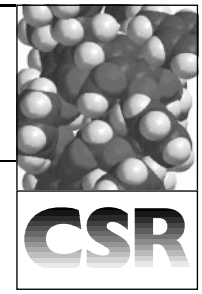
Photoinduced electron transfer in molecular systems: recent developments



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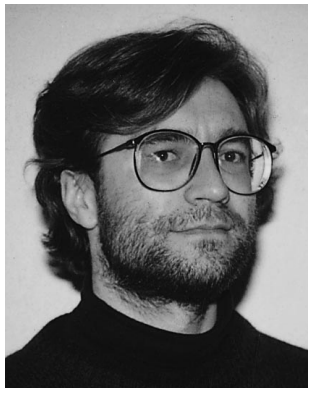
Highlights of new findings in electron transfer studies, in which elegant synthetic model systems were used to address important fundamental questions, are briefly described. The selected examples include: (i) efficient long distance electron transfer mediated by hydrogen bonds; (ii) energy and electron transfer through the walls of hemicarcerands; (iii) the influence of internal electric fields on the rate of electron transfer in α-helical peptides; (iv) construction of a biomimetic proton pump driven by photoinduced electron transfer. The review underscores the increasing role of synthesis in modern physical chemistry research.

1 Introduction

The principal aspects of long-range electron transfer processes, such as the driving force[1] and distance dependence,[2] the relationship with excitation transfer processes,[3] dependence on medium polarity, have been thoroughly investigated over the last decade and are now well understood. The recognition of the wide-ranging importance of these phenomena was underscored by the recent Nobel Prize awarded to R. A. Marcus. It is worthwhile to note that the solution of the most important fundamental questions in intramolecular electron transfer was possible thanks to unprecedented close collaboration between theorists, experimentalists and synthetic chemists. As a result of the success of this approach, a new and increasingly dominant style of physical chemistry research, in which the synthesis of the most appropriate model compound is an intrinsic part of a well designed experiment, has emerged. In the present review, the author sought to select highlights, which demonstrate the interdisciplinary nature of electron transfer studies, and which emphasize that the continuing development of this field, both in terms of basic science and applications, will increasingly depend on the involvement of skilful synthetic chemists. The review focuses on the newest findings in electron and energy transfer, which took place during the last three years. The first three chapters describe systems, which were designed to address specific fundamental questions, *i.e.*: (i) the role of hydrogen bonds in mediating long distance electron transfer; (ii) electronic coupling between the donor and the acceptor separated by impermeable 'molecular walls' of hemicarcerands; (iii) the influence of internal electric fields on the rate of electron transfer in α-helical peptides. The last chapter describes the construction of a highly complex biomimetic assembly, which is capable of ATP synthesis and which utilizes a photoinduced electron transfer system as the energy source. In addition to their biological relevance, all four examples are linked by an excellent design of model systems and a high level of synthetic skill being needed in order to prepare them.

Piotr Piotrowiak graduated from the University of Wrocław in 1982 (Magisterium with H. Ratajczak). After a brief stay at Stony Brook he joined the group of G. L. Closs at Chicago, where he received his PhD in 1988. In 1991, after a postdoctoral appointment with J. R. Miller at the Argonne National Laboratory, he took a faculty position at the University of New Orleans, where he became an Associate Professor in 1996. Since 1997 he has been an Associate Professor at Rutgers University. His recent research interests include vibronically mediated electron and excitation transfer in 'symmetry forbidden' systems, dynamics of non-aqueous electrolyte solutions, solvation in mixed solvents and various types of time resolved spectroscopy.



2 Electron transfer mediated by hydrogen bonds and salt bridges

It had been generally recognized that hydrogen bonds must play an important role in mediating electron transfer processes occurring in biological systems, and that their function most likely extends beyond simply providing the structural scaffolding for the donors and acceptors which participate in the redox process. However, it was not clear whether hydrogen bonds provide better or worse electronic coupling pathways than the widely studied covalent linkages, and both views had their loyal supporters, with the latter opinion being somewhat more popular on purely intuitive grounds (hydrogen bonds are much weaker, and therefore should result in weak donor–acceptor interactions). The controversy has been addressed and settled by Therien *et al*., who synthesized and investigated an elegant concise set of homologous compounds, which allowed a direct comparison of electron transfer proceeding through C–C σ-bonds, C=C double bonds, and hydrogen bonds.[4]

The model compounds employed tetraphenyl(porphinato)-zinc donors and (porphinato)iron(III) chloride acceptors linked by three types of bridging units (Fig. 1). It is crucial to note that in all three cases the number of intervening bonds is identical (six, counting from the phenyl groups of the donor and the acceptor). Furthermore, all bridges possess two equivalent electron transfer pathways, which contribute to the overall coupling. Interestingly, despite the lower driving force, photoinduced electron transfer mediated by hydrogen bonds (Fig. 1, top structure) was found to be nearly twice as fast as in the case

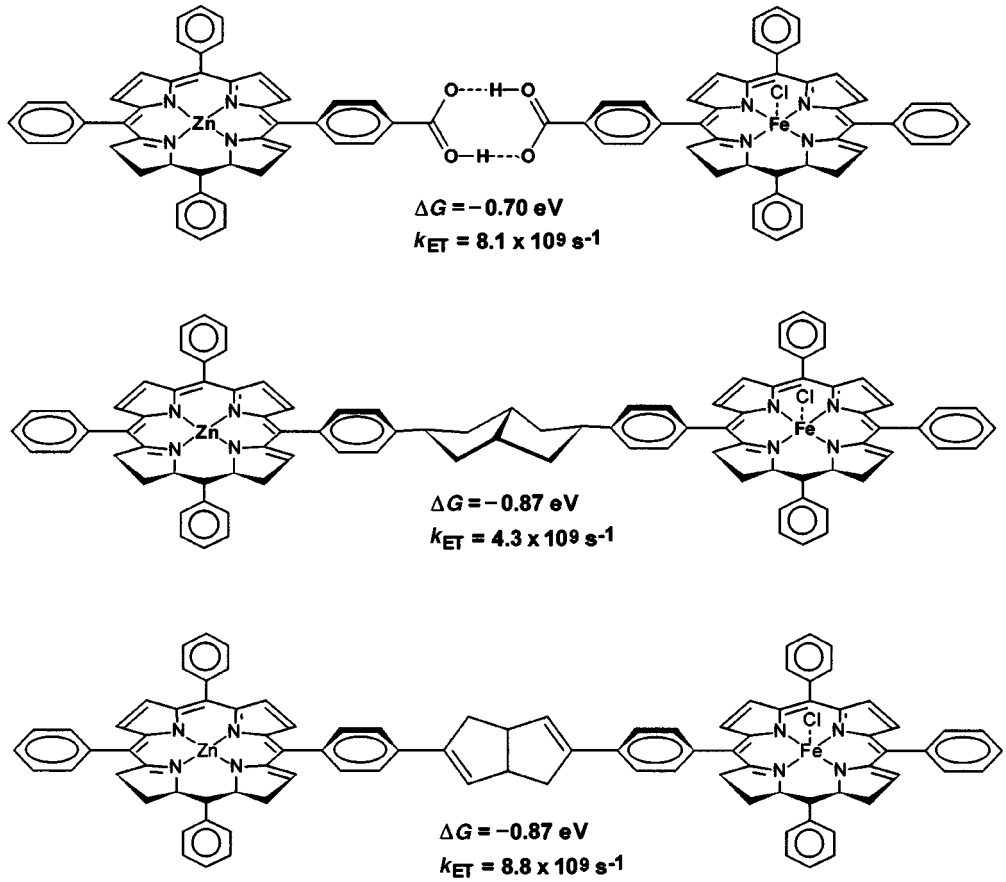


Fig. 1 Family of electron transfer model compounds with the donor and acceptor moieties linked by (from top to bottom): (a) hydrogen bond bridge; (b) all σ-bond bridge; (c) partially unsaturated bridge.

of σ-bonds (Fig. 1, middle structure). Indeed, when the correction for the 0.17 eV (~4 kcal mol^{-1}) difference in the driving force was included in the data analysis, the H-bond linked system emerged as the one with the largest donor–acceptor electronic coupling. This is a remarkable finding, because common chemical intuition would predict that even in the absence of full conjugation the partial unsaturation of the bridge (Fig. 1, bottom structure) should result in the strongest donor–acceptor interaction.

Nocera *et al*. observed a similar behavior in their salt-bridged and hydrogen bond linked donor–acceptor systems.[5] One of the model compounds utilized an asymmetric amidinium–carboxylate linkage (Fig. 2, top) resembling the arginine–aspartane bridge found in many biological systems, *e.g*. RNA stem loops and DNA complexes. The donor and acceptor in the second model were bridged by a symmetric arrangement of two carboxylic acid termini (Fig. 2, bottom). The authors used a classic combination of the $Ru^{II}(bpy)_3$ as the electron donor and the 3,5-dinitrobenzene as the acceptor. In both cases efficient photoinduced electron transfer was observed. The transfer rate in the symmetrically bridged compound was approximately twice as high as in the case of the amidinium–carboxylate link, even though the driving force was slightly more favorable (by ~1.6 kcal mol^{-1}) in the latter case. It is plausible that this behavior arises due to the different height and shape of the energy barrier for electron transfer in the highly polarized amidinium–carboxylate salt bridge. This type of an internal electric field effect within the bridging unit is not accounted for by the standard electron transfer theories.

Studies on compounds with linkages in which the ^{1}H-atoms of the amidine and the carboxylic acid were replaced by deuterium (Fig. 2, right), were performed to probe the possibility of coupling between electron transfer and the proton motion within the bridge. In both instances the rate of photoinduced electron transfer for the deuterated bridges was approximately 1.4 times slower than in the case of the original ^{1}H compounds. The authors explain this interesting effect in terms of modulation of the donor–acceptor electronic coupling by the vibrational motion of the proton (or deuteron) within the hydrogen bond.

To summarize, the work of both groups (Therien *et al*. and Nocera *et al*.) unambiguously demonstrates that hydrogen bonds, while weak in terms of bond enthalpy, are not a major impediment to long range electron transfer. Just the opposite, they can provide particularly efficient donor–acceptor interaction pathways, which can be enhanced by the coupling of the proton and electron motions. This interesting interplay between electron transfer and proton transfer within the bridging units, and the possible transition from the non-adiabatic to adiabatic regime, deserves further study.

3 Excitation and electron transfer through the walls of hemicarcerands

One of the interesting fundamental questions in the field of charge and electronic excitation transfer is the role of unbound medium separating the donor and the acceptor sites in providing the electronic interaction necessary for the transfer process to occur. A fascinating case of an intervening material which is not attached to either to the donor, or the acceptor, but where a fixed impermeable barrier is placed between the reactants, was investigated independently by Deshayes[6] and Balzani.[7] Both teams utilized Cram's closed surface hemicarcerand hosts[8] to encapsulate the triplet energy donor, and studied the electronic energy transfer to various acceptors in free solution. The carciplex systems are conceptually related to catenanes and rotaxanes, as they also do not involve any traditional bonding, or attractive potential, between the partners. The guest molecule

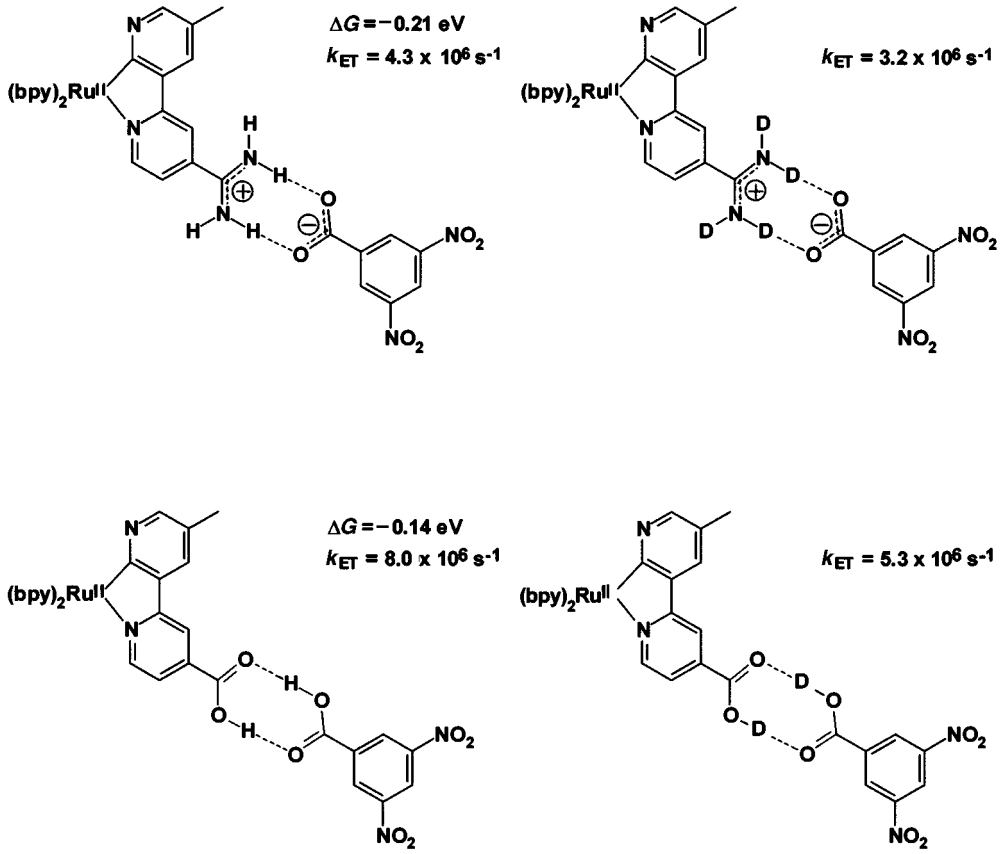


Fig. 2 Electron transfer model compounds with the asymmetric (top) and symmetric (bottom) hydrogen bond bridges.

remains trapped within the host purely as a result of the topological confinement.

The biacetyl donor is free to rotate inside its cage, however, as shown in Fig. 3, it cannot come into direct van der Waals contact with the organic triplet acceptors, and even such a small species as molecular oxygen cannot enter into the occupied hemicarciplex cavity. Consequently, triplet energy transfer must be mediated by the walls of the hemicarcerand, with an intervening center-to-center distance between the donor and the acceptor of approximately 7 Å. It is useful to remind the reader at this point that triplet energy transfer is mechanistically very closely related to electron transfer,[3,9] except that since it does not involve a major charge redistribution, it exhibits very little solvation dependence, and the relevant reorganization energy, λ, is dominated by the internal geometrical changes of the donor and the acceptor. Thanks to the greatly reduced electronic coupling in the encounter complex the rate constants for triplet energy transfer between the incarcerated biacetyl and a variety of acceptors fall well below the diffusion controlled limit. As a result, the characteristic Marcus relationship between rate

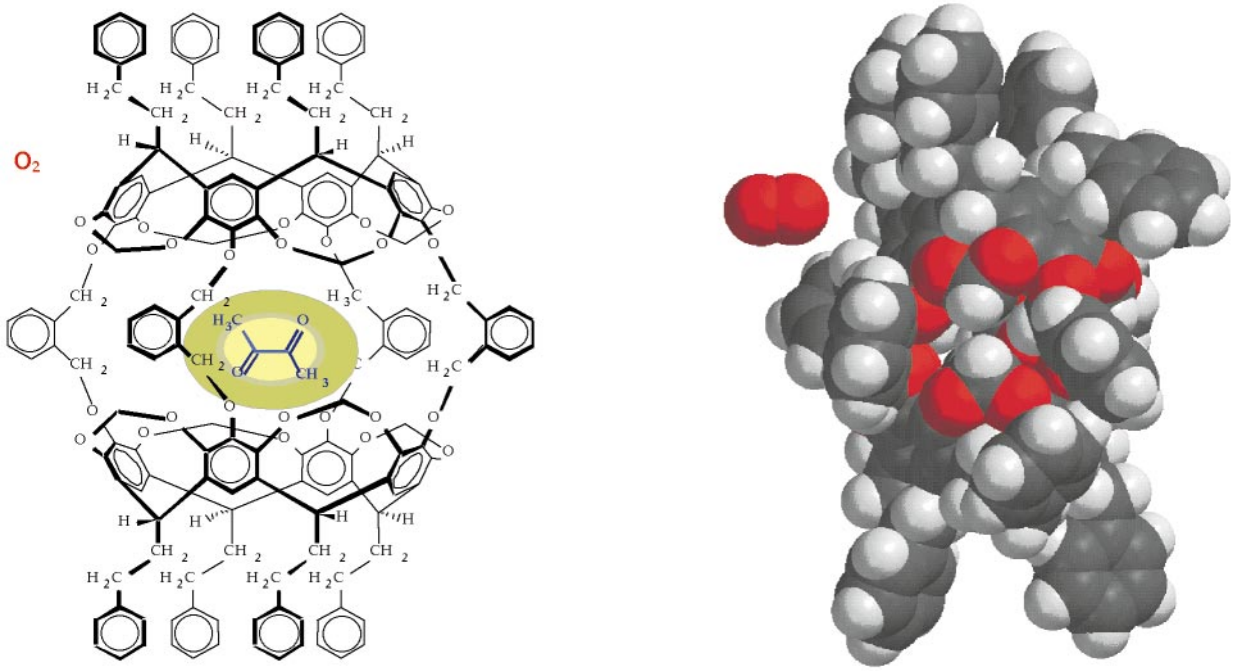


Fig. 3 The structure (left) and the space-filled model (right) of the hemicarcerand cage with the trapped biacetyl (butane-2,3-dione) triplet energy donor and a molecule of O_2 shown for size comparison.

constant and driving force is obtained (see Fig. 4), instead of the Sandros[10] or Weller[11] type behavior typical of a diffusion controlled process.

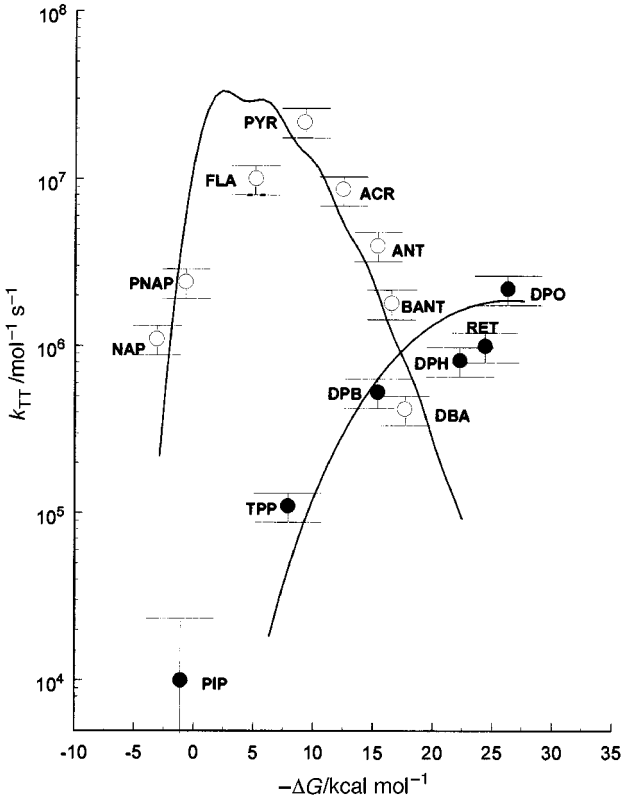


Fig. 4 The free energy dependence of triplet energy transfer from 'incarcerated' biacetyl to two classes of acceptors: (a) rigid aromatics (NAP = naphthalene, PNAP = 2-phenylnaphthalene, FLA = fluoranthene, PYR = pyrene, ACR = acridine, ANT = anthracene, BANT = 9-bromoanthracene, DBA = 9,10-dibromoanthracene); (b) olefins (PIP = *cis*-piperylene, TPP = triphenylethylene, DPB = 1,4-diphenylbuta-1,3-diene, DPH = 1,6-diphenylhexa-1,3,5-triene, RET = all-*E*-retinol, DPO = 1,8-diphenylocta-1,3,5,7-tetraene).

Perhaps the most surprising finding of both groups was that the 'incarcerated' excited triplet states are nearly immune to quenching by molecular oxygen, which is usually regarded to be a particularly efficient triplet quencher. This observation, which at first may seem to challenge the traditional organic photochemistry canon, is fully explained by the standard Marcus–Jortner[12] theory of non-radiative charge and excitation transfer: the biacetyl–molecular oxygen triplet donor–acceptor couple is characterized by an extremely small overall reorganization energy, $\lambda < 2$ kcal mol^{-1}, and a very large driving force, $-\Delta G^0 > 20$ kcal mol^{-1}. As a result, it falls deeply into the Marcus 'inverted region', very far from $-\Delta G^0 = \lambda$ thermodynamic optimum, and yields correspondingly slow rates (a pseudounimolecular rate of $\sim 1 \times 10^4$ M^{-1}s^{-1}, *i.e.* more than 5 orders of magnitude below the diffusion controlled limit, was measured by both the Deshayes and Balzani groups). Indeed, it is reasonable to conclude that oxygen's reputation for being a superb quencher should be attributed primarily to the fact that it diffuses much more rapidly than any of the larger triplet energy acceptors.

A detailed investigation of the dependence of the transfer rate on the internal reorganization energy (*i.e.* the magnitude of geometry change of the donor and the acceptor following the triplet transfer) was performed recently by Deshayes and Piotrowiak[13] for a broad variety of organic acceptors and incarcerated biacetyl donors. It was found that satisfactory quantitative agreement with the predictions of the Marcus–Jortner theory can be achieved only for families of related compounds with similar internal reorganization energies. The results obtained for rigid aromatic triplet acceptors (small geometry change in the excited state and correspondingly small reorganization energy) and olefinic triplet acceptors (large geometry change in the triplet state and large reorganization energy), are presented in Fig. 4. Please note the two separate curves, with maxima corresponding to $-\Delta G^0 = \lambda_{\text{aromatic}}$ and $-\Delta G^0 = \lambda_{\text{olefin}}$. The authors used variable temperature measurements to confirm which acceptors belong to the 'normal' and which to the 'inverted' region of the ΔG^0 dependence. In the first case, the classical Arrhenius type temperature dependence, with triplet transfer rates increasing at higher temperatures, and positive activation free energies are observed. In the second case, transfer rates decreasing with increasing temperature, and negative apparent activation free energies are obtained (the increasing efficiency of the nuclear tunneling in the 'inverted' region is responsible for this behavior).[14]

Both the Pina–Balzani and Deshayes–Miller groups also investigated electron transfer processes in analogous incarcerated systems. The Pina–Balzani team studied photoinduced electron abstraction from a variety of amines in free solution by the caged triplet state biacetyl,[15] while Deshayes and Miller monitored the rate of charge shift reactions from a number of electron donors to an 'imprisoned' quinone acceptor.[16] In both cases the measured rates were up to an order of magnitude faster than those obtained for triplet energy transfer, and the correlation with the predictions of the Macus–Jortner theory was much less satisfactory. Triplet energy transfer is mediated by a two-electron exchange interaction between the localized orbitals of the donor and the acceptor, which falls off very steeply with distance, approximately twice as rapidly as the analogous single electron exchange interaction which is responsible for electron transfer reactions.[3,9] Therefore, the considerably faster rates observed in the case of electron transfer are the expected result. The behavior of the electron transfer systems is complicated by the fact that the hemicarcerand cage, which contains eight trimethoxybenzene units, can serve both as a reasonably efficient electron donor and acceptor. Consequently, it is possible that in some instances the charge hopping mechanism involving reduced and/or oxidized hemicarcerand as an intermediate can compete with the superexchange mediated electron transfer. In addition, the possibility of formation of ground state complexes between the cage and the amines cannot be readily excluded.

4 Internal electric field effects in electron transfer

The large internal electric fields generated by the dipole moments of helical peptides were long expected to have an important influence on the rate of electron transfer in proteins. One of the speculative explanations of why only one of the two branches of the bacterial PSII reaction center is active, was based on the existence of such internal fields within the protein matrix. It has been estimated on the basis of vacuum electrostatics that the dipole of a long α-helix generates along its axis a field of 10^9 V m^{-1} (approximately 3.5 D per amino acid residue) directed from the N-terminus towards the carboxy-terminus.[17] Even after scaling for a more realistic relative permittivity, $\varepsilon > 1$, these intensities are well in excess of 10^6 V m^{-1} attainable in the laboratory by applying external electrical fields. A field of this magnitude can easily modify the driving force and the barrier height of an electron transfer reaction. Consequently, a strong dependence of electron transfer rates on the relative orientation of the helix axis and the direction of the electron transfer should be observed. Early support of this notion was provided by the electrochromic effect measurements,[18] however, the decisive confirmation was provided by the work of Fox and Galoppini, who prepared model com-

pounds (**1** and **2**) with the donor (dimethylaniline) and the acceptor (pyrene) covalently attached to a synthetic rigid helical peptide (Fig. 5).[19] The donor and the acceptor were separated by six amino acid residues ($R_{DA} \cong 10$ Å), and three additional residues were added at each end in order to prevent the unfolding of the termini. In both cases efficient quenching of pyrene fluorescence occurred as a result of electron transfer from dimethylaniline, Pyr^{*}—DMA $\rightarrow$ $Pyr^{\cdot -}$—$DMA^{\cdot +}$. A dramatic difference in the quenching rates was observed depending on whether the dipole moment of the peptide backbone was oriented parallel (compound **1**) or anti-parallel (compound **2**) to the direction of the motion of the transferred electron. The magnitude of the effect exhibited the expected dependence on the relative permittivity of the solvent: in low polarity media (THF, $\varepsilon = 7.5$) the ratio of the two rates , k_1^{ET}/k_2^{ET}, approached 30, while in the highly polar and strongly screening methanol ($\varepsilon = 32.7$) it was only 5. A straightforward explanation of these observations can be given on the basis of the energetics of **1** and **2**. The dimethylene–pyrene couple corresponds to the driving force for photoinduced electron transfer of $\Delta G^0 \cong -0.4$ eV, and thus falls well within the 'normal region' of the exothermicity dependence. Therefore, the orientation of the helix dipole which stabilizes the final $Pyr^{\cdot -}$—$DMA^{\cdot +}$, and increases the effective driving force, should correspond to the higher rate. Indeed, the authors measured the field induced difference between the driving forces in **1** and **2** by differential pulse voltametry in acetonitrile and found that the ΔG^0 of **1** is 100 meV more negative than that of **2**, in good agreement with the kinetic results. This driving force difference gives an estimate of the magnitude of the local internal field experienced at the donor and acceptor sites, $E \approx 1 \times 10^8$ V m^{-1}. Naturally, in solvents less polar than acetonitrile the magnitude of the effective field is larger.

In an important final test the authors studied the effect of helix unfolding on the ratio of electron transfer rates in the D–A and A–D systems.[20] Two approaches were used to disrupt the helicity of the peptide. In the first one, H_2O was added as a protic co-solvent to THF solutions of model compounds **1** and **2**. In all cases the ratio of k_1^{ET}/k_2^{ET} dropped abruptly from 27 in neat THF to 1.8–2.4 in the various mixtures. The second approach involved the synthesis of two new analogous model compounds, in which L-prolines were incorporated into the backbone of the peptide as the helix breaking residues. The same electron donor (dimethylaniline) and acceptor (pyrene) were employed, and they were attached to the backbone in the same manner as previously. The observed electron transfer rates exhibited only a very weak dependence directionality of the donor and acceptor attachment. The corresponding ratios of transfer rates ranged from 1 to 3.4, *i.e.* they were much lower than in the case of purely helical **1** and **2**, indicating that no strong internal electric fields are present in the proline containing systems.

It should be mentioned that while the work described above was aimed primarily at explaining an important aspect of electron transfer in proteins, related concepts of utilizing static or transient electric fields in the construction of 'molecular diodes', or 'light activated switches', were recently advanced by others. Wasielewski *et. al* synthesized a complex D_1–A_1–A_2–D_2 electron donor–acceptor system, in which the formation of either D_1^+–A_1^- or A_2^-–D_2^+ is selectively inhibited by the presence of the electric field setup by the adjacent radical ion pair.[21] The same group investigated the effect of electric field produced by a photogenerated ion pair on the on the electronic spectra of nearby molecules. The presence of internal electric fields as high as $\sim 2 \times 10^9$ V m^{-1}, *i.e.* even larger than those generated by the dipole of the α-helical oligopeptide, was deduced from the spectral response of a carotenoid fragment, which served as the probe.[22]

5 Light driven proton pump

The most spectacular synthetic feat in this field during the recent years was undoubtedly the construction of a functioning biomimetic 'photon driven proton pump'.[23] The team lead by Moore, Gust and Moore culminated their extensive work on artificial multi-step electron transfer assemblies by implanting one of their well characterized C–P–Q 'triads',[24] (composed of a quinone, Q, as the electron acceptor, free-base porphyrine, P, as the primary electron donor, and carotene C, as the final electron donor), into the lipid bilayer of a reconstituted liposome (Fig. 6). Photoinduced electron transfer in the triad molecule spanning the wall of the vesicle sets up an electrochemical potential difference between the interior and the exterior of the liposome and leads to directional proton transfer. The preference for the orientation of the triad within the layer is in part thermodynamic (the bulky porphyrin and quinone

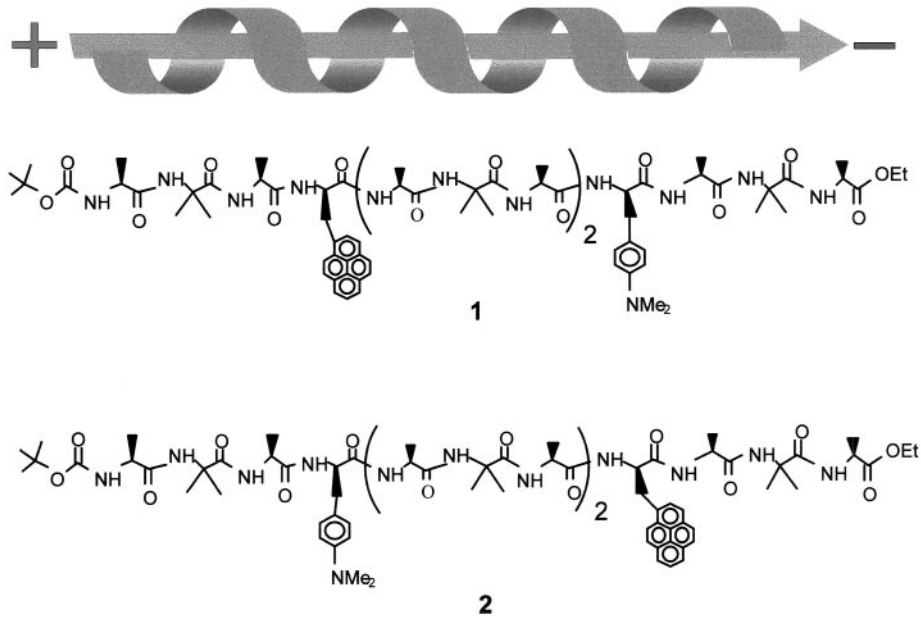


Fig. 5 Structures of the synthetic α-helical oligopeptides with covalently attached electron donor (*N*,*N*-dimethylaniline) and acceptor (pyrene). The direction of the electrical field set up by the helix dipole is indicated schematically above.

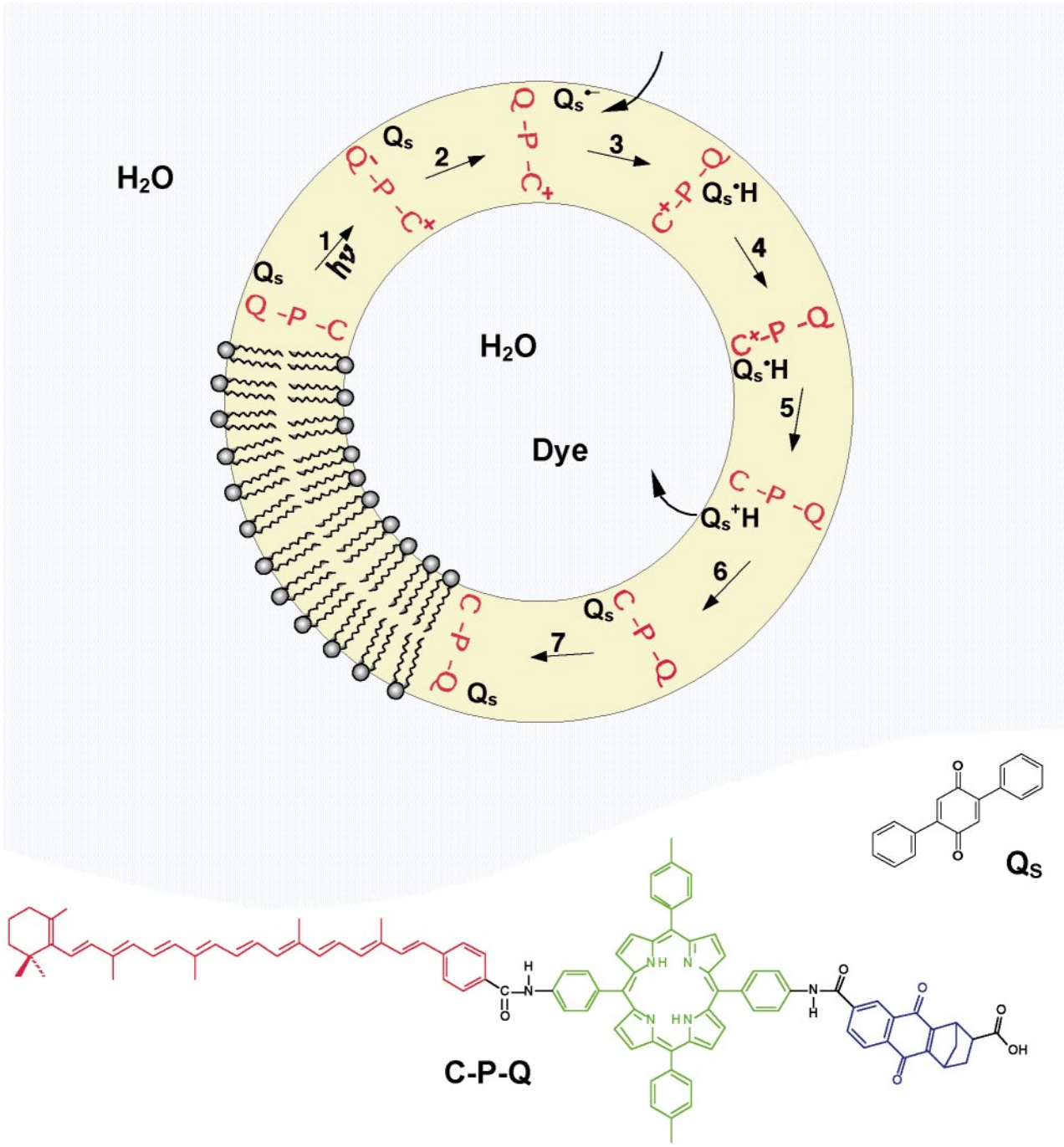


Fig. 6 Photoelectrochemical cycle of the 'proton pump' generating a pH gradient across the liposome bilayer with the structures of the essential components (bottom). See the text for detailed description of the cycle.

remain in the less densely packed outer layer), and in part kinetic (the activation barrier for the insertion of lipophilic carotenoid into the bilayer is much lower than for the polar quinone and carboxylic group).

Photoexcitation of the porphyrin moiety of C–P–Q results in the formation of the $C^{\cdot+}$–P–$Q^{\cdot-}$ charge separated state (quantum yield 0.1), which was detected by monitoring the transient absorbance of the carotenoid radical cation (Step 1). Electron transfer from -$Q^{\cdot-}$ to the lipid soluble 2,5-diphenylbenzoquinone (Q_s), with a reduction potential 0.6 V more positive than that of Q, results in the formation of the radical anion $Q_s^{\cdot-}$ (Step 2). The reduced form of Q_s accepts a proton from the external aqueous solution, forming the corresponding uncharged semiquinone $Q_sH^{\cdot}$, which diffuses through the membrane and performs the crucial function of a proton shuttle (Steps 3 and 4). Upon reaching the interior layer of the membrane $Q_sH^{\cdot}$ encounters the carotenoid radical cation, undergoes oxidation to $Q_s^{+}H$ (Step 5) and releases the proton into the aqueous medium (Step 6). Random diffusion of the regenerated Q_s closes the cycle (Step 7). The pH dependent fluorescence excitation spectrum of a water soluble dye was used to monitor changes in the proton concentration inside liposomes. The authors demonstrated that the efficiency of the system can be increased if a standard ionophore such as valinomycin is added in order to relax the membrane potential.

The pH gradient, which has been established across the bilayer membrane in the manner described above, gives rise to a proton motive force, *i.e.*, the biological analogue of the electromotive force, and potentially could be utilized to perform work. This challenging task was recently accomplished by Moore, Gust and Moore.[25] The researchers were able to reconstitute proteoliposomes with the ATP synthase built into the lipid bilayer, and to harness the pH gradient set up by the 'proton pump' to perform ATP synthesis. This is the first complete biomimetic system, which effectively couples electrical potential derived from photoinduced electron transfer to the chemical potential associated with the ADP–ATP conversion. The photoelectrochemical cycle is essentially identical with the one described above, except that when a pH gradient equivalent to a proton motive force of ~12 kcal mol^{-1} is

reached, the production of ATP from adenosine diphosphate (ADP) and inorganic phosphate begins. The functioning of the assembly was monitored by the luciferin-luciferase fluorescence assay.[26] On the basis of the ATP-dependent steady state luminescence of oxyluciferin the authors estimate that one molecule of ATP is synthesized per 14 absorbed photons of 633 nm light, and that up to 4% of the initial energy incident on the sample is stored by the system.

In order to surpass this impressive achievement, the Moore, Gust and Moore group is currently working on implanting the C–P–Q triad into inverted *E. coli* shells and converting them into hybrid, in part natural, in part man made, functioning photosynthetic assemblies.[27]

6 Concluding remarks

It is appropriate to close this brief review of recent achievements with an attempt at predicting future directions in electron transfer research. The future work will be characterized by increasingly complex molecular and hybrid molecule/nanoparticle systems, as well as by a progressive shift of emphasis to applied problems, such as the design of stable high yield dyes for photovoltaic devices, development of electroemissive polymers for displays, non-linear optical materials and sensors. Within the coming decade we will most likely witness the evolution of the current fascinating 'molecular tinker-toys' into truly applicable functional molecular devices.

Despite the relative maturity of this field, there still remains a wealth of important fundamental questions, which have been only slightly explored in the past, and which deserve a much more detailed attention. These topics include electron transfer through non-carbon based bridges (heteroatoms and metal atoms), concerted multielectron *vs*. stepwise electron transfer,[28] transition from non-adiabatic to adiabatic regime, molecular orbital symmetry effects,[29] vibronic state specificity,[30] and vibrational coherence effects in ultra-fast electron transfer. Addressing these fundamental issues will require the synthesis of new, specifically designed model compounds. Well-characterized electron transfer systems will find increasing use as static and dynamic probes of properties of unusual media, *e.g.* supercritical fluids, liquids at extreme pressures, liquid–liquid, liquid–gas and other interfaces.

Finally, one hopes that, as in any active field, there will be many surprising developments and applications of photo-induced electron transfer, which cannot be readily foreseen today. Indeed, only a few years ago most researchers working in this area, including the author of this review, would consider the construction of the described light-driven ATP synthesizing assembly to be a far-fetched project belonging to a very distant future.

7 Glossary of terms

Adiabatic electron transfer—When the donor–acceptor interaction is strong the rate of electron transfer can approach the rate of solvent fluctuations. The solvent dynamics begins to effectively control the transfer rate, *i.e.* the system behaves adiabatically.

Diffusion controlled limit—A bimolecular reaction, *e.g.* electron transfer between unattached donors and acceptors in solution, cannot proceed faster than the frequency of encounters between the reagents, which is determined by the rate of translational diffusion in a given medium.

'Inverted' region—If the driving force of an electron transfer reaction is larger than the corresponding reorganization energy, an increase of the ΔG^0 (or temperature) results in lowering the rate of the process, hence, the 'inverted behavior'.

Luciferin—4,5-dihydro-2-[6-hydroxy-2-benzothiazolyl]-4-thiazolecarboxylic acid, is the principal component of the firefly (*Photinus pyralis*) chemiluminescent apparatus. Luciferase–luciferin is a standard reagent for the determination of ATP in enzyme coupled systems.

Non-adiabatic electron transfer—When the donor–acceptor interaction is weak, and the rate of electron transfer is slower than the solvent fluctuations, the role of the medium is fully described by the reorganization energy. The solvent dynamics is of no consequence, and the process is non-adiabatic.

'Normal' region—If the driving force of an electron transfer reaction is smaller than the reorganization energy, the classical Arrhenius, or 'normal', dependence on the ΔG^0 (or temperature) is observed.

Nuclear tunneling—Eigenfunctions of a quantum mechanical harmonic oscillator extend beyond the classical bounds of the potential energy surfaces. Therefore, vibrational wavefunctions of the donor and the acceptor can mix, even if the thermal energy is not sufficient for reaching the top of the activation barrier. This effect is accounted for by the Marcus–Jortner theory. It is particularly important in the 'inverted' region.

Reorganization energy—The geometry of the donor–acceptor system, and the arrangement of a polar solvent around it, are different before and after the electron transfer takes place. The energy associated with these rearrangements is called the *internal*, and *solvent* or *medium* reorganization energy, respectively.

Superexchange coupling—Any electronic or magnetic interaction between two localized sites, *e.g.* electron donor and acceptor, which is mediated by the molecular orbitals of the intervening material (*e.g.* a covalent bridge, wall of a hemicarcerand, or a frozen solvent).

8 Acknowledgements

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