirical MO calculations.[9] The example thus reveals that once the appropriate paramagnetic state can be stabilized, and the proper measurement conditions can be found, hfcs can be directly read off the spectra.

Frontier Orbitals of Porphyrins

The frontier orbitals of porphyrins and chlorins are referred to in terms of the Gouterman four-orbital model shown in Figure 6. A minimum of four orbitals needs to be considered, since the two energetically lowest unoccupied MOs (LUMO and LUMO+1) are degenerate due to symmetry, and the two energetically highest filled orbitals (HOMO and HOMO−1) are accidentally nearly degenerate. For a given porphyrin derivative the energetic ordering of these orbitals (see insert in Figure 6) depends on the substituents. The distribution of MO coefficients between the orbitals is sufficiently different to justify the need to determine the frontier orbitals of the porphyrin derivative used in the model compound.

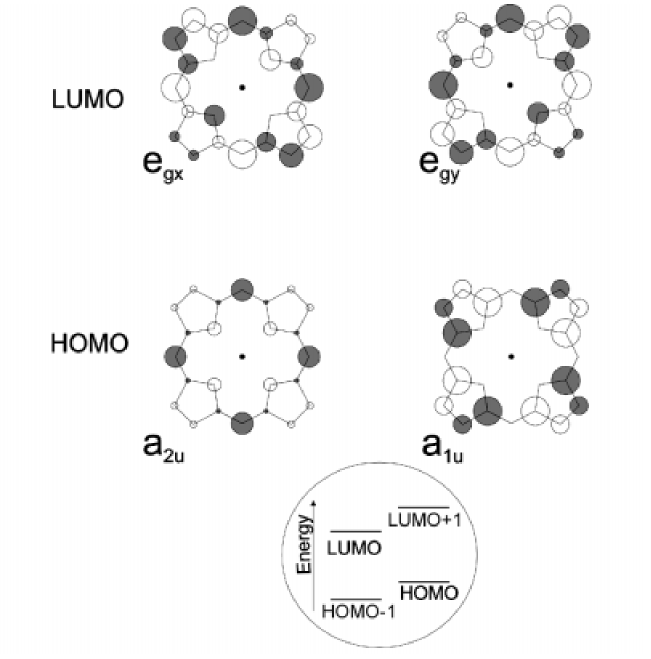

Figure 6. Frontier orbitals of the porphyrins according to the Gouterman four-orbital model; orbitals e_{gx} and e_{gy}: LUMO; a_{2u} and a_{1u}: HOMO; classification according to D_{4h} point group; insert: labeling of the frontier orbitals in the presence of a perturbation lifting the degeneracy

Previous investigations can be summarized as follows: In porphyrins, four aryl or alkyl substituents in the *meso* position (i.e. at position 5, 10, 15 and 20, see Figure 2) favor the a_{2u} HOMO, suggesting that the interaction of the aryl or alkyl substituents with the porphyrin π electron system raises the energy of the a_{2u} orbital, which has large MO coefficients at these *meso* positions (Figure 6), above the a_{1u}.

In the parent porphyrin, or the porphyrins with alkyl substituents at β-pyrrole positions, (i.e. positions 2, 3, 7, 8, etc. in Figure 2) an a_{1u} HOMO is found. Saturating the β-positions of one or two pyrrole rings to form a chlorin or a bacteriochlorin derivative also results in the a_{1u} orbital being the HOMO (see also Table 1).

Table 1. Frontier orbitals of porphyrins (**P**), chlorins (**Ch**), bacteriochlorins (**BC**), and (bacterio)chlorophylls (**Chl** and **BChl**)

	P-1	**P-2**	**P-3**	**P-4**	**Ch-1** **BC**	**Chl**[a] **BChl**
HOMO	a_{1u}	a_{2u}	a_{2u}	a_{1u}	a_{1u}	a_{1u}
LUMO	n.d.	n.d.	n.d.	e_{gx}-e_{gy}	e_{gx}	e_{gx}

[a] See refs.[33,34]

The LUMOs in porphyrins have received comparatively less attention than the HOMOs. Spectroscopic properties of **P-1** and **P-2** anion radicals investigated by Seth and Bocian[31] reveal that the degeneracy of the LUMOs dominate the EPR spectra. As a result, no hfcs could be determined. The LUMO of chlorophylls and bacteriochlorophylls was found to be the e_{gx} orbital.[32−34]

Results of EPR/ENDOR Investigations

In the following discussion, the theoretical framework described above is applied to the porphyrins and chlorins shown in Figure 2. First, we will discuss how the different substitution patterns affect the LUMO and the HOMO of the respective porphyrins, followed by a discussion of possible effects of attaching the acceptor. Finally, the consequences for ET properties are analyzed.

Effect of Substituents on Porphyrin LUMO

Anion radicals of symmetrically substituted porphyrins have EPR characteristics indicative of degenerate or nearly degenerate ground states: broad EPR signals, i.e. in the range of several mT, with Lorentzian lineshapes and fast-relaxing magnetization. These properties are attributed to the degeneracy of the LUMO e_{gx} and e_{gy} orbitals. Asymmetric substitution of the porphyrin lifts the degeneracy, but as long as the energy separation remains small, the nearby energy level is expected to enhance relaxation, and, for example lead to large EPR line widths. While such phenomena are interesting in their own right, and have spawned a class of research activities related to Jahn−Teller distortions in highly symmetrical molecules (for instance fullerenes C_{60}, C_{70}, etc.), in the present context they prevent the determination of MO coefficients because fast relaxation rates and large linewidths make it impossible to measure individual hfcs.

The series from **P-2** to **P-4** illustrates these trends; see ref.[7] Replacing one of the phenyl rings of **P-2** by cyclohexyl (**P-3**$^{-\cdot}$) reduces the EPR linewidth, but still retains the same overall features. Only the spectra of **P-4**$^{-\cdot}$ exhibit sufficient spectral resolution to determine hfcs in this state. The analysis revealed that in **P-4**$^{-\cdot}$, the orbital occupied by the unpaired electron is a linear combination of the e_{gx} and e_{gy} orbitals, as shown in Figure 7.

The fact that a linear combination of the wavefunction is appropriate is an immediate consequence of the degeneracy of the e_{gx} and e_{gy} orbitals, and reflects the way in which that degeneracy is lifted by the substituents. The symmetry imposed by the substituents, i.e. the positions to which the substituents are attached, determines which linear combination has to be chosen. It results in a drastic redistribution of MO coefficients relative to those of the e_{gx} and e_{gy} orbitals.

In the chlorins the saturation of one or two pyrrole rings reduces the symmetry of the molecule from the onset, and well-resolved anion radical EPR and ENDOR spectra are measured.[8,9] In other words, the splitting of the e_{gx} and e_{gy} orbital is sufficiently large to make one orbital dominant. From ENDOR studies, hfcs are obtained to high resolution, revealing the distribution of the coefficients of the LUMO over the molecule, which is the orbital relevant to charge separation. As the symmetry of the perturbation corresponds to the symmetry according to which e_{gx} and e_{gy} are classified, no linear combination is required in this case. The orbital is identified as the e_{gx} orbital, i.e. the same LUMO as in chlorophyll.[32−34]

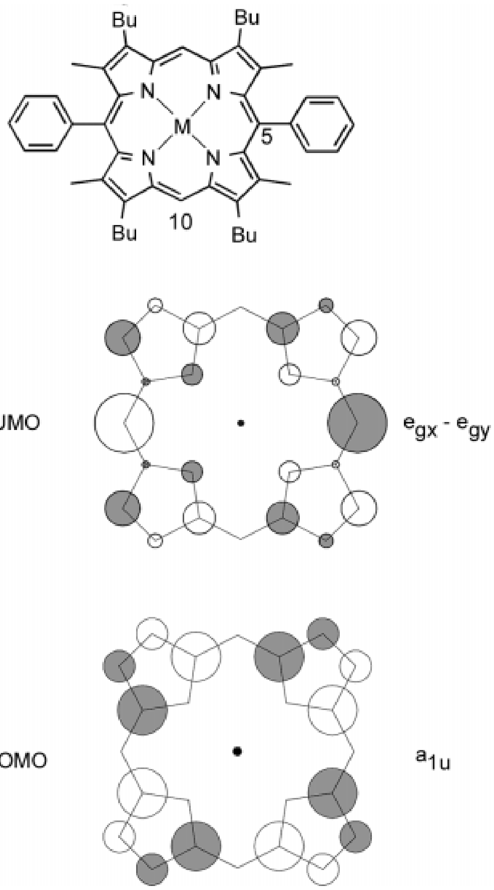

Figure 7. Frontier orbitals of asymmetrically substituted porphyrin **P-4**; LUMO: linear combination of e_{gx} and e_{gy} orbitals; HOMO: a_{1u}; large LUMO and small HOMO coefficient at position 5 make this a good linking position; for details, see ref.[7]

Effect of Substituents on Porphyrin HOMO

As mentioned above, *meso* substitution of porphyrins by alkyl or aryl groups causes sufficient elevation of the a_{2u} above the a_{1u} level to result in an A_{2u} ground state for the cation radical. Thus, an A_{2u} ground state of the cation radicals of **P-2** and **P-3** is hardly surprising. In **P-4**, competition between the β-alkyl and the two *meso*-phenyl groups was to be expected. An a_{1u}-like HOMO was found in this case, suggesting that two phenyl substituents are not sufficient to raise the a_{2u} above the a_{1u} orbital.[7]

Chlorins and bacteriochlorins: Another type of competitive effect is expected for the substitution pattern in **Ch-1**-, **Ch-2**-, and **BC-1**-type chlorins and bacteriochlorins: chlorophylls and bacteriochlorophylls are known to have a_{1u} HOMOs, but again, the *meso*-phenyl substituents in **Ch-1**, **Ch-2**, and **BC-1**, which are not present in the chlorophylls, should raise the a_{2u} in energy. In spite of this, an a_{1u} HOMO is found. In the chlorin example shown in Figure 5, the large hfc for the protons at positions 2 and 3 ($a_{2,3}$) is characteristic of an a_{1u} HOMO, since only the a_{1u} has large MO coefficients at the β-pyrrole positions (see Figure 6). There is some evidence, however, that the a_{2u} may be energetically not too far removed, as some difficulties in performing ENDOR experiments on these chlorins may be due to fast relaxation brought about by a close-lying orbital.[8,9]

Effects of Linking the Acceptor

If the acceptor is covalently linked to the porphyrin, also the linker acts as a substituent and thus can influence the porphyrin electronic structure. The linker, therefore, needs to be considered when determining the frontier orbitals of the porphyrin. The degree to which the linker−acceptor unit influences the electronic structure depends on the linking position and the electronic properties of the linker/acceptor. One example is shown in Figure 5, where linking the acceptor directly to a chlorin affects the hfcs of the chlorin.

Therefore, we investigated some acceptor-substituted porphyrins and chlorins. For porphyrins of type **P-2** and **P-3**, the cation radicals show no effect upon linking a quinone either directly or via a cyclohexylene bridge.[35] For chlorins, local, but generally small effects are observed when attaching the quinone directly to the *meso* position (see above), but none when the quinone is linked to the chlorin by a cyclohexylene bridge.[9] This finding is important because, as a result, the wavefunction of the parent porphyrin is expected to be a good model for the wave function of the quinone-linked model compound.

Use of the Triplet State to Determine Frontier Orbitals

An additional handle on the frontier orbital structure is provided by the triplet state of the porphyrin. The triplet state contains the same number of electrons as the excited singlet state and it is paramagnetic, with an unpaired electron in the HOMO and one in the LUMO, as shown in Figure 3. Given that **P*** (see Figure 1) is either a photoexcited singlet or the triplet state itself, in principle, the triplet is a better model for **P*** than the porphyrin anion radical. The hfcs of the triplet state can be determined by ENDOR, as shown by Kay et al.[36] Unfortunately, at present, the assignment of hfcs to specific molecular positions has turned out to be an even more difficult task than for the cation and anion radicals described above, which complicates the interpretation of the data.

Consequences for Electron Transfer

In the frontier orbitals of the porphyrins, the distribution of MO coefficients over the macrocycle is susceptible to small perturbations by the substituents and linkers. Given that the relevant HOMOs and LUMOs often have complementary MO coefficients (see Figure 6) it is to be expected that the orbital structure has an effect on the ET properties. This is illustrated using two examples, the frontier orbital structure of the asymmetric porphyrin **P-4** shown in Figure 7 and a chlorin−quinone system. For **P-4** the frontier orbitals shown in Figure 7 allow qualitative predictions about favorable linking positions. The large LUMO coefficient at position 5 of this porphyrin is combined with very small HOMO coefficients in the a_{1u} orbital, suggesting that linking the acceptor through the phenyl group at position 5 would be optimal. At position 10, the LUMO coefficient is much smaller making this position a bad linking position. In the case of this porphyrin, no quantitative predictions about the efficiency of the model compound could be made because of insufficient spectral resolution. The situation was different for the chlorin-based model compounds. In these cases, the information about the coefficients of the frontier orbitals was sufficiently accurate to be able to use (4) to quantify the efficiency of the model compound. The ratios calculated[9] show significant dependence on the linking position and the contribution of V_{DA} to the ratio k_{CS}/k_{CR} can be as large as 20 at certain positions, whereas at other positions it can be close to zero.[8,9]

From this estimate it seems clear that the electronic matrix element, and thus the electronic structure of the porphyrin contributes significantly to the efficiency of model compounds. Below are some general guidelines on how the porphyrin substituents could affect the efficiency. Given the approximations introduced in the model, the limitations of the present approach and possibilities for improving the theoretical models will be critically reviewed.

In model compounds consisting of larger aggregates, i.e. triads, tetrads etc., the above-mentioned model could be applied by considering the appropriate MOs. The second charge separation step from $\mathbf{P}^{+\cdot}\text{-}\mathbf{Q}_1^{-\cdot}\text{-}\mathbf{Q}_2$ to $\mathbf{P}^{+\cdot}\text{-}\mathbf{Q}_1\text{-}\mathbf{Q}_2^{-\cdot}$ would involve, for example, overlap of the LUMO of $\mathbf{Q}_1$ with the LUMO of $\mathbf{Q}_2$ for the charge separation (reaction 4) and the overlap of the HOMO of **P** with the LUMO of $\mathbf{Q}_1$ for the charge recombination (reaction 3).

Comparison of Porphyrins with Chlorophylls

As shown in Table 1 the frontier orbitals of most porphyrins (**P-2** to **P-4**) differ from those of chlorophylls and bacteriochlorophylls, and the analysis above suggests that this could be relevant for the ET rates. For example, with respect to the HOMO (the orbital that is relevant for charge recombination) porphyrins of the **P-1** type have a HOMO similar to that of the chlorophylls, whereas the *meso*-substituted porphyrins of type **P-2** and **P-3** have a HOMO that differs from those of the chlorophylls. As mentioned before, the complementary distribution of MO coefficients over the molecular positions in the a_{1u} and a_{2u} orbitals (see Figure 6) is expected to lead to significant differences in charge recombination between porphyrins of type **P-2** to **P-3** and chlorophylls. With respect to the charge separation, the obvious difference is that porphyrins have near degenerate LUMOs, whereas in chlorophylls the e_{gx} is energetically well below the e_{gy} orbital. The effect of the quasi-degeneracy of the LUMOs on V_{DA}, and thus k_{ET} is not well understood, which makes comparison to the chlorophyll systems, where this degeneracy is lifted, difficult at present.

The difference between the frontier orbital structure of chlorophylls and porphyrins suggests that within a given overlap situation V_{DA} parameters will differ if chlorophylls are replaced by porphyrins. The degree to which this affects the relevant k_{ET} values and ratios thereof will depend on the geometry of the overlap and, in model compounds, the linking position. Such factors could ultimately explain why nature has chosen chlorophyll as the origin of the primary charge separation rather than porphyrins.

Discussion of Literature Examples

In a publication from the group of Moore, Moore, and Gust,[14] a series of model compounds of the type **C−P-Q** are discussed, in which **C** is a carotenoid-type secondary electron donor, and **P** is a porphyrin of type **P-2** or **P-4**. The photophysical properties, in particular the ET rates were determined, and the FC factor in (1) was obtained from measured redox potentials. Once the FC term and k_{ET} is known, V_{DA} can be determined using (1). For model compounds based on porphyrins of the type **P-2**, V_{DA} values differ from those in the **P-4** model compounds. For example, in the charge recombination reaction $\mathbf{C{-}P^{+\cdot}\text{-}Q^{-\cdot}} \rightarrow \mathbf{C{-}P\text{-}Q}$, V_{DA}^2 is estimated to be a factor of 8 larger in the **P-2**-based model compound than in the model compound where **P** is of the **P-4**-type.[14] Qualitatively, this agrees with the difference in the HOMOs of **P-2** and **P-4**. In both cases, the acceptor is attached to the *meso* position 5 of **P**, where the HOMO of **P-4** has a significantly smaller coefficient c_i^D [see (3)] than the HOMO of **P-2**. In ref.[14] the differences between the two model compounds are attributed to a difference in orientation of the linking phenyl ring, i.e. a difference S_{ij} in (3).

Porphyrin diads ($\mathbf{P_1{-}P_2}$) are described by DeGraziano et al.[12] In one diad, $\mathbf{P_2}$ is attached to a *meso* position of $\mathbf{P_1}$, in the other diad $\mathbf{P_2}$ is attached to a β-position of $\mathbf{P_1}$. A similar approach, as used in ref.[14] yields estimates of V_{DA} for the different ET reactions. In ref.[13] porphyrin−quinone diads are investigated in which a naphthoquinone is attached by a bicyclic bridge to the *meso* and β positions (positions 5 and 7, Figure 2) of a porphyrin. In addition, the porphyrin bears a *meso* substituent at position 15, and alkyl groups at all remaining β positions, creating a porphyrin resembling **P-4**. The ET properties have been investigated in detail, in particular ET rates and their dependence on solvents and on the temperature were determined. Mechanistic aspects were discussed in detail. The ratios of k_{CS}/k_{CR} in these model compounds vary between 10 and 1000, and fast ET was observed even at low temperatures, suggesting that the rigid bridge promotes strong coupling between **P** and **Q**. The authors discuss the intriguing possibility that adiabatic ET specifically increases k_{CS}. The maximum value for V_{DA} of the charge separation reaction estimated is 100 cm^{-1}, which may lead to adiabatic ET for this reaction. Thus, while the large difference between k_{CS} and k_{CR} is mostly due to energetic factors entering the FC term, some of that enhancement could also be due to V_{DA}.

A study by Williamson and Bowler[15] explores the role of the linkers, which contain different numbers of through-bond vs. through-hydrogen-bond steps for ET, thus addressing a question that is discussed controversially also for biological ET reactions. Hyslop and Therien[16] present model compounds in which ET via the central metal ion of the porphyrin is compared to ET via the periphery of the porphyrin π electron system. This problem is particularly relevant to ET in heme-containing proteins.

The role of the bridge linking donor and acceptor is addressed in ref.[37], where the effect of a bridging porphyrin in chlorophyll−quinone model compounds was investigated. The ET rates for charge separation and recombination are given and redox potentials have been determined. Different models for the way the bridge contributes are discussed.

Future Developments

Novel Magnetic Resonance Techniques

Interesting developments can be expected from advanced EPR methods making use of time-resolved, pulsed EPR techniques.[38−40] With respect to determining the MO coefficients of the frontier orbitals, ENDOR on the triplet state will benefit from pulsed ENDOR techniques. Pulsed ENDOR has often been shown to result in a better signal-to-noise ratio than continuous-wave (cw) ENDOR, because pulsed ENDOR is less sensitive to relaxation rates and should therefore be more universally applicable.[41]

Perhaps more importantly, the improved time resolution of pulsed methods makes it possible to investigate charge separation by EPR in real time. Several examples of measurements on charge separated states have been performed (reviewed in refs.[39,40] and references therein). Long lifetimes (2.5 to 12.7 ms) of charge-separated states in chlorophyll-based triads have enabled Wasielewski et al.[42] to measure spin-polarized EPR signals by a cw-EPR method. From these signals the magnitude of the exchange interaction *J* of the state $\mathbf{P^{+\cdot}\text{-}Q^{-\cdot}}$ was derived. This parameter is identified with V_{DA} in their publication.[42] The results of Hanaishi et al.[43] show that FT-EPR spectra of weakly coupled radical pairs contain information on the molecular exchange interaction *J*, a quantity that can be related to V_{DA}.

Progress in Theoretical Methods

There are now several reports of the use of advanced MO methods such as ab initio or density-functional (DFT) methods on model compounds or related systems. These methods have become sufficiently efficient and fast to make them suitable for large systems. An example of using the DFT method is given in ref.[44] where, for example, the electronic coupling of NiOEP (i.e. **P-1** with Ni as central metal ion) dimers was investigated. For NiOEP, the method[44] predicts that the a_{2u} orbital lies above the a_{1u}, whereas the EPR/ENDOR experiments on ZnOEP discussed above suggest an a_{1u} HOMO. This difference could either be due to the fact that the central nickel ion favors an a_{2u} HOMO, or it reflects a shortcoming of the theoretical method. Given that the number of electrons in the NiOEP dimers is comparable to that of porphyrin−quinone diads, the DFT method is suitable to calculate biomimetic model systems. Presently, DFT methods are becoming increasingly better in calculating open-shell systems, and observables of EPR, such as hfcs. Therefore, it may be expected that these methods will in the near future replace the semi-empirical MO methods, such as those we have used in our model.

In order to calculate the structures of larger systems, a method proposed to combine molecular mechanics and quantum-chemical methods could also be of interest. An example is presented in ref.[45] where this method was applied to determine the structure of a porphyrin derivative, but it could also be beneficial to apply it to larger porphyrin−quinone model compounds.

Improvements to the Calculation of the Electronic Matrix Element

Two different approaches to calculate V_{DA} have been used to date. The first one is to calculate the combined donor−acceptor system and determine V_{DA} from the splitting of the energy levels at the proper nuclear configuration. This requires that the complete energy hypersurface is known, and the method is still difficult to perform for larger systems. The second approach is to calculate overlap integrals using the perturbative approach discussed above. We have taken that model to the extreme by approximating the sum of overlap integrals in (3) with the MO coefficient at the linking position. An improved calculation of the electronic matrix element would have to involve a calculation of the overlap integral as the sum over all atomic orbitals on D and A (and potentially of the spacer) which contribute to (3). Such calculations have been performed, for example on the natural photosynthetic system discussed by Plato et al.[21] It has been observed that in some cases pairwise interactions of centers may produce large, but almost canceling contributions to the sum to be evaluated in (3). In covalently linked model compounds, dominant contributions arise from porphyrin−spacer atomic overlap integrals, suggesting that the orientation and the nature of the bridge will have to be closely investigated. This is illustrated in a recent theoretical treatment[17] where ab initio calculations of V_{DA} for porphyrin quinone diads with different linkers are presented. Explicitly, the effect of the spacer orbitals is considered. The study illustrates that today ab initio methods are sufficiently powerful to calculate such large systems. The authors demonstrate that their calculations yield a satisfactory agreement with measured values. Given the high level of the theory it does not seem surprising that approximations have to be introduced, one of them is related to the uncertainty of the energetic ordering of the MOs, particularly the frontier orbitals, of the porphyrin. We propose that some of the ambiguities can be taken care of by comparing information about the frontier orbitals obtained by EPR/ENDOR methods as described above. A detailed theoretical treatment of solvent effects on ET rates in porphyrin−quinone model compounds has been presented by the same authors.[46]

What one would like to achieve is demonstrated by Kumar et al.,[47] where nonbiomimetic model compounds are investigated. The electronic matrix element is extracted from experimental ET data by measuring the parameters entering the FC factor. The ratio of the FC factors relative to the measured ET rates yields V_{DA}. For model compounds with different bridge structures, V_{DA} is compared to ab initio theoretical calculations, and specifically couplings through solvent molecules are investigated. Theory and experiment agree to the same order of magnitude, which is satisfactory given the difficulties in calculating that parameter, and certainly when compared to other approaches discussed in the literature to date. It would be desirable to use the approach demonstrated for biomimetic model compounds. This would require the inclusion of the electronic structure of biomimetic **D** and **A** moieties, which seems well within the range of the theoretical methods available to date.

At present, calculations with advanced theoretical methods that allow one to explicitly determine the electronic matrix element are still too time-consuming to be applied to a large number of model compounds. While that limitation is clearly becoming less restrictive as computational methods advance and better theoretical treatments become available, at present the information is too limited to be used as practical guideline in the synthesis. As the simple model presented here allows us to assess some general properties of model compounds, albeit in a less quantitative way, we consider it as a crude, but hopefully useful tool. Ultimately, the choice of the method will be a balance between the computational effort, the precision needed, and the type of model compound.

Summary and Conclusions

It has been demonstrated that EPR/ENDOR spectroscopy is an excellent tool to determine the frontier orbitals of the redox-active components in model compounds. In the present account the frontier orbitals of the donor were analyzed. The effect of the donor electronic structure on the electronic matrix element, specifically the efficiency of charge separation in diad model compounds, which we have defined as k_{CS}/k_{CR}, was investigated, suggesting that k_{CS}/k_{CR} could be increased by a factor of 20 in a chlorin derivative. Such a contribution would be substantial, but has not yet been verified experimentally (see below). Qualitative predictions about preferred linking positions of donor and acceptor were made for several types of porphyrin and chlorin derivatives. From the non-uniform distribution of MO coefficients over the macrocycle we have concluded that part of the difference of ET rates in model compounds with different linking positions must be due to electronic factors. The fact that the MO coefficients of the HOMO and LUMO at a given linking position can be complementary suggests an influence of electronic factors on the efficiency.

Experimental studies have been discussed in the present account, in which values for V_{DA}, or for ratios of V_{DA} in different model compounds, are given. The contribution of V_{DA} to k_{CS}/k_{CR} has not yet been determined, however. Therefore, a quantitative comparison between the estimates of V_{CS}/V_{CR} given in the present account and experiments cannot be made. It should be possible, however, to compare the published data of ratios of V_{DA} in different model compounds to MO coefficients, an approach that is planned for the future.

Irrespective of the theoretical treatment used to obtain V_{DA}, the electronic structure of the redox components as obtained by EPR/ENDOR techniques is sufficiently accurate and detailed to serve as a critical test of the theory, particularly with respect to the wavefunctions calculated. Also, the experimental evidence about which orbitals feature as HOMO or LUMO can help in cases where the calculations are not sufficiently accurate to reliably determine the energetic ordering of the orbitals, as discussed in one example in the present account.

In summary, considering the available information about V_{DA} from experiments and the investigation of the frontier orbitals performed here, a quantitative analysis of the electronic matrix element is within reach. Unfortunately, the link is still missing. The hope is that research in this direction can be triggered as that will lead to a better understanding of the complementary factors that regulate and optimize ET properties.

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