

Photoinduced Electron Transfer III

Editor: J. Mattay

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With 72 Figures and 13 Tables



Springer-Verlag

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ISBN 3-540-53257-9 Springer-Verlag Berlin Heidelberg New York
ISBN 0-387-53257-9 Springer-Verlag New York Berlin Heidelberg

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Printed in Germany

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Typesetting: Th. Mützer, Bad Langensalza; Printing: Heenemann, Berlin;
Bookbinding: Lüderitz & Bauer, Berlin
51/3020-543210 — Printed on acid-freepaper

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Preface to the Series on Photoinduced Electron Transfer

The exchange of an electron from a donor molecule to an acceptor molecule belongs to the most fundamental processes in artificial and natural systems, although, at the primary stage, bonds are neither broken nor formed. However, the transfer of an electron determines the chemical fate of the molecular entities to a great extent. Nature has made use of this principle since the early beginnings of life by converting light energy into chemical energy via charge separation. In recent years man has learnt, e.g. from X-ray analyses performed by Huber, Michel and Deisenhofer, how elaborately the molecular entities are constructed within the supermolecular framework of proteins. The light energy is transferred along cascades of donor and acceptor substrates in order to prevent back electron transfer as an energy wasting step and chemical changes are thus induced in the desired manner.

Today we are still far away from a complete understanding of light-driven electron transfer processes in natural systems. It is not without reason that the Pimentel Report emphasizes the necessity of future efforts in this field, since to understand and “to replicate photosynthesis in the laboratory would clearly be a major triumph with dramatic implications”. Despite the fact that we are at the very beginning of knowledge about these fundamental natural processes, we have made much progress in understanding electron transfer reactions in “simple” molecular systems. For example most recently a unified view of organic and inorganic reaction mechanisms has been discussed by Kochi. In this context photochemistry plays a crucial role not only for the reasons mentioned above, but also as a tool to achieve electron transfer reactions. The literature contains a host of examples, inorganic as well as organic, homogeneous as well as heterogeneous. Not surprisingly, most of them were published within the last decade, although early examples have been known since the beginning of photochemistry (cf. Roth's article in Vol. 156). A reason is certainly the rapid development of analytical methods, which makes possible the study of chemical processes at very short time ranges. Ebersson in his monograph, printed by this publishing company two years ago,

nicely pointed out that "electron transfer theories come in cycles". Though electron transfer has been known to inorganic chemists for a relatively long time, organic chemists have still to make up for missing concepts (cf. Eberson).

A major challenge for research in future, the "control of chemical reactions" as stated by the Pimentel Report, can be approached by various methods; light-driven processes are among the most important ones. Without interaction of the diverse scientific disciplines, recent progress in photochemistry, as well as future developments would scarcely be possible. This is particularly true for the study of electron transfer processes. Herein lies a challenge for science and economy and the special fascination of this topic – at least for the guest editor.

The scope of photochemistry and the knowledge about the fundamentals of photoinduced electron transfer reactions have tremendously broadened within the last decade, as have their applications. Therefore I deeply appreciate that the Springer-Verlag has shown interest in this important development and is introducing a series of volumes on new trends in this field. It is clear that not all aspects of this rapidly developing topic can be exhaustively compiled. I have therefore tried to select some papers which most representatively reflect the current state of research. Several important contributions might be considered missing by those readers who are currently involved in this field, however, these scientists are referred to other monographs and periodical review series which have been published recently. These volumes are meant to give an impression of this newly discovered reaction type, its potential and on the other hand to complement other series.

The guest editor deeply appreciates that well known experts have decided to contribute to this series. Their effort was substantial and I am thankful to all of them. Finally, I wish to express my appreciation to Dr. Stumpe and his coworkers at the Springer-Verlag for helping me with all the problems which arose during the process of bringing the manuscript together.

Münster, December 1989

Jochen Mattay

Preface to Volume III

This book is the third of a four-volume series on photoinduced electron transfer (PET) that attempts to bring together some representative accounts on new trends in photochemistry. While the first volumes (Volume 156 and 158) have mainly covered the history and the fundamentals in a broad sense as well as contributions from organic and inorganic chemistry, this issue is concerned with the control of PET by various methods, starting from heterogeneous systems, covering three- and multicomponent photosynthetic model systems, and ending with ion pair interactions in homogeneous medium.

PET across membranes is extensively discussed in the first contribution with emphasis on primary photochemical charge separation processes and secondary recombination reactions. Mainly vesicles and planar bilayer membranes serve as models which allow the spatial separation of photochemically generated oxidants and reductants.

The second article also deals with PET in arranged media, however, this time by discussing comprehensively the various types of heterogeneous devices which may control supramolecular interactions and consequently chemical reactions. Before turning to such applications, photosynthetic model systems, mainly of the triad type, are dealt with in the third contribution. Here, the natural photosynthetic electron transfer process is briefly discussed as far as it is needed as a basis for the main part, namely the description of artificial multicomponent molecules for mimicking photosynthesis. In addition to the goal to learn more about natural photosynthetic energy conversion, these model systems may also have applications, which, for example, lie in the construction of electronic devices at the molecular level.

After getting somewhat acquainted with PET in natural and artificial systems, the reader may become aware of its tremendous implications by studying the next article. There, heterogeneous and homogeneous catalysts as well as biocatalysts are described for artificial photosynthetic applications dealing with H_2 evolution, CO_2 fixation, hydrogenation, and hydroformylation processes.

The final contribution turns back to the more “simple” aspects of PET in homogeneous media. As was shown for ion pairs in one of the golden ages of physical organic chemistry, the controlled formation of various types of radical ion pairs by photochemical methods can be utilized to control the course of chemical reactions. At this point, the medium effects which govern the formation and the fate of radical ion pairs resemble the supramolecular effects of the arranged systems discussed in the first articles.

I hope that these contributions again will show the high potential of PET and that further developments will be stimulated. The efforts of the authors of the first four articles were substantial and I deeply acknowledge their consent to contribute to this series.

Münster, June 1990

Jochen Mattay

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Photoinduced Electron Transfer Across Membranes

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Vectorial photoinduced electron transfer (PET) across bilayer lipid and surfactant membranes provides a unique opportunity for the spatial separation of photochemically generated oxidants and reductants. In this chapter a review is given of the data on vectorial PET across the membranes of vesicles and planar bilayer membranes. The key steps that determine the efficiency of PET across membranes are discussed, i.e. (i) primary photochemical charge separation processes, (ii) secondary recombination reactions and (iii) electron transfer across membranes that provides stabilization of the charges generated in step (i). Step (iii) can be performed by three mechanisms: (1) via the diffusion of electron (or hole) carrier through the membrane, (2) via reactions of electron exchange between molecules located in different monolayers of a bilayer membrane and (3) via intramolecular electron transfer along bridging molecules, molecular wires and ultrafine semiconductor particles embedded into membranes. The possibility of conjugating PET across membranes with catalytic redox reactions is discussed with the emphasis on the water cleavage.

1 Introduction

The past decade has been marked by the growing interest in photochemical processes in structurally-organized molecular assemblies. The interest in this area of photochemistry was stimulated by its importance for: (i) rapidly developing technologies like photography and molecular electronics and, (ii) the development of artificial molecular systems for solar energy conversion via mimicking photosynthesis. Natural systems providing photosynthesis in bacteria and in the chloroplasts of green plants demonstrate rather high extent of molecular order. Indeed, the reaction centers and electron transfer chains in these systems are spatially organized in lipid-protein membranes that provide extremely high efficiency of light-to-chemical energy conversion

A reason for the necessity to have an appropriate structural organization for natural photosynthetic systems and their artificial analogs appears to be clear. It can be demonstrated if one consider, e.g. artificial molecular systems for light-to-chemical energy conversion via photochemical water cleavage into dihydrogen and dioxygen. Systems of this type are under development now as simplified functional analogs of plant photosynthesis that can provide an ecologically attractive route for solar-to-chemical energy conversion (see reviews [1–7]).

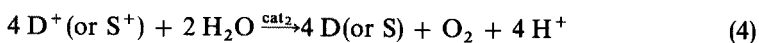
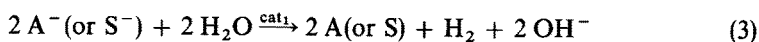
A design of photocatalytic systems to perform water cleavage is most often based on the following approach. The first stage of the cleavage reaction involves a photoinduced charge separation, i.e. electron transfer from the excited photosensitizer, $^*S$, to an acceptor, A:



or to a photosensitizer from a donor, D:



Dihydrogen and dioxygen which are the final stable products of water cleavage, are formed via subsequent dark catalytic processes of water reduction and oxidation by the A^- or S^- and D^+ or S^+ species, respectively:



Mechanistically this pathway is rather similar to the scheme of light-to-chemical energy conversion during photosynthesis of plants. However the difference between these two processes is that during photosynthesis, energy is stored as the chemical energy of carbohydrates, whereas the photocatalytic water cleavage accumulates energy as the chemical energy of dihydrogen.

The major difficulty in constructing the molecular systems for water cleavage is the necessity to inhibit the recombination reactions between energy rich particles

S^+ and A^- or S^- and D^+ . This recombination appears to be much faster than the complicated catalytic processes of water reduction and oxidation. That is why at present the possibility of accomplishing photocatalytic water cleavage in a simple homogeneous system seems rather vague. Inhibition of the recombination between oxidizing and reducing agents is likely to be accomplished by an analogy with natural photosynthesis, i.e. via spatial separation of these particles in the system. It implies that the system must contain spatially organized molecular structures wherein the S^+ and A^- or S^- and D^+ particles formed are spatially separated.

The widely used approach to developing such systems is based on the self-organizing ability of some microheterogeneous systems. This approach was also suggested by analogy with natural photosynthesis, where the reaction centers are spatially organized in biomembranes. Indeed, an interesting peculiarity of biological systems is the ability of their components to self-assemble, which allows the latter to take certain favorable positions in the membrane.

The design of artificial self-organizing systems is based on the ability of some molecules which contain simultaneously hydrophobic and hydrophilic groups to form molecular assemblies of definite structure in solution. Examples of the assemblies that can be used to suppress undesirable recombination processes are polyelectrolytes, micelles, microemulsions, planar lipid membranes covering an orifice in a film separating two aqueous solutions, unilamellar vesicles, multilamellar vesicles and colloids of various inorganic substances (see reviews [8–18] and references therein).

Particular progress in suppressing undesirable back recombination of photo-separated charges was achieved while using the vesicles, i.e. microscopic spherical particles formed by closed bilayer membranes. On the inside and outside of the vesicle one can obtain immiscible water solutions of different ionic compositions. It is also possible to introduce into the suspension of vesicles all the necessary components of the photocatalytic system: the photosensitizer, electron donor and acceptor, electron carriers, as well as the catalysts of dihydrogen and dioxygen evolution providing an appropriate spatial location of all the components. When embedding the photosensitizer or an electron carrier into the vesicle membrane, it proves possible to perform vectorial photoinduced electron transfer across the membrane from donor D to acceptor A , located in aqueous phases at the different sides of the membrane. As a result the products of photochemical electron transfer reaction, e.g. D^+ and A^- , appear to be separated by the membrane which inhibits their direct recombination and allows in principal these products to be used in subsequent dark reactions for production of desired substances, e.g. H_2 and O_2 . Thus in these systems the regions of molecular dimensions with different values of redox potentials are able to coexist.

In this paper we discuss results obtained in constructing the organized molecular systems for PET based on the use of ultrathin lipid or surfactant membranes, and in studying the mechanisms of PET in such systems. The state of the art in conjugation of PET across membranes with catalytic reactions of water reduction to dihydrogen and its oxidation to dioxygen will be also briefly discussed.

2 Membrane Systems Providing Vectorial PET

2.1 Preparation and Structure of Vesicles

The traditional substances for vesicles preparation are lipids [19, 20], which also appear to be the main structural components of biological membranes, including those of the chloroplasts. For photochemical experiments, lecithin vesicles are usually used because their properties have been studied in detail and they can be prepared with high reproducibility. In lecithin of natural origin (its structural formula is shown in Fig. 1a) the hydrocarbon substituents R_1 and R_2 can be either saturated or unsaturated. Among synthetic lipids, lecithins with identical, $R_1 = R_2$, nonbranched and saturated substituents, (for example, dipalmitoyllecithin (DPL), dimyristoyllecithin (DML)) are commonly used for vesicle preparation. One may also use some other surfactants possessing an ionic group and one, two or three hydrocarbon chains, for example dihexadecylphosphate (DHP) [21–23] (see Fig. 1b) and others [24–32].

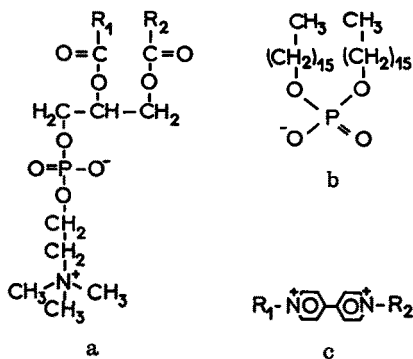


Fig. 1. Structural formulae of lipids and surfactants: (a) – lecithin; (b) – dihexadecylphosphate; (c) – viologen

The ability of the above mentioned substances to self-organize into bilayer membranes is caused by their amphiphility. During the formation of the vesicles the amphiphilic molecules orient themselves in such a way that their polar “heads” contact aqueous phases outside and inside the vesicle, while their nonpolar “tails” are directed towards the interior of the bilayer as shown in Fig. 2c. Vesicles can be classified in multilamellar, small unilamellar ($d = 200\text{--}500\text{ \AA}$) and large unilamellar ($d = 1000\text{--}5000\text{ \AA}$) ones. Since these are small unilamellar vesicles that are typically used for studying PET, in further discussion the term “vesicle” will always refer to the vesicles of this type, unless otherwise specified.

One of the most popular methods of vesicle preparation was suggested by Huang [33]. It is based on sonification of the lipid or surfactant in water (see Fig. 2a). Another widely used method of vesicles preparation is a fast injection of an alcohol or ether solution of a lipid into an aqueous solution. Numerous studies concerning the structure and properties of vesicles obtained by these procedures are analyzed in Refs. [19, 20, 34–36].

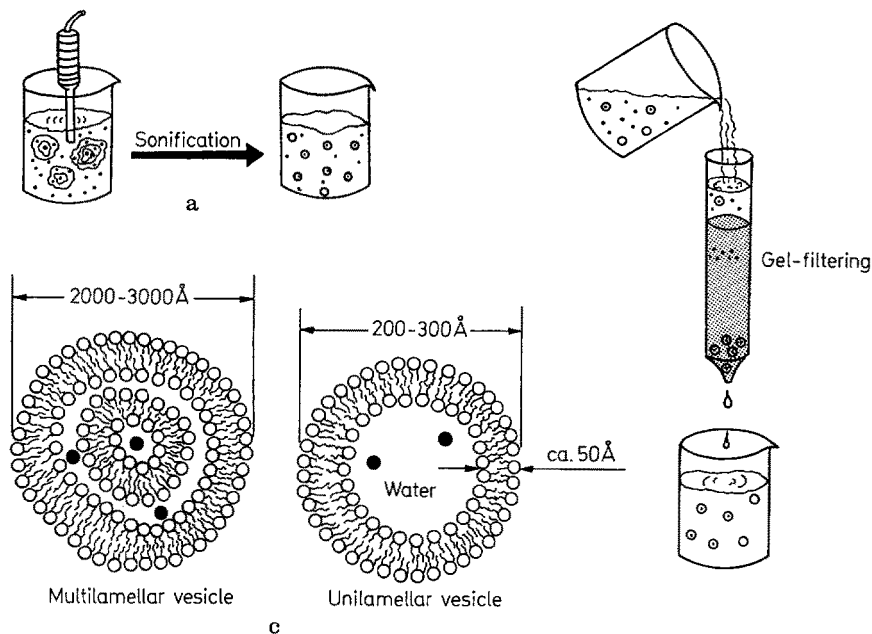


Fig. 2. The procedures for the preparation of vesicles with the desired content of inner cavities. The *black points* denote be molecules to be placed only inside the vesicles: (a) — the stage of preparation of unilamellar vesicles; (b) — the stage of replacement of the bulk solution content; (c) — structure of vesicles

Components of a photosystem can be inserted selectively into the lipid wall or the inner cavity of the vesicle. For this purpose the lipid and components insoluble in water are dispersed together in aqueous solution by sonification. This leads to an occlusion of water insoluble components within the lipid bilayer. The vesicle membrane is sufficiently stable and impermeable for a number of ions. This allows one to prepare, by gel-filtering, the media of different ionic composition inside and outside the vesicle as shown in Fig. 2b. Such asymmetry of chemical content can be preserved for a rather long time (from several hours to several days). Recently the surfactant molecules with double bonds, which can be polymerized after vesicle preparation, were used for further enhancement of vesicle stability [37–39]. Such polymerized vesicles are stable for several months.

One of the peculiarities of reactions in suspensions of vesicles is the possibility of obtaining a much higher local concentration of reagents located in membranes or the inner cavity than their average concentration in suspension. For instance, the presence of one molecule in the inner cavity of a DPL vesicle (diameter 220 Å, membrane thickness ≈ 50 Å [40]) corresponds to the local concentration of about 3×10^{-3} mol/l. These values correspond to only about 10^{-6} mol/l average concentration of the same species in the suspension containing 3×10^{-3} mol/l of the DPL lipid, since the overall volume of the vesicle cavities in such suspensions

comprises only 0.1% of the total volume of the suspension. Another peculiarity of the vesicle suspension is the large total surface area of lipid membranes, which at lipid concentration of 4 mg cm^{-3} reaches 1 m^2 per 1 cm^3 of the suspension.

2.2 Direct and Carrier-Mediated Pathways of PET Across Membranes

The direct electron transfer from $^*S$ to A separated by a lipid membrane looks like the most attractive way of charge separation in membrane systems. Since $^*S$ and A are separated in this case by a distance of about $50 \text{ \AA}$, a possible mechanism of the reaction may be electron tunneling across membrane as schematically shown in Fig. 3a. The back electron transfer via tunneling from A^- to S^+ is expected to be slowed down considerably due to the rapid dissipation of the reaction exothermicity resulting in the increase of potential barrier for the back electron tunneling (see also the chapter by Zamaraev and Khairutdinov). Note that the actual distance of electron tunneling in the process of PET across membranes can be notably smaller than the thickness of the membrane, because the partners in electron tunneling are expected to be able to penetrate to a certain distance inside the lipid membrane. A more detailed discussion of electron transfer across membrane via tunneling will be presented in Sect. 4.2.

The other way of PET across membrane is carrier-mediated transfer as shown in Fig. 3b. This way suggests the use of an intermediate acceptor, A_1 , embedded into the membrane and capable in the reduced form, A_1^- , to carry electron across the membrane to the ultimate acceptor, A_2 . In this case $^*S$, S^+ , A_2 and A_2^- should

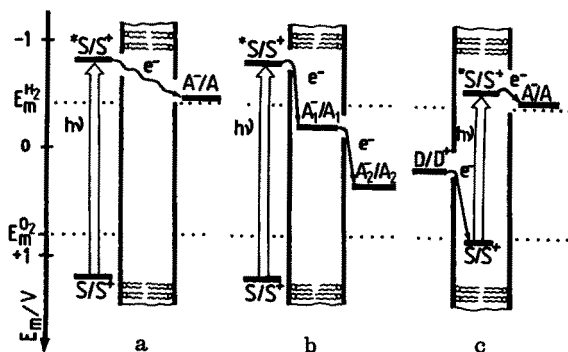


Fig. 3. The possible design of systems for PET across membranes: (a) — electron tunneling in $S // - // A$ system; (b) — carrier-mediated transport in $S // A_1 // A_2$ system; (c) — sensitizer-mediated transport in $D // S // A$ system

The particular values of redox potentials E_m are shown for: (a) — $S = \text{Ru}(\text{bpy})_3^{2+}$, $A = \text{MV}^{2+}$; (b) — $S = \text{Ru}(\text{bpy})_3^{2+}$, $A_1 = \text{C}_{16}\text{V}^{2+}$, $A_2 = \text{Fe}(\text{CN})_6^{3-}$; (c) — $S = \text{Chl}$, $D = \text{Asc}$, $A = \text{MV}^{2+}$.

The redox potentials at pH 7 of dioxygen ($E_m^{O_2}$) and dihydrogen ($E_m^{H_2}$) are given for comparison

be hydrophilic so that they could not penetrate through the membrane, and the redox potential of A_1^-/A_1 should be more negative than that of A_2^-/A_2 . Apparently the photosensitizer S itself can also serve as electron (or hole) carrier if it is embedded into the membrane. This situation is shown in Fig. 3c.

The systems shown in Fig. 3 can be made more complicated via further introduction into the electron transfer chain of the intermediate electron donors and/or acceptors possessing required redox potentials. In the next section we shall demonstrate that this method which mimics the multistep electron transfer chains of photosynthesis sometimes may allow to increase substantially the efficiency of PET across lipid membranes.

2.3 Vesicle Systems

An observation of vectorial PET across the membranes of lipid vesicles was first reported in 1976 by Mangel [41]. Since then numerous systems for vectorial PET across the membranes of vesicles have been reported (see Table 1, part 1). In spite of the differences between the systems of Table 1, all of them have one important common feature. This feature is the asymmetry of the content of aqueous phases inside and outside the vesicle which is required to provide vectorial PET across the membrane in any system. Note also that each vesicle system of Table 1, may have an analog with reversed topology (i.e. with the reversed contents of the inner and outer aqueous phases).

Regarding the design of PET across membranes, the systems studied can be divided into two large groups: (i) — the systems with the photosensitizer embedded into vesicle membrane and (ii) — the systems with the photosensitizer located outside the membrane. These two types of membranes can be named as photoactive and photopassive, respectively.

2.3.1 Photoactive Membranes

In most systems of this group chlorophyll, Chl, was used as a photosensitizer. This reflects great expectations associated with Chl-containing vesicles as models of the natural photosynthetic apparatus. The earlier works in this field were reviewed by Hurley and Tollin [103]. As mentioned above, the first observation of PET across the vesicle membranes containing chlorophyll and β -carotene (System 1, Table 1) was reported by Mangel [41]. The presence of β -carotene and Chl dimers in the membrane was assumed to be necessary for transmembrane electron transfer. However in later works [43, 44, 48, 51–53] it was suggested that in fact the presence of neither β -carotene nor Chl dimers is crucial for PET. It is also worth noting that the high quantum yield of electron phototransfer, reported by Mangel [41] also has not yet been confirmed by other investigations.

The proposed mechanism of electron transfer across Chl-containing membranes of vesicles in $A // \text{Chl} // D$ (i.e. for systems containing Chl as a photosensitizer in the membrane and donor, D, and acceptor, A, particles outside and inside the vesicle, respectively) and $D // \text{Chl} // A$ systems was outlined in early papers [42, 43,

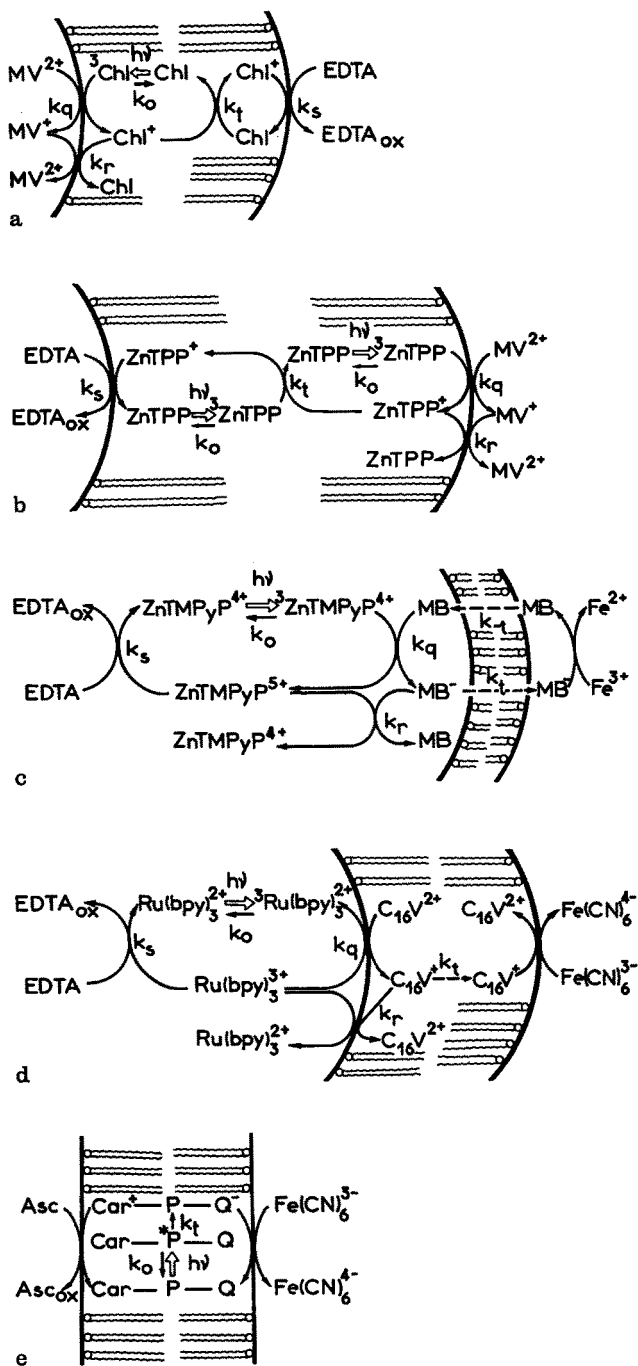


Fig. 4. Schematic representation of suggested mechanisms of PET across membrane for some systems of Table 1: (a) – System 3; (b) – System 12; (c) – System 27; (d) – System 21; (e) – System 45. White and black arrows indicate, respectively, reaction steps that do and do not require light quanta to occur. Dotted arrows indicate transmembrane diffusion of substances

Table 1. Membrane systems providing vectorial PET^{a, b}

Part I. Vesicles

system number	inner aqueous phase content	membrane content	outer aqueous phase content
Systems of A // S // D type			
1	Fe ³⁺	Chl and β-carotene	Asc
2	Fe(CN) ₆ ³⁻	Chl and carotenoids	—
3	MV ²⁺	Chl a	EDTA
4	MGNQ	Chl a	GSH
5	Fe(CN) ₆ ³⁻	Chl a or Chln a	EDTA
6	Cyt	Amphiphilic flavins	
Systems of D // S // A type			
7	Asc	Chl a	Cu ²⁺
8	Asc	Chl a	Fe(CN) ₆ ³⁻
9	Asc	Chl a	Methyl red
10	Asc or NADH	Chl a	MV ²⁺
11	Asc	Phe	MV ²⁺ or EVS
12	EDTA or NADH	ZnTPP	MV ²⁺
13	EDTA	ZnTPP	MV ²⁺
14	EDTA and Ru(bpy) ₃ ²⁺	ZnTPP	MV ²⁺
15	EDTA	H ₂ MP ²⁻	C ₇ V ²⁺ or MV ²⁺
16	EDTA	ZnC ₁₂ TPyP ⁺ or AF	AQDS ²⁻
17	EDTA or Asc	ZnC ₁₈ TMPyP ³⁺ and (ZnTPP or H ₂ TPP or UQ ₁₀)	MV ²⁺
18	EDTA	MgC ₁₈ TMPyP ³⁺ or MgTPyP	MV ²⁺

membrane material	max quantum yield, $\Phi/\%$ °	comments	Refs.
eggL	7.5	No PET across membrane is observed without carotene. Photoactive are Chl-dimers	41
eggL	—	$\text{Fe}(\text{CN})_6^{3-}$ reduction is conjugated with H_2O oxidation to O_2	42
eggL	0.1–0.01	Direct observation of the stage of trans-membrane electron transfer using flash-photolysis	43
eggL	20	Φ was estimated from the rate constants of various steps of electron transfer, obtained by flash-photolysis	44
eggL	—	$\Phi(\text{Chln a}) > \Phi(\text{Chl a})$	45
DPL	—	—	46, 47
eggL	—	—	48
eggL	—	Ionophores accelerate electron transfer due to proton co-transport	49, 50
eggL	0.1	—	51
eggL	1.7	The products of transmembrane PET slowly recombine due to MV^+ radical penetration inside vesicle	52, 53
eggL	15–20	The products of transmembrane PET slowly recombine due to MV^+ radical penetration inside vesicle	54, 55
eggL or DPL	0.24	Consecutive two-quantum activation of electron transfer across membrane, therefore Φ is proportional to the square of the light intensity	56–59
eggL	—	Electron phototransfer across membrane proceeds via two-quantum photoionization of porphyrin dimers in membrane	60
eggL	0.6	Φ was obtained at simultaneous photoexcitation of $\text{Ru}(\text{bpy})_3^{2+}$ and ZnTPP	58, 61
eggL	0.2	Depolarization of membrane induced by K-valinomycin raises Φ	62
DPL	—	Intermediate acceptors (alloxazine or vitamin K_1), when inserted into the membrane, increase Φ . Two-step photoactivation of electron transfer. $\Phi(\text{ZnC}_{12}\text{TPyP}^+) \cong 100 \Phi(\text{AF})$	63
DPL	—	Two-step photoactivation of electron transfer at simultaneous excitation of both photosensitizers in the membrane	64, 65
DPL	—	$\Phi(\text{MgC}_{18}\text{TMPyP}^{3+}) \cong 30 \Phi(\text{MgTPyP})$	66

Table 1. (continued)

system number	inner aqueous phase content	membrane content	outer aqueous phase content
19	EDTA	$(\text{bpy})_2\text{Ru}(2\text{C}_{16}\text{bpy})^{2+}$	MV^{2+} or C_7V^{2+}
20	—	$\text{ZnC}_{16}\text{TPyP}^+$ and PVS	$\text{MnC}_{16}\text{TPyP}^{2+}$
Systems of D + S // A ₁ // A ₂ type			
21	EDTA + $\text{Ru}(\text{bpy})_3^{2+}$	$\text{C}_{16}\text{V}^{2+}$	$\text{Fe}(\text{CN})_6^{3-}$
22	(EDTA or $\text{K}_2\text{C}_2\text{O}_4$) + $(\text{Ru}(\text{bpy})_3^{2+})$ or ZnTMPyP^{4+}	$\text{C}_{18}\text{V}^{2+}$	$\text{Fe}(\text{CN})_6^{3-}$ or MB
23	S^{2-} , CdS	$\text{C}_{16}\text{V}^{2+}$	$\text{Fe}(\text{CN})_6^{3-}$
Systems of A ₂ // A ₁ // S + D type			
24	$\text{Fe}(\text{CN})_6^{3-}$	$\text{C}_{14}\text{V}^{2+}$	ZnTPPS^{4-} , Tricine
Systems of D + S + A ₁ // A ₂ // A ₃ type			
25	EDTA + $\text{Ru}(\text{bpy})_3^{2+}$ + $\text{Rh}(\text{bpy})_3^{3+}$	Quinones	$\text{Fe}(\text{CN})_6^{3-}$
Systems of A ₃ // A ₂ // A ₁ , S + D type			
26	$\text{Fe}(\text{CN})_6^{3-}$	$\text{C}_{16}\text{V}^{2+}$	MV^{2+} + ZnTMPyP^{4+} + EDTA
Systems of D + S + A ₁ // — // A ₂ type			
27	EDTA + ZnTMPyP^{4+} + MB	—	Fe^{3+}
28	$\text{Na}_2\text{S}_2\text{O}_3$ + ZnTPPS^{4-} + C_4V^{2+}	—	FMN
Systems of D + S // — // A type			
29	Asc + HCD	—	$\text{Fe}(\text{CN})_6^{3-}$
Systems of A // — // S + D type			
30	$\text{Fe}(\text{CN})_6^{3-}$	—	MB + (Asc or Fe^{2+})
31	$\text{Fe}(\text{CN})_6^{3-}$	—	(AQDS ²⁻ or MV^{2+}) + $\text{C}_2\text{H}_5\text{OH}$
32	MV^{2+}	—	CdS + benzyl alcohol
Systems of D ₂ // D ₁ // S + A type			
33	$\text{Os}(\text{bpy})_3^{2+}$	$(\text{bpy})_2\text{Os}(2\text{C}_{17}\text{bpy})^{2+}$	$\text{Ru}(\text{bpy})_3^{2+}$ + $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$

membrane material	max quantum yield, $\Phi/\%$ °	comments	Refs.
eggL	0.04–0.44	Addition of ionophores and K-valinomycin raises Φ	67–69
DHP	—	Mn(III) reduction to Mn(II) is conjugated with DHP membrane oxidation. No electron transfer without PVS	70
eggL	10–20	—	71, 72
DPL	10–20	—	73–76
eggL	—	Electron donor D is S^{2-} ion coming with CdS and/or membrane material	77
DHP	—	Only indirect evidence for transmembrane electron transfer was obtained	78
DPL	10–20	—	79
eggL	—	Electrical polarization caused by transmembrane electron transfer slows the latter down	77
eggL	60	Electron is carried across the membrane by A_1^-	77, 80
eggL	10	Other C_nV^{2+} dications ($n = 1, 3, 5, 6$ and 10) were also used as A_1 . In the system with reversed topology $\Phi = 3\%$	81
eggL	—	HCD^- serves as electron carrier across the membrane. Being protonated it simultaneously carries proton	82
eggL	—	Only UV light is active	83, 84
eggL	—	Electron transfer across membrane is accompanied by co-transport of proton. Only UV light is active	85
DHP	5	The mechanism of transmembrane electron transfer is not reported	86
DPL	10–30	Strong oxidant $Os(bpy)_3^{3+}$ is accumulated in the inner cavities of the vesicles	87

Table 1. (continued)**Part II. Planar bilayer lipid membranes**

system number	donor D in aqueous phase	photosensitizer S in membrane	acceptor A in aqueous phase
34	QH ₂	Chl and carotene	Fe ³⁺
35	Asc	Chl and carotene	Ce ⁴⁺ or Fe ³⁺
36	Asc	Chl	TMPD
37	MV ²⁺ or MB	Chl	Fe ³⁺
38	Fe ²⁺	Chl and carotene	Fe ³⁺
39	EDTA	ZnTPP	MV ²⁺ or C ₇ V ²⁺
40	Asc	ZnTPP or ZnTPP-Ac	Fe ³⁺
41	Asc	ZnTPP-Ac	Fe(CN) ₆ ³⁻
42	Fe(CN) ₆ ⁴⁻	MgOEP	Fe(CN) ₆ ³⁻
43	Na ₂ SO ₃	TCNQ	MV ²⁺
44	Asc	P or P-Q or Car-P	Fe ³⁺
45	Asc	Car-P-Q	Fe(CN) ₆ ³⁻

^a Only components active in redox reactions are indicated. Abbreviations of the names of compounds are explained in Section 8

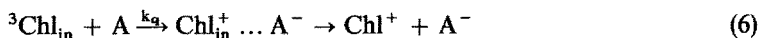
^b Designations for vesicle systems: Inner aqueous phase content // Membrane material // Outer aqueous phase content. Notation D + S // A₁ // A₂ means that the donor D and sensitizer S are located in the inner aqueous phase, the first acceptor A₁ is embedded into the membrane, and the second acceptor A₂ is located in the outer aqueous phase. Sign // stands for interface between the membrane and water phase

^c If not specially mentioned, Φ was determined in steady-state photolysis

membrane material	measured value	comments	Refs.
mixture of lipids	photo voltage	Photocurrent is proportional to square root of light intensity. Quantum yield of PET across the membrane is estimated as 2–7.5%	88,89
mixture of lipids	photo current	Quantum yield of PET across the membrane is estimated as 0.01%	90, 91
eggL	photo current	—	92
eggL	photo voltage	BLM is made of spinach or chlorella extract	93
eggL	photo current	No photocurrent is observed without carotene	94
mixture of lipids	photo current and photo voltage	Two-quantum PET across membrane is considered. Proton carriers raise the photocurrent by one order of magnitude	95
PS	photo current	One-quantum PET across membrane. Zn-TPP-Ac is 30 times more photoactive than ZnTPP	96
GMO	photo current	PET across membrane is accompanied by co-transport of proton, which is also carried by photosensitizer	97
mixture of lipids	photo voltage	Transmembrane diffusion of MgOEP^+ is supposed to perform charge transport	98
cyano-biphenyl	photo current	TCNQ-cyanobiphenyl complex is photoactive	99
mixture of lipids	photo voltage and photo current	Photovoltages obtained for Car-P and P-Q are much larger than those obtained with simple porphyrin	100
PS	photo current	Intramolecular PET across membrane	101, 102

51]. For the systems of A // Chl // D type the mechanism, schematically represented in Fig. 4a, has been suggested. Later on, Ford and Tollin [43, 44] have comprehensively examined the kinetics and mechanism of PET across the Chl-containing membranes. They have demonstrated that only the triplet-excited chlorophyll is involved in PET, as shown in Fig. 4a.

The sequence of the reactions leading to PET across membrane looks as follows:



Here and in what follows the subscripts "in" and "out" indicate the Chl molecules localized near the inner and outer surfaces of the vesicle membranes. If no more than one pair of Chl^+ and A^- particles is generated on the inner surface of each vesicle, the recombination by reaction (7) may be described in terms of first-order kinetics. Having in mind that the number of D, A and Chl_{out} molecules considerably exceeds the number of ${}^3\text{Chl}$ and Chl^+ particles, one can treat all the remaining rate constants of reaction sequence (5)–(9) also as pseudo first-order ones. In accord with this reaction scheme, the quantum yield of the transfer of the first electron through the vesicle membrane can be expressed as:

$$\Phi = \Phi_T \frac{k_q}{k_q + k_0} \varphi_c \frac{k_t}{k_t + k_r} \quad (10)$$

Here Φ_T is the quantum yield of ${}^3\text{Chl}$ and φ_c is the yield of the ion-radical products from a ${}^3\text{Chl} \dots \text{A}$ geminate pair in the primary photochemical act. Particular stages of reaction scheme (5)–(9) will be discussed in more detail in Sects. 3 and 4.

Calvin and his co-workers [67–69] have used as the photosensitizer $(\text{bpy})_2 \cdot \text{Ru}(2 \text{ C}_{16}\text{bpy})^{2+}$, a surfactant analog of $\text{Ru}(\text{bpy})_3^{2+}$ complex (System 19, Table 1), rather than the natural pigment Chl. Just as Chl, $(\text{bpy})_2\text{Ru}(2 \text{ C}_{16}\text{bpy})^{2+}$ is embedded into the membrane owing to long hydrocarbon substituents, while EDTA and MV^{2+} serve as electron donor and acceptor respectively. To our knowledge, this is the first experimental realization of PET across the vesicle membrane that leads to energy storage. The scheme of PET across the membrane suggested for this system [67–68] is similar to schemes (5)–(9).

When using heptylviologen, C_7V^{2+} , which is more hydrophobic than MV^{2+} and can also serve as an excellent electron carrier, a larger value of Φ is observed under similar conditions. This is associated with a higher efficiency of $\text{A} = \text{C}_7\text{V}^{2+}$ in reaction (6) as compared to $\text{A} = \text{MV}^{2+}$. In fact, C_7V^{2+} is better adsorbed on

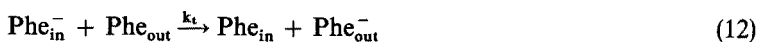
the membrane than MV^{2+} and thus possibly penetrates into it somewhat deeper than MV^{2+} [104]. At the same time, unlike MV^+ , the radical cation C_7V^+ formed upon PET across membranes is capable of penetrating fast through lecithin membranes from the outer surface into the inner water phase of the vesicle (see Table 2, Sect. 4.1 and Refs. [81, 105]). As a consequence the electron transferred through membrane is able to readily return back (in the form of C_7V^+) in the secondary dark process.

Matsuo et al. [106] have reported the data which do not quite agree with the mechanism proposed in Refs. [67, 68]. They found that MV^{2+} does not quench the luminescence of $(bpy)_2Ru(2 C_{12}bpy)^{2+}$ located in the lipid membrane. This suggests that electron transfer at the outer surface of the vesicles in System 19 cannot take place, which contradicts the mechanism suggested in Refs. [67, 68]. Even for $(bpy)_2Ru(2 C_{12}bpy)^{2+}$, insertion into the membrane of decylviologen, which quenches the luminescence of the $(bpy)_2Ru(2 C_{12}bpy)^{2+}$ complex, does not give rise to the formation of the MV^+ radical cation [106]. Thus it may be concluded that $(bpy)_2Ru(2 C_{12}bpy)^{2+}$ is located deep enough inside the membrane core and is not accessible for the acceptors from the solution. Nevertheless, according to Ford's and Calvin's opinion [106a], analysis of the absorption spectra of $(bpy)_2Ru(2 C_{16}bpy)^{2+}$ in media with different polarities gives evidence that this complex is in the contact with the water phase at the surface of the membrane and thus can react with MV^{2+} . Further studies are needed to resolve the controversy between the data obtained by various groups for the similar systems described above.

In all the systems of A // S // D and D // S // A type from Table 1, except for System 11, the primary photochemical act appears to be oxidation of the photosensitizer via reactions of type (6). For System 11, where pheophytin, Phe, is used as the photosensitizer, the primary reaction is its reduction:



In this situation the transmembrane electron transfer is assumed to occur in a reaction similar to reaction (8):

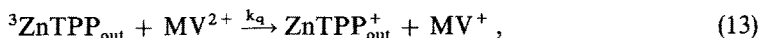


with subsequent reduction of the acceptor A at the outer side of the membrane. Comparison of Φ values for Chl- and Phe-containing vesicles (Systems 10 and 11) shows that in the latter case the value of Φ is higher by one order of magnitude. Krasnovsky and his co-workers [52–55] explain this in terms of larger values of k_q and ϕ_c as well as smaller values of k_r for Phe-containing vesicles (see eqn. (10)).

The scheme of the (5)–(9) type suggests that only one quantum of light is consumed for the transmembrane transfer of one electron. However, when using tetraphenylporphyrinatozinc(II), ZnTPP, as the photosensitizer it was found (Systems 12 and 13) that the initial rate of PET across the membrane is proportional

to the square of the light intensity [56–58, 60]. This suggests the participation of two rather than one light quanta in the transfer of one electron across the membrane.

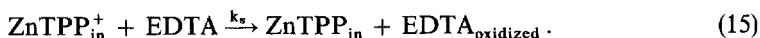
Flash photolysis experiments have shown that for these systems the primary photochemical act is the transfer of an electron from $^3\text{ZnTPP}$ to MV^{2+} , and the intermediate particles involved in the transfer are $^3\text{ZnTPP}$ and ZnTPP^+ [56, 58, 59]. The whole set of the data obtained makes it possible to suggest the scheme for PET across the membrane which is shown in Fig. 4b. This scheme assumes the electron transfer at the outer boundary of the vesicle membrane as the first act:



which is followed by electron transfer to $\text{ZnTPP}_{\text{out}}^+$ across the membrane from the other excited molecule $^3\text{ZnTPP}_{\text{in}}$ located near the inner surface of the membrane:



Finally the irreversible oxidation of EDTA takes place:



This scheme suggests the participation of two $^3\text{ZnTPP}$ particles in the transfer of one electron and explains why the total rate of transmembrane PET is proportional to the square of light intensity.

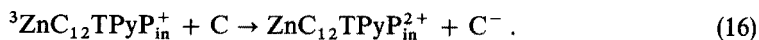
If this scheme is valid, one can expect that, when both EDTA and MV^{2+} are located in the bulk solution and the membranes are used only as carriers of water-insoluble ZnTPP, electron transfer from EDTA to MV^{2+} sensitized by ZnTPP can occur on the outer surface of the vesicle with the participation of only one $^3\text{ZnTPP}$ particle. In this case the initial rate of MV^+ accumulation is expected to be directly proportional to the light intensity, and indeed such dependence was observed experimentally [57].

Another mechanism of the transmembrane electron transfer in the system under discussion has been proposed by Khairutdinov and co-workers [60]. This mechanism assumes the two-quantum ionization of porphyrin dimer located in the inner membrane monolayer with the capture of the electron by MV^{2+} dication to be the primary redox photochemical process. However, this interpretation is based on the data obtained when studying vitreous suspensions of vesicles at 77 K, and further experiments seem to be needed to justify their applicability to liquid suspensions at ambient temperatures.

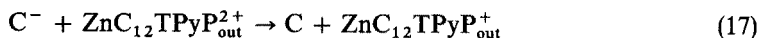
Reaction (14) and hence the overall rate of electron phototransfer across the membrane can be enhanced by providing additional excitation of the ZnTPP_{in} molecules on the inner membrane surface. It could be done by virtue of energy transfer from some “antenna” collecting light and then transferring the excitation to the “reaction centers”, i.e. the ZnTPP_{in} molecules embedded into the membrane; this approach reproduces the action of a pull of the “antenna” chlorophyll in chloroplasts. In corresponding experiments (System 14 of Table 1) a water-soluble

$\text{Ru}(\text{bpy})_3^{2+}$ complex placed into the inner cavity of the vesicle was used as such "antenna". The lifetime of the triplet-excited state of this complex ($\approx 0.6 \mu\text{s}$) is sufficiently long, so that before its deactivation it can experience numerous collisions with the inner surface of the vesicle membrane and thus with the porphyrin molecules embedded into the membrane. Indeed, it was found that the introduction of $\text{Ru}(\text{bpy})_3^{2+}$ into the inner volume of the vesicle leads to the sixfold increase of the rate of the transmembrane PET [58, 61]. This effect results, first, from the spectral sensitization due to the light absorption by the ruthenium complex in the spectral region where porphyrin does not absorb, and, second, from the two-three fold increase of Φ due to the energy (or electron) transfer from $^3\text{Ru}(\text{bpy})_3^{2+}$ to ZnTPP_{in} .

A two-step photoactivation of electron transfer across the membrane was also assumed for the System 16 of Table 1, wherein a surfactant porphyrin, $\text{ZnC}_{12}\text{TPyP}^+$, served as a photosensitizer [63]. The presence of an intermediate electron carrier in membranes (vitamin K_1 or derivatives of alloxazine) leads to a significant increase in the electron phototransfer rate. Such an influence of the carriers, which are known to be the quenchers of the excited porphyrin, is explained in terms of the two-quantum mechanism of electron phototransfer activation involving the participation of electron carriers. According to the scheme suggested by Matsuo and his co-workers [63], the absorption of the light quantum on the outer side of the membrane results in the reduction of AQDS^{2-} and in the oxidation of $\text{ZnC}_{12}\text{TPyP}_{\text{out}}^+$ by the reaction of the type (13). Absorption of the second light quantum on the inner surface leads to the formation of the triplet excited porphyrin and subsequent reduction of the electron carrier, C, embedded into the membrane:



The reduced form of the carrier diffuses to the outer surface of the membrane and reduces in its turn the molecules of $\text{ZnC}_{12}\text{TPyP}_{\text{out}}^{2+}$ formed during the first photochemical act:

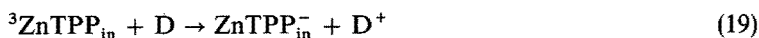
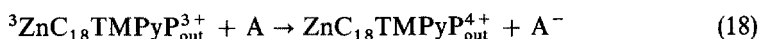


The irreversible oxidation of the EDTA donor at the inner surface of the membrane by a reaction of the type (15) regenerates $\text{ZnC}_{12}\text{TPyP}_{\text{in}}^+$. This scheme explains qualitatively the experimental data on PET in the presence of the carriers. However, it does not explain the data on a more slow PET observed when there are no carriers inside the membrane.

In all the systems considered above the photosensitizer was embedded in the membrane symmetrically, i.e. identical S molecules are located near both the inner and the outer surfaces of the vesicle membranes. Of great interest would also be to create asymmetric membranes providing a specially organized gradient of the redox potential across the lipid bilayer. Asymmetry of a membrane can be realized, e.g. if one locates the molecules with different redox potentials within the membrane near its inner and outer interfaces. An asymmetric membrane containing the components required for photochemical separation of charges at the lipid // water

interface and also for the vectorial transfer of electrons across membrane would be an even closer analog of the reaction center of photosynthesis. Theoretical analysis of electron transfer by a chain of electron acceptors through the nonpolar region of such a membrane was given in ref. [107].

Experimentally, electron transfer across vesicle membranes with an asymmetrically embedded photosensitizers was first observed in System 17 of Table 1. Katagi et al. [64, 65] succeeded in embedding a photosensitizer ($\text{ZnC}_{18}\text{TMPyP}^{3+}$) into the bilayer membrane both uniformly and selectively in its outer monolayer, i.e. asymmetrically. In the latter case no electron transfer across the membrane took place until the other photosensitizer (ZnTPP) was introduced into the membrane uniformly. The proposed mechanism of electron transfer involved two photochemical steps:



with further recombination of the radical cation and radical anion of the porphyrins in the membrane via a reaction of the type (17). Note however that according to refs. [56, 60, 62] one fails to observe a reaction of the type (19). Thus further studies of the mechanism of PET across the membrane in this system seem to be needed.

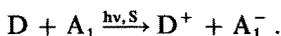
Other examples of the systems with photosensitizers asymmetrically embedded into membranes, are Systems 17 and 19 of Table 1.

2.3.2 Photopassive Membranes

For the systems with photoactive membranes discussed in the previous section the photosensitizer embedded into the vesicle membranes not only participated in photochemical and dark redox reactions with substances which are located in water phases on both sides of the membrane, but also served as the carrier of the electron across the membrane. In the presence of the appropriate electron carrier which is capable of penetrating through the membrane core it is also possible to perform electron transfer between membrane-separated water phases when photosensitizers are located in these phases rather than in the membrane. Membranes containing no photosensitizers can be called photopassive ones since no photo-physical and photochemical processes occur in them, and their role is only to (i) provide electron transfer from one water phase to the other leading to the formation of spatially separated oxidant and reductant and (ii) to suppress recombination reactions.

The possibility of using vesicle membranes in such a way has been demonstrated in systems of the type $\text{D} + \text{S} + \text{A}_1 // - // \text{A}_2$ (i.e. systems in which the inner volume of the vesicle contains the donor D, photosensitizer S and primary acceptor A_1 ; no special carrier is inserted into the membrane; and the outer volume of the vesicle contains the ultimate acceptor A_2). Systems 27 and 28 of Table 1 belong

to this class. In these systems particles A_1^- are generated in the inner water phase of the vesicle by virtue of the irreversible photosensitized oxidation of the donor D:



If A_1^- particles are hydrophobic enough, they can penetrate through the membrane and transfer the electron to the ultimate acceptor A_2 in the water phase outside the vesicle. The electron transport in the systems like those is schematically shown in Fig. 4c (in this figure MB stands for the methylene blue and ZnTMPyP⁴⁺ – for tetramethylpyridiniumporphyrinatozinc(II)). Note that owing to the efficient suppression of S^+ and A_1^- recombination because of fast irreversible reduction of S^+ (under experimental conditions of Refs. [80, 81] $k_s[D]_{in} > k_r[A_1^-]_{in}$), the quantum yield of PET across the membrane is equal to that of A_1^- generation:

$$\Phi = \Phi_T \phi_c k_q [A_1]_{in} / (k_q [A_1]_{in} + k_o). \quad (20)$$

In D // S // A systems with photoactive membranes the electron transfer across the membrane via electron exchange mechanism (reactions of the type (8), (12) and (14)) does not lead to the redistribution of substances between the inner and outer water phases. In case of D + S + A_1 // – // A_2 systems with the diffusion mechanism of electron transfer such a redistribution should be taken into account [77, 81, 105]. Note that for the System 27 of Table 1 the value of Φ was shown to decrease from 60% to 20% as the intensity, I, of light absorbed by the suspension increased from 1 mW/cm² to 100 mW/cm². This effect is accounted for by a light-induced decrease in the concentration of a quencher A_1 inside the vesicle because of its escape into the outer water phase (see Fig. 4c). At high light intensities the rate of A_1^- photogeneration (and hence the rate of PET across the membrane) ceases to be dependent on the light intensity and is only determined by the rate of A_1 diffusion through the membrane back inside the vesicle. Under these conditions:

$$\Phi = k_{-1} [A_1]_{out} / I, \quad (21)$$

where k_{-1} is the rate constant of A_1 transport across the membrane. Thus in order to achieve high stationary rates of PET across the membrane it is necessary to ensure an appropriate conjugation of A_1^- and A_1 flows across the membrane. This is true not only for the Systems 27 and 28, but also for other systems considered below in this section.

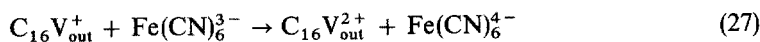
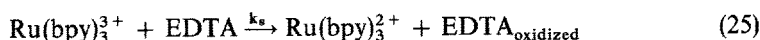
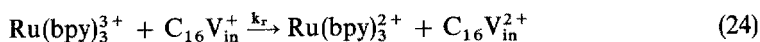
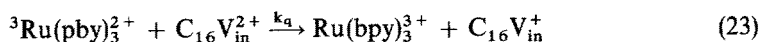
In Systems 29 and 30 suggested by Sudo and Toda [82–84] no intermediate acceptor A_1 was added. Instead of A_1 the photosensitizer itself which is able to penetrate through a lipid bilayer both in oxidized and reduced states, performs electron transfer across the membrane. System 30 allows one to accumulate and store the products of electron transfer from the reversible donor, Fe^{2+} , to the reversible acceptor, $Fe(CN)_6^{3-}$. Note that in homogeneous solution it is impossible to accumulate and store the products of this reaction. It is well known that back recombination of the products formed upon PET from Fe^{2+} to thiazine dyes

(thionin, methylene blue) is rather slow [108]. This is the reason, why the diffusion of the reduced methylene blue across the membrane inside the vesicle to ultimate acceptor, $\text{Fe}(\text{CN})_6^{3-}$, can successfully compete with the recombination reaction in the water phase outside the vesicle. Thus the possibility to accumulate the products of PET in System 30 is totally accounted for by the specificity of the compounds chosen.

System 31 is similar to System 30. However, UV light is required to excite the photosensitizer in System 31.

The above systems with photopassive membranes do not utilize such an advantage of membranes as the possibility of accomplishing the primary act of photoinduced charge separation at the membrane // water interface. When this primary act occurs in the bulk of the inner or outer water phases, recombination of the separated charges remains to a large extent unsuppressed and usually competes strongly with the secondary process of electron transfer across the membrane. It is also possible to use the photopassive membranes that provide the primary charge separation between the photosensitizer located in the water phase and the electron (or hole) carrier embedded into the membrane close to the membrane // water interface. Provided that the reduced (or oxidized) carrier formed in this process is transported rapidly enough through the membrane core to its opposite side, a higher efficiency of PET across the membrane can be achieved.

The examples of this type are Systems 21 and 22 of Table 1. The scheme for PET across membrane in System 21 is given in Fig. 4d. It assumes the following sequence of reactions:



Reaction (26) means that C_{16}V^+ radical cation changes its location, i.e. it migrates from the inner surface to the outer surface of the membrane.

Within this scheme the quantum yield (Φ) of PET across the membrane is determined by the product of the yield of the triplet state (Φ_T), fraction of ${}^3\text{Ru}(\text{bpy})_3^{2+}$ molecules quenched by $\text{C}_{16}\text{V}^{2+}$ (φ_q), yield of radical-ion products from the geminate pair in the primary photochemical act (φ_c) and the probability (η) for these products avoiding recombination:

$$\Phi = 2\Phi_T\varphi_q\varphi_c\eta \quad (28)$$

Coefficient 2 takes into account that the product of the one electron oxidation of EDTA is capable of reducing the second viologen molecule [109]. Note that for $\text{Ru}(\text{bpy})_3^{2+}$ the Φ_T is close to 100% [110].

For steady-state photolysis and flash photolysis at comparatively low flash intensity one can easily obtain the conditions, under which no more than one pair of $\text{Ru}(\text{bpy})_3^{2+}$ and C_{16}V^+ particles is generated at a time at the inner surface of the vesicle membrane, and all the processes with the participation of these particles are completed long before the next light quantum reaches the vesicle. In this case one may describe the recombination kinetics by the first order kinetic law [111] with the rate constant:

$$k_r = k_b[\text{C}]_{\text{in}}, \quad (29)$$

where k_b is the bimolecular rate constant for the recombination of the same products, and $[\text{C}]_{\text{in}} \simeq 10^{-3} \text{ mol/l}$ is the local concentration corresponding to a pair of recombining molecules per vesicle. Expressing Φ via the rate constants of the reactions (22)–(27) and local concentration of viologen in the membrane, $[\text{C}_{16}\text{V}^{2+}]_m$, and of EDTA inside the vesicle, $[\text{EDTA}]_{\text{in}}$, as well as taking into account that the stage of EDTA oxidation is irreversible, one obtains:

$$\Phi = 2\Phi_T \frac{k_q[\text{C}_{16}\text{V}^{2+}]_m}{k_0 + k_q[\text{C}_{16}\text{V}^{2+}]_m} \varphi_c \frac{k_s[\text{EDTA}]_{\text{in}} + k_t}{k_s[\text{EDTA}]_{\text{in}} + k_t + k_r}. \quad (30)$$

The high value of Φ for Systems 21 and 22 is ascribed to the efficient suppression of reaction (24) by a faster reaction (25) ($k_s \simeq 10^7 \text{ l/mol s}$ at pH 6.5 [112]). Indeed, at high local concentration of $[\text{EDTA}]_{\text{in}} > 0.01 \text{ mol/l}$ in the vesicle cavity, the condition $[\text{EDTA}]_{\text{in}} k_s \gg k_r$ is fulfilled. Hence $\eta = (k_s[\text{EDTA}]_{\text{in}} + k_t)/(k_s[\text{EDTA}]_{\text{in}} + k_t + k_r)$ is close to unity, Φ becomes independent of the concentration and nature of A_2 and is determined only by the rate of C_{16}V^+ photogeneration:

$$\Phi = 2 \frac{k_q[\text{C}_{16}\text{V}^{2+}]_m}{k_0 + k_q[\text{C}_{16}\text{V}^{2+}]_m} \Phi_c. \quad (31)$$

It can be seen from Eq. (28) that in order to obtain a high quantum yield of PET across the membrane both $\varphi_q = k_q[\text{C}_{16}\text{V}^{2+}]_{\text{in}}/(k_0 + k_q[\text{C}_{16}\text{V}^{2+}]_{\text{in}})$ and φ_c should be sufficiently large. For example, if one inverts the topology of System 21, i.e. exchanges the contents of the inner and outer water phases of vesicles, the value of Φ decreases from 15% to 0.021% [113]. This is due to a decrease of φ_q resulting from a dramatic drop in the probability of diffusion collisions between $^3\text{Ru}(\text{bpy})_3^{2+}$ and the membranes during the lifetimes of excitation. This drop occurs because the volume of the bulk solution considerably exceeds the volume of the vesicle inner cavity.

In System 22 a water-soluble porphyrin, ZnTMPyP^{4+} , was used as the photosensitizer. However, the quantum yield of transmembrane PET $\Phi = 0.5\%$ is considerably lower in this case than for $\text{Ru}(\text{bpy})_3^{2+}$, since viologen $\text{C}_{18}\text{V}^{2+}$

inserted in the vesicle wall does not practically quench excited porphyrin [114]. It is possible to achieve a more efficient generation of the $C_{16}V^+$ radical cation by $ZnTMPyP^{4+}$ photosensitizer introducing an intermediate electron acceptor MV^{2+} which oxidizes $^3ZnTMPyP^{4+}$ in the outer water phase and transfers the electron to the membrane-bound $C_{16}V^{2+}$ (System 26 of Table 1).

In natural photosynthesis the quinones are widely used as electron carriers. Unfortunately, the low values of ϕ_e in the reaction of quinones with $^3Ru(bpy)_3^{2+}$ make the direct use of these important electron carriers rather inefficient. However, introduction of the electron carrier $Rh(bpy)_3^{3+}$ into the inner volume of the vesicle in addition to photosensitizer $Ru(bpy)_3^{2+}$, provides much more efficient electron transfer from $^3Ru(bpy)_3^{2+}$ to a quinone embedded into the membrane. This was found for System 25 of Table 1.

As has already been mentioned, in the above systems with hydrophobic viologens embedded into the membranes as electron carriers, a high value of Φ of transmembrane PET is achieved due to the irreversibility of reaction (25). In the absence of EDTA the value of η (see Eq.(28) and (30)) decreases drastically since the recombination reaction effectively competes with the transmembrane diffusion of the carrier. The quantum yield of PET across membrane under these conditions is:

$$\Phi = \Phi_0 k_t / 2(k_t + k_r) = \Phi_0 \eta / 2, \quad (32)$$

where $\Phi_0 = 15\%$ is the quantum yield in the presence of EDTA and $\eta = k_t / (k_t + k_r)$ is the efficiency of the charge separation.

For direct observation of the transmembrane electron transfer by membrane-bound viologens the system shown in Fig. 4d was studied by flash photolysis technique [115, 116]. At high concentration of EDTA the only channel for the decay of $C_{16}V^+$ radical generated at the inner surface of membrane remains electron transfer to the outer membrane interface via reaction (26) followed by the oxidation of $C_{16}V_{out}^+$ via reaction (27). As the concentration of the final acceptor $A_2 = Fe(CN)_6^{3-}$ increases, the rate constant for the pseudofirst order decay of the viologen radical cation increases and achieves the maximum value k_p , which is independent of the concentration and nature of A_2 . This means that the oxidation of the viologen radical cation occurs in the non-limiting stage and, therefore, k_p may be interpreted as the rate constant for the transmembrane electron transfer.

Recombination constants k_r of a pair of primary products of PET at the inner membrane // water interface were also measured for the system of Fig. 4d using flash photolysis in the absence of EDTA and $Fe(CN)_6^{3-}$. The values k_p , k_t and η for a series of membrane-bound viologens are listed in Table 2. Taking into account that Φ_0 amounts to 15%–20%, it is easy to calculate (using Eq. (32)) that even in the absence of an irreversible electron donor, the value of Φ for PET across the membrane can achieve several percent.

Let us finally discuss System 33 of Table 1 wherein an electron donor, namely the amphiphilic osmium complex, rather than acceptor is embedded into the membrane as the electron carrier. The high quantum yield of PET across the membrane in this system is due to the fact that the primary oxidation of the

excited photosensitizer $^*S = {}^3Ru(bpy)_3^{2+}$ by the acceptor $A = Co(NH_3)_5Cl^{2+}$ proceeds irreversibly because it is followed by the cobalt complex decomposition. Therefore, during the steady-state photolysis all the further processes $D_1 + S^+ \rightarrow D_1^+ + S$ and $D_2 + D_1^+ \rightarrow D_2^+ + D_1$, where $D_1 = (bpy)_2Os(2C_{17}-bpy)^{2+}$ and $D_2 = Os(bpy)_3^{3+}$, occur in the non-limiting steps. Since $Os(bpy)_3^{3+}$ formed upon irradiation in the inner volume of the vesicle is a rather strong oxidant ($E_m = 0.84$ V, vs NHE), this system is of certain interest for modeling an oxygen evolving center of photosynthesis (see Sect. 5.2).

Note that the transfer of electrons across the membranes leads to the appearance of the opposite electric charges in the inner and outer water phases and, hence, causes an electric polarization of the membrane, that must retard further transfer of electrons. Therefore, in order to maintain high values of Φ during the steady-state photolysis, it is necessary to compensate such polarization, e.g. via providing the transfer of the ions through the membrane simultaneously with electron transfer. Indeed, in Systems 8 and 19 a significant (by a factor of 3 to 10) increase of Φ has been found after efficient carriers of protons were added into the system [49, 50, 67–69]. A similar effect is exerted by valinomycin – a carrier of potassium ions, or gramicidin which creates ion channels in membranes [69]. Moreover, the creation of the negative potential (50–100 mV) inside the vesicle prior to the illumination leads at room temperature to rising Φ of PET to outside the vesicle up to 0.44%, while $\Phi = 0.04\%$ is observed in the absence of the potential [69]. If none of the indicated ionophores is present, the electric charge appearing upon electron transfer is compensated apparently due to either the electric breakdown of the membrane or the diffusion across the membrane of the components of the buffer which is always present in vesicle suspensions. The influence of the electrical polarization of the membrane on the transmembrane electron transfer will be discussed in more detail in Sect. 4.1.3.

2.4 Planar Bilayer Lipid Membranes

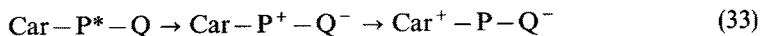
The planar bilayer lipid membranes (BLM), which were first prepared in 1963 by Mueller et al. [117], are bilayer lipid membranes covering an orifice of 1 to 2 mm in diameter in a partition between two macroscopic water volumes. The properties of such membranes were discussed in detail by Tien [118]. Experimental studies of vectorial PET across planar BLM have both advantages and disadvantages compared with vesicles. An important advantage is the possibility of using sensitive electrometric techniques. Placing electrodes in water phases at both sides of the membrane containing a photosensitizer, one can directly observe the appearance of a photovoltage and/or photocurrent resulting from the transmembrane PET. The works in this field are reviewed in Refs. [118–125]. On the other hand, both the low optical density and small surface area of BLM complicate the application of the powerful techniques such as flash photolysis with spectroscopic registration of PET's intermediates. Note, that an observation of photovoltage alone cannot demonstrate unambiguously that PET across the membrane actually occurs. For

example, Hong and Mauzerall [126, 127] have shown that the phototransfer of the electron from a photosensitizer located in the membrane to a water-soluble acceptor, which takes place at only one of the membrane // water interfaces, leads to the appearance of a transmembrane voltage even when no further transfer of the electron across the membrane core takes place. Moreover, as it has been pointed out by Yong and Feldberg [128] for a MgOEP-containing planar BLM even the appearance of photocurrent is not always associated with PET across the membrane, since it may be caused also by phototransfer or H^+ and OH^- ions across the membrane.

The systems, wherein PET across planar BLM separating a donor of electron in water phase I and an acceptor of electron in water phase II was observed, are listed in Table 1 (Part II). Note, that when reporting the observation of the photocurrent, the authors often omit the discussion of the mechanisms of PET across planar BLM. For Chl-containing BLM the regularities and mechanism of PET across the membrane seem to be similar to those discussed above for the Chl-containing vesicles. The only exception is System 36 where the charge transfer across the membrane was suggested as resulting from the diffusion of radical-cation $TMPD^+$ across the membrane rather than from electron exchange via reaction (8) involving Chl^+ radical; $TMPD^+$ is supposed to be generated in System 36 by virtue of the photoreduction of ^3Chl at the membrane // water phase II interface (reaction type (11)).

Some discrepancy is found between the points of view of various authors on the mechanism of PET across the planar BLM containing ZnTPP. For instance, Tien and Yoshi [95] suggest for System 39 the mechanism which is analogous to that discussed for vesicle System I2 (see Fig. 4b). Addition of $Ru(bpy)_3^{2+}$ into water phase I increases the photocurrent, i.e. the effect is similar to that described above for System 14. At the same time Bienvenue et al. [96] suggest another mechanism of PET across the membrane, in System 40, which is based on the transmembrane diffusion of $ZnTPP^+$ radical cation formed in reaction type (13). This latter mechanism is shown to agree with the experimentally observed dependency of the photocurrent on the light intensity, on the external voltage applied to the membrane, as well, on the concentration of the acceptor in water phase II. Substitution of ZnTPP for ZnTPP-Ac containing the carboxy group (System 40 and 41) drastically increases the photocurrent. The photocurrent also increases when water phase II is made more acidic than phase I. This is explained by the fact that the photosensitizer ZnTPP-Ac serves as both electron and proton carrier across the membrane, transferring upon illumination the proton and electron in the opposite directions.

Of particular interest is System 45 described by Seta et al. [101] in which the possibility of PET across lipid membrane by virtue of intramolecular charge separation process has been demonstrated (see Fig. 4e). Photoexcitation of porphyrin in a Car – P – Q covalently-linked triad (see the structure of Car – P – Q in Fig. 21a of the Chapter by Zamaraev and Khairutdinov) leads to a two-step transfer of an electron from the Car fragment to the Q fragment:



The length of the triad ($> 40 \text{ \AA}$) and its molecular conformation in BLM apparently permit the triad to practically span the bilayer, so that its terminal groups Car^+ and Q^- can oxidize Asc and reduce $\text{Fe}(\text{CN})_6^{3-}$ at the interfaces of the membrane and water phases I and II, respectively. The whole set of the above reactions results in electron transfer from phase I to phase II with the regeneration of the initial triad, the turnover of the triad in the PET cycle across BLM being quite high [101].

Note that the studies of vectorial PET across planar BLM were initiated earlier than for vesicles. In spite of this the number of works published so far on PET across BLM is notably smaller than for vesicle systems. The reason for this seems to be some drawbacks that are intrinsic to planar BLMs as a potential component of practically interesting redox photocatalytic systems. It is known that the necessity of providing high reaction rates per unit volume implies the use of heterogeneous catalysts with large enough specific surface area. In this respect, heterogeneous photocatalytic systems are not likely to be an exception. Note, e.g. that chloroplasts of photosynthesizing organisms indeed have membranes with an extremely developed surface. The area of the membrane // water interface for vesicle suspensions is also much higher than that for planar BLM.

3 Stages of Charge Separation and Recombination

As seen from the previous sections, transmembrane PET does not result from one elementary reaction, but includes several elementary steps: photoexcitation and deactivation, redox quenching of the excited photosensitizer with formation of the radical-ion products and recombination of these products, subsequent redox reactions or diffusion of electron (or hole) carriers needed for electron transport across the hydrophobic core of the membrane. Of course the heterogeneity of the membrane-containing systems which appears in the presence of the developed lipid // water interface, local electric fields, and anisotropy of the membrane properties exerts a serious influence on the mentioned processes. To clarify the regularities of this influence is important because of two reasons. First, processes of photoinduced and dark electron transfer across bilayer membranes serve as models of similar processes in the chains of electron transport of natural photosynthesis and phosphorylation. It is expected that clarification of the regularities of electron transport in more simple model systems may help us to understand better the behaviour of more complicated natural systems. Second, if one learns how to control PET across the membranes, this may help to increase the efficiency of light-to-chemical energy conversion in membrane systems, as well as improve the properties of electrogenic membranes for molecular electronics.

3.1 Fate of Electron Excitation Inside Membranes

It is well known that the high quantum efficiency of photosynthesis is provided, first of all, by minimizing a useless dissipation of electron excitation energy in

rigidly structured reaction centers. Moreover, in the course of evolution of the photosynthesizing organisms, Nature has invented the special apparatus for green plants, i.e. "antennae" — the pool of chlorophyll molecules, allowing the harvesting and transfer of the excitation energy almost without losses to the photochemically active site. Such antennae provide a very high efficiency of light harvesting.

Of course, nowadays it is still impossible to utilize in the artificial membrane systems the primary electron excitation with the same efficiency as in natural ones. One of the reasons for this is the lack of sufficient knowledge about the fate of the electron excitation in these systems. The quantitative data about the dissipation of the electron excitation in such systems are quite scarce. In the present section we shall discuss these data.

Synthetic or natural porphyrins are most widely used as photosensitizers of PET across the membranes. It is well known that in homogeneous solutions the electron excited states of porphyrins are efficiently quenched upon the increase of the concentration of the porphyrins [129]. If porphyrins are located in the membranes of the vesicles, these processes are expected to manifest themselves especially strongly due to rather high local concentration of the porphyrins. Note that this concentration may be high enough for the quenching even when only a few molecules of a porphyrin are located in the membrane.

For Chl-containing vesicles it has been shown that an increase of the local concentration of Chl in the membrane indeed leads to a decrease in the lifetimes of the excited singlet and triplet states of Chl molecules via the concentration quenching of these states by Chl molecules in the ground state. This quenching was assumed to be of a dynamic character [130–132]. The concentration quenching was also observed for ZnTPP in membranes of lecithin vesicles [133]. Note that the lifetime of $^3\text{ZnTPP}$ decreases abruptly with the increase of temperature. This jump coincides with the phase transition of the membrane from a gel to a liquid crystal, accompanied by the sharp increase of $^3\text{ZnTPP}$ mobility in the membrane. This fact also points to the dynamic character of the concentration quenching.

The non-exponential decay of the triplet excited states of the photosensitizers is observed for Chl-, Phe- and ZnTPP-containing vesicles [132–135]. The reason for the non-exponentiality may be, first, a statistical distribution of the concentrations of porphyrin molecules in the membrane, and, second, a simultaneous decay of the triplet excited states via several parallel channels such as spontaneous deactivation, concentration quenching and triplet-triplet annihilation which are known to be characteristic of porphyrins in organic solvents [129]. For ZnTPP and Phe in vesicles, the process of triplet-triplet annihilation is indeed observed [56, 134], while according to [132] this process is surprisingly absent for Chl.

The kinetics of concentration quenching in vesicles can be described quantitatively in terms of the stochastic approach. This approach takes into account, first, the small (1–100) number of photosensitizer molecules in one vesicle and, second, the statistical character of their distribution in the vesicles. The small number of the photosensitizer molecules in a vesicle leads to a significant influence of the fluctuations of this number on the quenching kinetics. As shown in Phe-containing vesicles [134], under these conditions the stochastic approach describes the

experimental data on the concentration quenching more correctly than the traditional deterministic one.

Only few data are available concerning the processes of the intermolecular energy transfer in membranes. Efficient intramembrane energy migration is reported by Kunitake [136] for bilayers that contain chromophores as a part of membrane-forming molecules. Even in frozen Chl-containing lecithin vesicles the energy of excitation migrates rather fast between Chl molecules [137].

Since the radius of the vesicle exceeds considerably the thickness of the membrane, it may seem possible to describe the quenching of excited states inside the membrane via energy transfer mechanism in terms of the two-dimensional Förster's kinetic equations [138, 139]. However, for the quenching of rodamine 6G fluorescence by malachite green, Tamai et al. [140] have shown that the energy transfer in vesicles is more adequately described by the superposition of the two- and three-dimensional Förster's kinetics. The quenching radii in this system are large (ca. 60 Å) and comparable with the size of the vesicles. The effective spatial dimensionality of the reaction media in this case may indeed be considered as an intermediate between two and three. It seems possible to apply the fractal approach [141] for the description of the kinetics of quenching. According to Refs. [140, 142], resonance energy quenching processes in membranes become important starting with the mean statistical distance between the interacting particles of 60–65 Å, and their rate increases with the decrease of this distance. However, when this distance decreases by up 10–18 Å, the quenching due to electron transfer may prevail over the quenching due to energy transfer.

3.2 Photoinduced Charge Separation and Recombination at Membrane // Water Interface

The primary processes of photoinduced charge separation in lipid membranes were studied in detail for Chl-containing vesicles by Tollin and co-workers [132, 143, 144]. It has been shown possible to reach 100% quenching of ^3Chl by introducing benzoquinone, BQ, into the membrane. However, due to the geminate recombination the yield of the radical-ion products of PET, Chl^+ and BQ^- , is only 60% of the amount of the quenched ^3Chl . The electric charge of the membrane surface has a significant influence on the quantum yield of BQ^- and Chl^+ and their subsequent recombination. The membrane // water interface can be charged negatively, for example, by the insertion of anionic surfactants into lecithin membranes. The interfacial electric field produced by this charge not only increases the yield of BQ^- and Chl^+ by diminishing the probability of their geminate recombination, but also pushes BQ^- into the bulk water phase, thus inhibiting significantly the secondary recombination of BQ^- with membrane-bound Chl^+ . Cationic surfactants have the opposite influence.

Tollin and his co-workers [145, 146] have observed a number of interesting peculiarities using water-soluble MV^{2+} , AQDS^{2-} and $\text{Fe}(\text{CN})_6^{3-}$ as redox quenchers of ^3Chl . The inner and the outer surface of the vesicles membrane were

found to be asymmetrical (i.e. non-identical) with respect to the local concentration and physical state of Chl, as well as to processes involving ^3Chl . It has been found that the efficiency of quenching, yields of radical-ion products and rate constants of their recombination are different at the inner and outer membrane // water interfaces. For example, at maximum about 50% of ^3Chl molecules are quenched when the quencher MV^{2+} is added into the inner cavity of the vesicle, while only 16% at maximum are quenched when MV^{2+} is added to the water phase outside vesicles.

The kinetics of the recombination of Chl^+ and MV^+ radical ions formed during the quenching of ^3Chl , consists of the fast and slow stages. The corresponding rate constants also occurred different at the inner and outer surfaces of the vesicles. The observed difference in the recombination rates was explained by different structural and dynamic characteristics of the inner and outer monolayers of the membrane.

Note that asymmetry between the inner and outer interfaces was observed also for large unilamellar vesicles [146]. However, the ratios of the rates of ^3Chl quenching and the yields of radical-ion products on the inner and outer membrane surface for large unilamellar vesicles are of the opposite character compared with small unilamellar vesicles.

As follows from the data from Sect. 2, the primary photochemical stage in the majority of the membrane systems studied is the redox quenching of the excited photosensitizer by an electron acceptor or donor leading to electron transfer across the membrane // water interface. For electron transfer to occur from the membrane-embedded photosensitizer to the water soluble acceptor, it is necessary for the former to be located sufficiently close to the membrane surface, though the direct contact of the photosensitizer with the aqueous phase is not obligatory. For example, Tsuchida et al. [147] have shown that electron transfer to MV^{2+} from photoexcited Zn-porphyrin inserted into the lecithin membrane, is observed only until the distance from the porphyrin ring to the membrane surface does not exceed about 12 Å.

Important factors controlling the formation of the radical-ion products of the PET, their escape from the geminate pair, as well as recombination at the membrane // water interface, are the electrostatic and hydrophobic interactions of the reagents with the membrane.

3.2.1 The Influence of Electrostatic Interactions

It is possible to regulate the electric potential of the membrane // water interface introducing ionogenic surfactants into the lecithin membranes or using the vesicles from pure ionogenic surfactants. The potential of the membrane surface may reach 100–150 mV [148], depending on the amount of the surfactant in the membrane and on the presence of the salts in the aqueous solution. It is possible to increase significantly the efficiency of photoinduced charge separation reactions and inhibit recombination reactions on the membrane // water interface by designing appropriate matching between the electric charges of the membrane surface and the partners of PET reactions.

For example, Hurst et al. [149] have shown that the quenching of $^3\text{ZnTPPS}^{4-}$ by dications of alkylviologens in a homogeneous solution produces no radical-ion products due to the intensive ion-pairing of the reagents, which leads to geminate recombination. At the same time the quantum yield of the radical-ion products reaches 50% in the suspension of negatively charged DHP vesicles, which adsorb the radical cations of viologens and repulse ZnTPPS^{3-} . The influence of the electric charge of the membrane surface on the recombination of electron phototransfer products (porphyrin and viologen radicals) was also studied (Refs. [150–152]). When one of the reagents was highly hydrophilic and had a charge with the sign opposite to that of the membrane, it was possible to decrease the rate of recombination by several orders of magnitude.

The systematic study of the influence of the surface charge alteration on the yield and recombination of the PET products was undertaken by Tollin and co-workers [153–157] for Chl-containing lecithin membranes. Electron transfer between excited Chl and electrically charged or neutral electron acceptors was studied. It was shown that the repulsion of the anionic primary electron acceptor, e.g. naphthaquinonesulfonate, NQS^- , from the negatively charged lecithin membrane modified with DHP leads to an increase in the quantum yield of the primary products of electron phototransfer and to the inhibition of their recombination. The use of the primary electron acceptor which is attracted by the membrane, e.g. MV^{2+} (or NQS^- in the vesicles with the positively charged surface), leads to an increase of the efficiency of ^3Chl quenching due to an increase of the local concentration of the primary electron acceptor near the membrane surface. For example, the lifetime of ^3Chl becomes 8 times shorter with an increase of DHP content in the membrane from 0 to 30 mol.% in the system with MV^{2+} as the electron acceptor. However, the efficiency of charge separation, i.e. the quantum yield of the primary products of electron phototransfer, significantly decreases rather than increases upon addition of DHP due to a more efficient geminate recombination. Similar regularities were observed also when using ferricytochrome c rather than MV^{2+} as electron acceptor.

Apparently, the electric charge of the membrane can be neutralized by an increase of the inorganic salts concentration. This neutralization is believed to decrease mutual repulsion of the molecules in the membrane, and thus to increase the density of molecules packing in the membrane and its viscosity. The probability for the products of PET reaction to escape geminate recombination is expected to decrease in this case due to the cage effect.

3.2.2 The Influence of Hydrophobic Interaction

If upon electron transfer one of the products becomes significantly more hydrophobic (or, vice versa, hydrophilic) than in the initial state, this product may leave the water // membrane interface and immerse itself in the depth of the membrane (or, vice versa, desorb into the aqueous phase). It has been demonstrated that such spatial separation of the products may lead to a significant inhibition of their recombination [158–160].

Ford and Tollin [161, 162] have studied the influence of hydrophobic nature of the electron acceptor (symmetrical dialkylviologens, C_nV^{2+} , have been used) on the yield of electron phototransfer and on the rate of recombination of the products formed. It has been shown that the rate constant of ^3Chl quenching in the lipid membranes increases with the increase of the length of alkyl substituent in viologens due to an increase of the local concentration of the quencher in the membrane (because of the strengthening of C_nV^{2+} binding to the membrane with the increase of its hydrophobicity). However, simultaneously an increase is observed of the probability of the geminate pair recombination accompanied by a notable decrease of the lifetime of PET products. This lifetime is controlled by the rate of the C_nV^+ radical cation escape from the membrane to the aqueous phase. It should be noted that in this system it is difficult to achieve simultaneously the high efficiency of ^3Chl quenching by C_nV^{2+} and the inhibition of the recombination of the radical-ion products. For this to be achieved, C_nV^{2+} should be bound to the membrane as strongly as possible, whereas radical cation C_nV^+ — as weakly as possible. Though in reality C_nV^{2+} , being a more hydrophilic molecule, is expected to be bound to the membrane more weakly than C_nV^+ . Indeed, according to Tabushi and Kugimiya [161 a], the equilibrium constants of radical cations C_nV^+ binding with the lipid membrane are 3 orders of magnitude greater than those for dications C_nV^{2+} . These constants are also found to increase with the increase of the number of methylene groups n in the alkyl fragments of viologens.

The influence of hydrophobic interactions on the recombination of the primary products of electron phototransfer can be well illustrated if we consider Systems 21 and 22 of Table 1. For these systems (see Fig. 4d) the recombination of $\text{Ru}(\text{bpy})_3^{3+}$ with the viologen radical cation on the inner membrane surface was studied using flash photolysis technique. It can be seen from Table 2 that the values of k_t for the series of membrane-embedded viologens, which were found from the observed first-order recombination constants k_r using Eq. (29), are significantly smaller than recombination rate constants k_h for the same species in homogeneous solution. Such a stabilization of electron transfer products at the membrane // water interface may be explained by the fact that the radical cations of the membrane-embedded viologens are more hydrophobic than the initial dications, while $\text{Ru}(\text{bpy})_3^{3+}$ complex is more hydrophilic than the initial $\text{Ru}(\text{bpy})_3^{2+}$. Therefore, just after the formation of viologen radical and of $\text{Ru}(\text{bpy})_3^{3+}$, these particles find themselves in non-equilibrium surrounding. This leads to the fast escape of $\text{Ru}(\text{bpy})_3^{3+}$ to the inner aqueous phase, and, vice versa, to the immersing of the viologen radical cation deeper into the lipid bilayer. This hinders direct encounter between the products of electron phototransfer and decelerates their recombination. Note, that this mechanism of the primary stabilization of the separated charges via the increase of the distance between them looks somewhat similar to the mechanism in natural photosynthesis. The difference, however, lies in the fact that in the reaction center of photosynthesis the increase of the distance is caused by the electron transfer from primary acceptor to the secondary one, while in our case the reagents themselves change their location to be more distant from each other. The proposed interpretation of the deceleration of the recombination process at the interface between the membrane and the inner aqueous solution is also supported by the

Table 2. Rate constants of transmembrane electron transfer (k_t) by viologen radical cations, their recombination with $\text{Ru}(\text{bpy})_3^{3+}$ in homogeneous solution (k_h) and inside the vesicle cavity (k_r and k_b) and efficiencies of spatial charge separation (η) for viologens with various substituents [201]

substituent ^a R	k_t 10 s^{-1}	k_r 10^2 s^{-1}	k_b ^b (10^6 l/mol s)	k_h ^c (10^8 l/mol s)	$10^2 \eta$ ^c
heptyl	11	46	22	15	2.3
hexadecyl ^d	9	70	33	—	1.3
benzyl	9	91	43	56	0.98
phenacyl	16	47	22	20	3.3
2,4-dinitrophenyl	12	28	13	38	4.1
phenyl	4	89	42	98 ^e	0.45
4-biphenyl	4.5	39	19	28 ^e	1.1
4-methoxycarbonylphenyl	1	90	43	50	0.11
4-cyanophenyl	4	86	41	3.8 ^e	0.46
4-chlorophenyl	0.5	72	34	76 ^e	0.07

a) see viologen structure in Fig. 1;

b) k_b was calculated from experimentally observed k_r using equation (29);

c) $\eta = k_r/(k_t + k_r)$;

d) data for vesicles from eggL, other data — for vesicles from DPL;

e) data for acetonitrile:ethanol = 2:1 solution, other data for aqueous solution

fact that for hydrophilic viologen radical cations, which are not embedded into the membrane, the recombination rate constant has nearly the same large value as for the homogeneous aqueous solution. E.g. for the recombination in the inner volume of the vesicle of $\text{Ru}(\text{bpy})_3^{3+}$ and the water-soluble methyltrimethylammoniumpropylviologen radical cation the bimolecular rate constant $k_b = 2.4 \times 10^9 \text{ l/mol s}$ found using Eq. (29) is close to the recombination rate constant for the same particles in homogeneous solution $k_h = 1.5 \times 10^9 \text{ l/mol s}$ [163]. Close values of the rate constants in homogeneous solution and in the inner aqueous phase of the vesicles are also obtained for the recombination of $\text{Ru}(\text{bpy})_3^{3+}$ with other hydrophilic reduced electron acceptors: methylviologen radical cation and $\text{Rh}(\text{bpy})_3^{2+}$ complex [163, 164].

The detailed study of the recombination between the membrane-embedded octadecylviologen radical cation, C_{18}V^+ , and $\text{Ru}(\text{bpy})_3^{3+}$ complex has shown [115] that the kinetics of this process at the inner surface of the vesicle is non-exponential. The process slows down sharply after approx. 60% of the C_{18}V^+ and $\text{Ru}(\text{bpy})_3^{3+}$ have recombined. This fact was explained [115] by the slow immersion of C_{18}V^+ into the membrane. The recombination was assumed to proceed via electron tunneling, the rate of which is known to decrease exponentially with the increase of the distance between the reagents. To our mind, an alternative explanation can be given in terms of the fast, in comparison with the recombination, escape of $\text{Ru}(\text{bpy})_3^{3+}$ into the inner aqueous volume of the vesicle and the immersing of the viologen radical cation into the bilayer. In this case the observed kinetics should be controlled by the diffusion of the viologen radical cation back from the depth of the membrane to its inner surface, where this radical cation becomes accessible

for $\text{Ru}(\text{bpy})_3^{3+}$. As shown by Nadtochenko et al. [165, 166] for the recombination of Phe^- with Asc^+ , such a model allows one not only to describe quantitatively the non-exponential character of the recombination kinetics, but also to take into account correctly the influence of the electrical polarization of the membrane on the recombination kinetics.

The 1–2 order of magnitude decrease of the rate constant for the recombination of PET products, in comparison with the homogeneous solution, was also observed by Matsuo and co-workers [167, 168]. In their studies one of these products was hydrophilic and thus located in the aqueous phase, while the other was hydrophobic and thus immersed in the membrane. Such a decrease of the rate is, apparently, a common feature of the reactions providing electron transfer across the membrane // water interface between the reagents with substantially different hydrophobicity.

4 Mechanisms of Electron Transfer Across Membranes

As it has been already indicated in Sect. 2, electron transport through the hydrocarbon core of the bilayer (see reactions (8), (14), (26)) is a key step of any transmembrane PET, and usually it controls the rate and efficiency of the PET process as a whole. Therefore, the data concerning the mechanism of this stage of PET and the factors which affect it are of crucial importance for the development of photochemical systems based on PET across the membranes. Unfortunately, for the majority of the systems listed in Table 1 the proposed mechanisms of electron transfer across the membrane seem to be rather tentative because of insufficient information about the localization of the redox-active components and their diffusion mobility inside the membranes. Only for few systems the studies were detailed enough to propose convincing mechanisms and to give a quantitative description of the kinetics of electron transfer across the membrane.

As already mentioned in Sect. 2, there are two alternative pathways of transmembrane electron transfer: (i) direct transfer via electron exchange reactions between the molecules located in the inner and outer monolayers of the membrane, such as reactions (8) and (14), and (ii) carrier-mediated transfer, provided by the diffusion of an electron carrier or a hole carrier from one side of the membrane to the other, such as reaction (26).

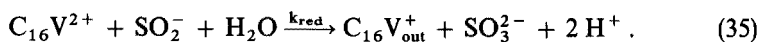
In this Section we shall discuss experimental data concerning both these pathways. We shall start our discussion with the carrier-mediated mechanisms since it has been studied in more detail.

4.1 Transfer via Translocation of Electron Carriers

4.1.1 Experimental Data

For many systems of Table 1 excited molecules are not themselves involved in the stage of the electron transfer across the membrane. They are rather used in the previous stage for the generation of the intermediate radicals which serve as electron carriers.

As an example let us consider System 21 of Table 1, where electron transfer across the membrane is provided by dihexadecylviologen radical cation $C_{16}V^+$, generated via reaction (23). To clarify the mechanism of transmembrane electron transfer in this system the stopped-flow technique was used [169]. The suspension of the vesicles, containing $C_{16}V^{2+}$ in the membrane and $K_3Fe(CN)_6$ in the inner cavity, was mixed with the borate buffer solution of the strong reducing agent, sodium dithionite (see Fig. 5a). This leads to the fast reduction of about 70% of $C_{16}V^{2+}$ present in the sample. After that the reoxidation of $C_{16}V^+$ via the reaction with $Fe(CN)_6^{3-}$ was observed (Fig. 5b, curve 1). First-order rate constants of these two reactions are $k_1 = 16 \text{ s}^{-1}$ and $k_2 = 0.4 \text{ s}^{-1}$, respectively, and are independent of both the molar fraction of viologen in the membrane and the nature and concentration of the oxidizing agent placed inside the vesicle. Assuming that the distribution of dihexadecylviologen between the outer and the inner membrane monolayers is uniform, it is possible to ascribe the first stage of the process to the reduction of $C_{16}V_{out}^{2+}$ located in the outer monolayer. Note, that the volume of this monolayer amounts to approx. 70% of the total membrane volume [170]. The reduction of $C_{16}V_{out}^{2+}$ proceeds via the following scheme:



Note that equilibrium (34) is shifted to the left. Because of this, with excess dithionite, the measured value of k_1 is proportional to the square root of dithionite concentration [171, 172]:

$$k_1 = k_{red} K_{eq}^{1/2} [S_2O_4]^{1/2}.$$

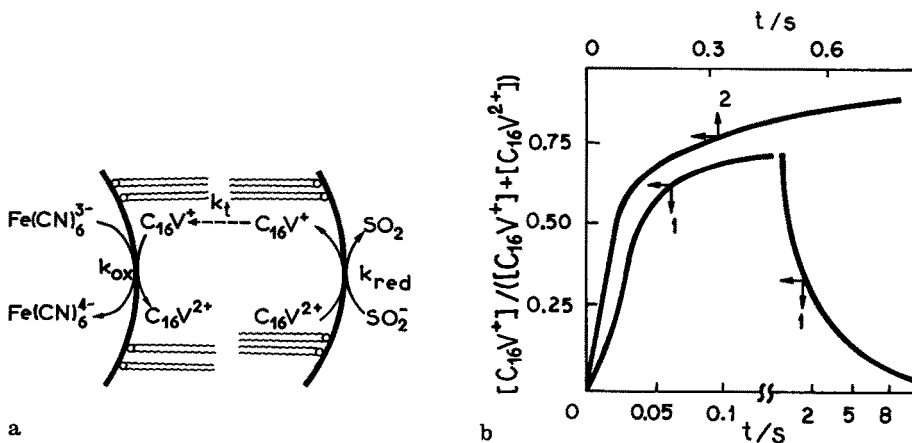
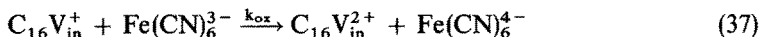


Fig. 5. Viologen-mediated electron transport across the vesicle membrane: (a) — scheme of the process; (b) — variations of viologen radical cation concentration in the presence (1) and the absence (2) of $0.75 \text{ mol/l } K_3Fe(CN)_6$ in the inner cavity. Sodium dithionite concentration is 0.01 mol/l . The molar ratio viologen:lipid = 1:20

The reoxidation of $C_{16}V_{out}^+$ is controlled by its migration to the inner membrane surface:



with the subsequent oxidation by ferricyanide:



proceeding in a non-limiting step (that is why k_2 is independent of the $K_3Fe(CN)_6$ concentration). Thus reaction (36) is the rate-determining step of the overall reaction sequence (36)–(37), and the rate constant of electron transfer across the membrane $k_t = k_2 = 0.4 \text{ s}^{-1}$.

Note that $C_{16}V^+$ radical cations are absent in the final stationary state of the system, despite the presence of a significant excess of dithionite in the outer solution. This can be explained only assuming that all $C_{16}V^{2+}$ particles become inaccessible for the reduction by dithionite, because of the migration of all viologen particles to the inner membrane surface. Apparently, in this case, the ions $C_{16}V_{in}^{2+}$ cannot migrate across the membrane back to its outer surface within the experiment time scale ($\tau \gg 10 \text{ s}$). In other words, for the process



the rate constant $k_{-1} \ll 0.1 \text{ s}^{-1}$. The destruction of the vesicles by a detergent again makes all $C_{16}V^{2+}$ molecules accessible for the dithionite and leads to the reduction of both all $C_{16}V^{2+}$ and $Fe(CN)_6^{3-}$.

It is obvious that the electric field should arise in the membrane during the migration of $C_{16}V^+$ radical cations. This field will inhibit their further diffusion across the membrane. However, if besides $C_{16}V^+$ some other ions are added to the sample and they can penetrate across the membrane and compensate its charge, then, starting with a certain instance, when the rates of $C_{16}V^+$ transfer through the membrane and charge compensation process become equal, the rate of $C_{16}V^+$ transfer will stop decreasing and reach a constant value. It will be shown in Sect. 4.1.3 that under the conditions of the described stopped-flow experiments (when the initial number of $C_{16}V^+$ radicals formed via reaction (35) is more than 100 per one vesicle), the rate constant of reaction (36) $k_t = 0.4 \text{ s}^{-1}$ depends on the rate of ion transfer compensating the membrane charge. These ions, perhaps, can be buffer components and also H^+ and OH^- [173–178].

The direct evidence for the fact that transmembrane electron transfer is provided by the migration of the reduced carrier across the membrane from one aqueous phase to another was obtained also for such water-soluble carriers as methylviologen and methylene blue [77, 179]. The corresponding rate constants are 5.3×10^{-2} and $9 \times 10^{-3} \text{ s}^{-1}$.

Tabushi et al. [161] studied the dependence of the stationary rate of dark electron transfer across a lipid membrane by dialkylviologen radical cations C_nV^+ on the number n of carbon atoms in the alkyl substituents ($n = 1, 3, 4, 8$ and 16) in the

system similar to that shown in Fig. 5a. It turned out that the rate has a maximum at $n = 4$, and for the water-soluble viologens ($n = 1, 3$ and 4) the stationary rate is controlled by the transfer of radical cations from the outer aqueous phase into the membrane. For $n = 8$ and 16 the rate-controlling stage is the oxidation of C_nV^+ by $Fe(CN)_6^{3+}$ on the inner membrane // water interface. Unfortunately, from the data of Ref. [161] one cannot find the values of k_t for reaction (36).

Hurst and co-workers [172, 180–185] extensively studied the mechanisms of dark electron transfer by alkylmethylviologen radical cations across the membranes of DHP vesicles. The experiments carried out and the results obtained are quite similar to those described above. In particular, it has been demonstrated that during transmembrane electron transfer in steady-state conditions viologen radical cations migrate from one side of the membrane to the other with the rate constant $k_t = 2 \times 10^{-2} \text{ s}^{-1}$.

4.1.2 Models of Transmembrane Transport

Various models describing the motion of molecules across membranes have been proposed in the literature (see reviews [186, 187]). In 1949 Zwolinsky, Eyring and Reese [188] proposed that we should consider the membrane as being a structureless medium and to characterize the migration of molecules across membrane by the isotropic diffusion coefficient, D . The same assumption was used by Hardt [189] to derive the expressions for the characteristic time, τ , of the particle diffusion from one side of the spherical membrane to the other:

$$\tau = (d^2/2D) (2R_2 + R_1)/3R_1$$

for the movement inside and:

$$\tau = (d^2/2D) (2R_1 + R_2)/3R_2$$

for the movement outside. Here R_1 and R_2 are the radii of the inner and outer surfaces of the membrane and d is its thickness.

Note, however that the concepts about the lipid membrane as the isotropic, structureless medium are oversimplified. It is well known [19, 190] that the rates and character of the molecular motion in the lateral direction and across the membrane are quite different. This is true for both the molecules inserted in the lipid bilayer and the lipid molecules themselves. Thus, for example, while it still seems possible to characterize the lateral movement of the egg lecithin molecule by the diffusion coefficient D_l , its movement across the membrane seems to be better described by the so-called flip-flop mechanism when two lipid molecules from the inner and outer membrane monolayers of the vesicle synchronously change locations with each other [19]. The value of $D_l = 1.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [191] corresponds to the time of the lateral diffusion jump of lecithin molecule, i.e. about 10^{-7} s . The characteristic time of flip-flop under the same conditions is much longer (about 6.5 hours) [19]. The molecules without long hydrocarbon chains migrate much more rapidly. For example for pyrene $D_l = 1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [192].

The lipid membrane is not only anisotropic, but also inhomogeneous in the transmembrane direction. It contains relatively hydrophilic polar layers adjacent to the membrane // water interfaces, which include the polar “heads” of lipid molecules, and highly hydrophobic non-polar central core, containing the hydrocarbon chains.

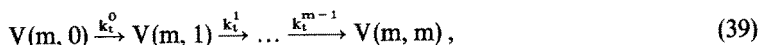
Träuble [193] made an interesting attempt to take into account the influence of the membrane molecular structure on the transmembrane transfer of small molecules. The transmembrane motion of these molecules was considered under the assumption that the thermal motion of the hydrocarbon chains of the membrane lipid leads to the appearance of the mobile structural defects (so called “kinks”) in the membrane. The “kinks” are small free volumes in the hydrocarbon phase of the membrane diffusing in the membrane. The molecules from the aqueous phase may be captured by these “kinks” and, moving together with them, transferred to the other side of the membrane. Such a model was shown to describe satisfactorily the translocation of small neutral molecules such as water.

For the transmembrane transfer of ions containing hydrophobic substituents the model was proposed that takes into account the variations of dielectric properties across the membrane. According to this model [194–200] the lipophilic ions are adsorbed at the minima of the potential energy near to the membrane // water interface (see Fig. 6b). The transfer of the ions across the membrane is considered to be monomolecular reaction of the ion’s surmounting of the hydrophobic barrier in the center of the membrane with the first order rate constant k_p .

Such a mechanism appears to be adequate enough for the description of the carrier-mediated electron transfer across membranes. It allows, for example, one to describe quantitatively the influence of electrical polarization on the transmembrane electron transfer.

4.1.3 The Influence of Electrical Polarization

The influence of electrical polarization of the membrane on electron transfer provided by dihexadecylviologen radical cation was studied in Refs. [77, 201]. These studies were made in order to verify the assumption that the electric field, arising in the membrane during reaction (36), decelerates further electron transfer. $C_{16}V_{out}^+$ radical cations were generated only in the outer monolayer of the membrane by means of flash photolysis of the vesicle suspension containing $Fe(CN)_6^{3-}$ in the inner cavities. If, at the initial moment of time, on average less than one $C_{16}V_{out}^+$ particle is present per vesicle, then the kinetics of electron transfer from $C_{16}V_{out}^+$ to $Fe(CN)_6^{3-}$ (reactions (36), (37)) is well described by the first order law. If the initial concentration of radicals is higher than one molecule per vesicle, than with long reaction times the process is slowed down and its kinetics deviates from the first order law (Fig. 6c). One can describe this kinetic behavior using the stochastic approach and assuming, that the electron transfer into the inner cavity of the vesicle with the initial number of generated $C_{16}V^+$ radical cations m takes place through the sequence of steps:



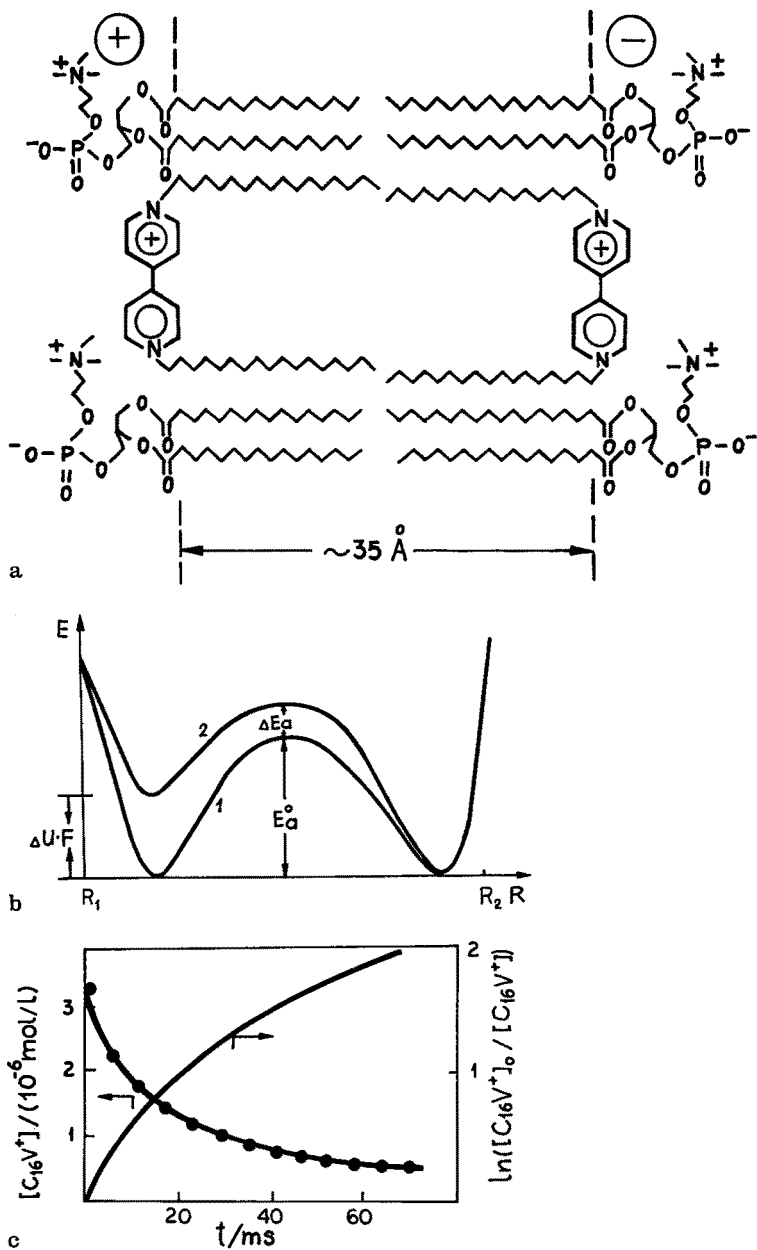


Fig. 6. The influence of membrane polarization on the viologen-mediated electron transport across the membrane: (a) — location of viologen radical cation in DPL membrane; (b) — suggested potential energy profiles and activation energies for $C_{16}V^{+}$ transport across the membrane in the absence (curve 1) and in the presence of the transmembrane voltage ΔU (curve 2). R_1 and R_2 are the inner and outer radii of the membrane; F is Faraday constant; E_a is the activation energy in the absence of the voltage; ΔE_a is the increase of the activation energy induced by the voltage; (c) — kinetics of $C_{16}V^{+}$ radical cation decay in suspension of vesicles containing 0.75 mol/l $K_3Fe(CN)_6$ in their inner cavities. The average initial content of $C_{16}V^{+}$ in the outer membrane monolayer is 1.2 molecule per vesicle. Solid line — experiment, points — calculation (see text)

where $V(m, i)$ denotes the vesicle which contains initially m $C_{16}V^+$ particles and in which the transfer of i electrons has been carried out. It is possible to calculate the rate constants k_i^j assuming that the transmembrane transfer of each $C_{16}V_{out}^+$ radical cation increases the activation energy of the next $C_{16}V_{out}^+$ transfer by the value $\Delta E_a = F \Delta U/2$, where F is the Faraday constant, ΔU is the potential difference between the membrane surfaces caused by the transfer of one elementary positive charge (see Fig. 6b):

$$k_i^j = k_i^0 \exp(-i \Delta E_a/RT), \quad (40)$$

where k_i^0 is the rate constant of the movement of the first $C_{16}V_{out}^+$ particle across the membrane. Note, that the value of k_i^0 found from the initial part of the curve in Fig. 6c coincides with the value of k_i found earlier for the transfer of the first electron across the same membrane but in the opposite direction (see Table 2).

The high rate of the lateral diffusion of the ions along the membrane surfaces allows one to assume that the membrane charge has a uniform distribution along its surface and to estimate ΔU using the well known expression for the spherical capacitor. In the calculations made [77] the dielectric constant of the membrane core was assumed to be 2.1, and the inner and the outer radii to be equal to 85 and 125 Å, respectively [19, 202]. The kinetics of $C_{16}V^+$ decay was calculated according to the following scheme: the average initial number of $C_{16}V_{out}^+$ radical cations per vesicle was obtained experimentally, and the initial concentration of the vesicles with various number of $C_{16}V_{out}^+$ particles was found according to the Poisson distribution. After that, the current concentration of $C_{16}V^+$ in vesicles with various m was calculated for each m from the kinetic equation for the sequence of reaction (39). Further, the total current concentration of $C_{16}V_{out}^+$ was found by summing up the concentrations of $C_{16}V^+$ for vesicles with various m . As seen from Fig. 6c, the calculations are in good agreement with the experiment which confirms the validity of the proposed model.

Note that after eight $C_{16}V^+$ particles are transferred across the membrane, the deviations of the reaction kinetics from the first-order law again disappear. This apparently corresponds to the above mentioned case when the rate of $C_{16}V^+$ transfer becomes controlled by the rate of charge neutralization (see Sect. 4.1.1). The rate constant of the transfer here amounts 0.64 s^{-1} , and is close to that (0.4 s^{-1}) measured for reaction (36) by the stopped-flow method.

Bienvenue et al. [96] used the expression similar to Eq. (40) to describe quantitatively the dependence of the photocurrent through the planar BLM upon the applied photovoltage ΔU in the System 40 of Table 1. Photocurrent was caused by the transfer through membrane of $ZnTPP^+$ radical cations. Note that in this case the potential difference affecting the motion of $ZnTPP^+$ cation is equal to only 60% of the external voltage apparently due to the location of $ZnTPP^+$ sufficiently deep below the surface of the membrane.

The influence of the electric polarization of the membrane, either specially created or aroused during the transmembrane PET, on the overall rate of PET process was also observed for Systems 8, 15, 19, 31 of Table 1. However, the experimental data available for these systems do not allow one to connect directly

this influence with the stage of electron transfer across the membrane and to give a quantitative description of it.

The above results indicate that in order to maintain the high rate of transmembrane electron transfer, it is necessary to provide efficient neutralization of the arising polarization. For this purpose lipophilic ions and proton carriers were successfully used (see Table 1). These compounds are known to act as the uncouplers of the mitochondrial oxidative phosphorylation and are able to remove the gradients of electric fields across lipid membranes.

4.1.4 The Influence of Temperature

The rate and character of the molecular motions of both the molecules embedded in the lipid bilayer and lipid molecules themselves are strongly dependent on the temperature [19, 203]. At a certain temperature t_m , the gel-liquid crystal phase transition is known to occur for the membrane made of a synthetic lipid. For example, $t_m = 41.5^\circ\text{C}$ for the membranes from DPL. In the vesicles formed by a mixture of lipids, e.g. egg lecithin, the phase transition occurs smoothly rather than jumpwise and starts below 0°C . Note that the permeability of lipid membranes increases notably upon transition from the liquid crystal state to the gel state [204].

The study of k_i dependence on the temperature shows that the phase state of the lipid bilayer has a strong influence on the rate of transmembrane electron transfer by viologen radical cations. The dependencies of k_i on $1/T$ for the vesicles of dipalmitoyl-, distearoyl- and dimiristoyllecithins have characteristic salient points corresponding to the decrease of the effective activation energy from 105–125 to 25–40 kJ/mol with the increase of the temperature [75]. The temperature, where the salient points are observed, correspond to the phase transition temperatures for the bilayers constructed of these lipids. The phase transition of the membrane is accompanied by a jumpwise increase of the mobility of viologen molecules embedded in the bilayer and, as the consequence, by the sharp increase of k_i . No jumpwise change in k_i upon increasing the temperature was observed for the vesicles made of dioleylecithin and egg lecithin which are known to be in the liquid crystal state over all the available temperature range.

4.1.5 Attainable Rates of Transmembrane Transport

To get an idea about the scale of the attainable rates of carrier-mediated electron transfer across membranes, we have compiled in Table 3 the data about the rate constants and characteristic times for various translocation processes. It can be seen that for the similar carriers, the translocation time τ increases strongly with the increase of the charge of the carrier (compare, e.g. the data of Table 3 for proton carriers). This is quite natural, taking into account that the particle should pass through the core region of the bilayer with the polarity equal to that of a non-polar organic solvent. For the ions with their charges equal to 2 and more the membranes are practically impenetrable. Naturally τ also depends on the membrane thickness. The increase of the length of the aliphatic residue in the lecithin molecule from C_{16} to C_{24} leads to the increase of τ by more than one

Table 3. Rate constants k_t and characteristic times $\tau = k_t^{-1}$ of translocation of various compounds across lipid membranes

compound	charge	k_t/s^{-1}	$\tau/10^{-3} s$	lipid ^a	Refs.
<i>Electron carriers</i>					
dihexadecylviologen ($C_{16}V^+$)	+1	90	10	eggL	201
dioctadecylviologen ($C_{18}V^+$)	+1	20	50	DPL	75
ubiquinone-10	0	> 23	< 40	DML	205
dichlorobenzoquinone	0	8	130	DPL	206
hemin dimethyl ester	0	4	250	eggL	207
<i>Proton carriers^b</i>					
CCCP	-1	1.7	600	eggL/Chol	208
CCCP	-1	175	6	DFL	209
CCCP	0	440	2.3	eggL/Chol	208
CCCP	0	$12 \cdot 10^3$	0.08	DFL	209
FCCP	-1	400	2.5	DFL	210
FCCP-H	0	$7.6 \cdot 10^3$	0.13	DFL	210
DTFB-H	0	$20 \cdot 10^3$	0.05	PE	211
<i>Lipid-soluble ions</i>					
dipicrylamine	-1	670	1.5	DFL	203
dipicrylamine	-1	430	2.3	DOL	203
tetraphenylborate	-1	6.5	150	DOL	212

a) Abbreviations of the compounds notions are explained in Section 8;

b) CCCP stands for carbocyanide-*m*-chlorophenylhydrazone;

FCCP stands for carbocyanide-*p*-trifluoromethylhydrazone;

DTFB stands for 5,6-dichloro-2-trifluoromethylbenzimidazole

order of magnitude [203]. However, the most essential fact that one can see from Table 3, is the strong specificity of the translocation process, i.e. strong dependence of τ on the combination of the nature of the penetrating compound and the membrane material.

It can be seen from Table 3 that radical cations of viologens move across the membrane rather slowly, their rate being significantly smaller than that of some proton carriers and lipophilic ions. For the fastest processes the time for crossing the membrane is only a fraction of a millisecond. If the viologens had the same rates, the efficiency of the spatial separation of the charges during the transmembrane PET, as defined by Eq. (32), would be near 100%. The existence of the compounds with such high rates of transmembrane motion allows one to expect that in the future it will be possible to find reversible transmembrane electron carriers which have simultaneously the necessary redox potentials and high enough transmembrane mobility.

4.2 Transfer via Electron Exchange Reactions

While describing in Section 2 the systems providing PET, it was noted that for some of them the transmembrane electron transfer could be explained in terms of electron exchange reactions of the (8), (12) or (14) types. In this connection,

two questions arise — first, why the data cannot be explained by the transmembrane diffusion of the oxidized or reduced photosensitizer, so that no assumption is needed on electron exchange between the photosensitizer molecules that are located in the different membrane monolayers? Second, what is the nature of the electron exchange reaction, i.e. does the electron exchange take place in a direct collision of reactants or at large distances via electron tunneling? In order to answer these questions we shall discuss in this section in more detail the systems, where the transmembrane electron transfer via electron exchange reactions was assumed.

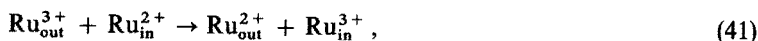
4.2.1 Chlorophyll-containing Membranes

The main arguments in favor of the transmembrane electron transfer in Chl-containing vesicles via reaction (8) (see also Fig. 4a) are provided by the data concerning the rate of this reaction and Chl-localization in the membranes. It was suggested that Chl molecules are located just below the membrane surface [213]. The spectroscopic and fluorescence data point to the polar environment of Chl tetrapyrrol macroring rather than to its direct contact with the aqueous phase [214, 215]. Most likely this polar environment is formed by the domains of the ester groups of lecithin molecules. Such a location of Chl molecules is confirmed by the experiments on Chl fluorescence quenching and on ^3Chl oxidation by spin labels embedded at various depths in the membrane [216, 217]. It has been shown that the most efficient in photooxidation are the labels closest to the surface. On the other hand Chl occlusion by the lecithin membrane does not inhibit its reactions with ions located in the aqueous phase. For example, oxidation of membrane-bound Chl by persulfate located in the aqueous phase has been observed [218–220].

The measurement of the characteristic time of the transmembrane electron transfer performed by Ford and Tollin [43] for System 3 of Table 1 has given the value of $\tau < 10^{-4}$ s; τ decreases with the increase of the Chl local concentration in the membrane as it should be for the bimolecular reaction (8). According to the data of Birrell et al. [221] the characteristic time of the transmembrane diffusion of a spin labeled Chl molecule comes to about 4 min at 0 °C, i.e. exceeds the characteristic time of electron transfer by about 6 orders of magnitude. One can hardly imagine the charged radical anion Chl^- or radical cation Chl^+ moving through the membrane faster than the neutral Chl. Therefore the transmembrane migration of Chl^- or Chl^+ cannot explain the observed rates of electron transfer, and the conclusion by Ford and Tollin about transmembrane electron transfer via reaction (8) looks rather plausible.

4.2.2 $\text{Ru}^{2+}/\text{Ru}^{3+}$ -containing Membranes

In System 19 of Table 1 the transmembrane transport of electrons was ascribed to the electron exchange reaction:



where Ru^{2+} and Ru^{3+} stand for amphiphilic complexes $(\text{bpy})_2\text{Ru}(2\text{C}_{16}\text{bpy})^{2+/3+}$ embedded in the membrane (see Ford et al. [67, 68]). Ford and Calvin [106] have shown that the position of the UV-VIS absorption bands of the ruthenium complex corresponds to a high polarity of its environment, which suggests its location close to the membrane // water interface. The characteristic time of electron transfer across the membrane, as estimated from steady-state kinetics of the transmembrane PET in System 19, is found to be within the range of $\tau \simeq 10^{-4} - 10^{-6}$ s. Such a short value of τ suggests that electron transfer is more likely to proceed via reaction (41), than via transmembrane migration of the triple-charged $\text{Ru}_{\text{out}}^{3+}$ complex. Indeed one can hardly imagine this complex diffusing across the membrane core in such a short time (see Sect. 4.1.5). The activation energy for the transmembrane electron transfer in the discussed system was found to be 67 ± 20 kJ/mol [222].

The electron exchange reaction of the (41) type was also suggested by Lee and Hurst [223] to provide the dark electron transfer across the lecithin membranes that contained the amphiphilic 4-alkylpyridinepentaamineruthenium(III) complex. The basis for this conclusion was provided by kinetic data on the two-step character of Ru^{3+} reduction to Ru^{2+} by a reducing agent added to the vesicle suspension. The kinetics of Ru^{3+} reduction is qualitatively similar to the one shown in Fig. 5b. The first faster step is attributed to the reduction of Ru^{3+} species located in the outer membrane monolayer. The second slow step with the characteristic time $\tau \simeq 10^3$ s, which is independent of the reductant concentration, is attributed to the reduction of Ru^{3+} species located in the inner membrane monolayer. The spectral data again suggest the location of ruthenium complex in the domain of the polar head groups of lipid, i.e. close to the membrane surface. The independent measurements have shown the rate of transmembrane diffusion of the ruthenium complex to be negligibly small, compared to the rate of $\text{Ru}_{\text{in}}^{3+}$ reduction. In this situation the only imaginable way of $\text{Ru}_{\text{in}}^{3+}$ reduction seems to be reaction of the (41) type.

4.2.3 Porphyrin-containing Membranes

In System 12 of Table 1 the transmembrane electron transfer is ascribed to electron exchange via reaction (14) between the non-charged molecule ZnTPP_{in} located in the inner monolayer and radical cation $\text{ZnTPP}_{\text{out}}^+$ located in the outer monolayer. To determine the location of excited ZnTPP molecules in the membrane, the photoreduction of amphiphilic spin-labeled molecules of stearic acid embedded into the membrane by ZnTPP was studied [57]. It turned out (see Fig. 7) that the rate of photoreduction of the N–O fragments located close to the bilayer surface (at the fifth carbon atom counting from the carboxy group) exceeds significantly that for the N–O fragments embedded more deeply in the membrane (with the paramagnetic substituent at the 16th carbon atom). These results suggest that ZnTPP is located mainly near the bilayer surface. The ZnTPP location in the domain of the polar groups of lecithin molecules is also demonstrated by the bathochromic shift of the porphyrin absorption bands with respect to its spectrum in the nonpolar toluene solution [59]. Note that such a location close to the membrane surface is considered to be typical for porphyrins embedded in

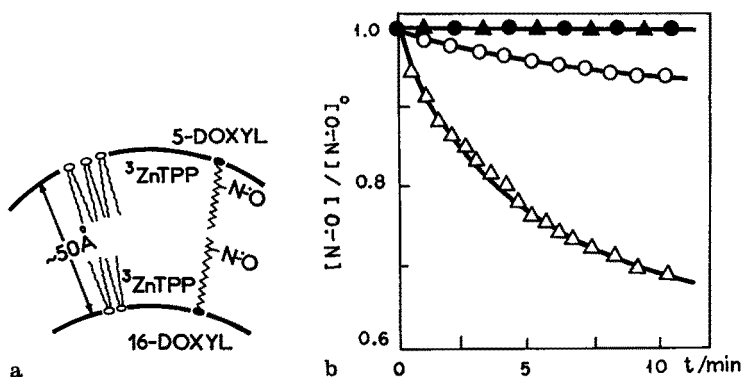


Fig. 7. (a) — Location of ZnTPP and spin labelled stearic acid in vesicle membrane; (b) — kinetics of ZnTPP-sensitized reduction of spin-labels: *black circles and triangles* — without light; *white circles and triangles* — upon illumination into absorption band of ZnTPP. Spin-labels: *triangles* — 5-doxylstearic acid, *circles* — 16-doxylstearic acid; the numbers 5 and 16 indicate the number of the carbon atom at which the N–O fragment is located, starting with the carboxy group

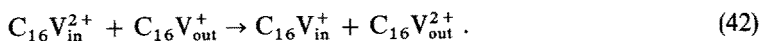
membranes [224]. The fact, that the rate of transmembrane PET in System 12 of Table 1 is proportional to the square of the light intensity, suggests the participation of two excited ZnTPP molecules in the electron transfer step across the membrane (see Sect. 2.1.3). This provides evidence of inability of the $\text{ZnTPP}_{\text{out}}^+$ intermediate to provide efficient electron transfer via its diffusion from one membrane surface to the other. Note, that if the rate of $\text{ZnTPP}_{\text{out}}^+$ transmembrane migration were high enough, the participation of the second excited porphyrin particle in PET would not be necessary, as it is actually observed for the photoreduction of MV^{2+} with EDTA located at the same side of the membrane in the presence of ZnTPP photosensitizer embedded in the membrane [57]. In the absence of $\text{ZnTPP}_{\text{out}}^+$ diffusion across the lipid membrane, the most likely channel of electron transport across the membrane is electron exchange reaction (14), occurring within the lifetime of $^3\text{ZnTPP}_{\text{in}}$ molecules, i.e. 0.1–1 ms. The same reaction is also suggested by Tien and Joshi [225] for PET across ZnTPP-containing planar BLM.

Feldberg et al. [226] also came to the conclusion about the existence of the transmembrane electron transfer via exchange reactions of the type of (8), when they found a square dependence of the membrane electrical conductivity on the concentration of the membrane-bound porphyrin (ethiochlorin of Mg(II)).

4.2.4 Viologen-containing Membranes

Sometimes electron transfer via the transport of electron carrier and via electron exchange reactions occur simultaneously. Co-existence of both these channels was observed for dark electron transfer across the viologen-containing vesicle membrane [169, 201]. To illustrate this let us turn back to the experiments shown schematically in Fig. 5a. In accordance with the reaction sequence (34)–(37) and

bearing in mind the slow rate of $C_{16}V^{2+}$ backward diffusion to the outer vesicle surface via reaction (38), one may expect that the amount of $Fe(CN)_6^{3-}$ reduced upon the total disappearance of $C_{16}V_{in}^+$ radical cations at the second segment of curve 1 in Fig. 5b should not exceed the amount of $C_{16}V_{out}^+$ produced at the first segment of the curve. However, the actual decrease of the amount of $Fe(CN)_6^{3-}$ turned out to be more than twice as much as expected [169, 201]. This suggests the existence of an additional channel of electron transfer inside the vesicle, besides process (36) of $C_{16}V_{out}^+$ migration. The information concerning this additional channel was obtained in experiments similar to those described above, but without an electron acceptor in the vesicle cavity. As seen from curve 2 in Fig. 5b, addition of dithionite causes a two-step reduction of viologen embedded in the membrane, with the characteristic times of 0.06 s and 0.43 s. At these steps, respectively, about 70 and 30% of the overall viologen contained in the membranes are reduced. The kinetics of the first step coincide with those observed at the first segment of curve 1 and apparently correspond again to the reduction of viologen located on the outer water // membrane interface via reactions (34) and (35). The second step results from the reduction of the remaining viologen which is located in the inner monolayer. Taking into account that reaction (38) is slow, i.e. $C_{16}V^{2+}$ cations do not migrate between the membrane inner and outer monolayers within the time scale of the experiment, it seems natural to attribute the slow step of kinetic curve 2 (Fig. 5b) to the electron exchange reaction:



$C_{16}V_{out}^{2+}$ formed in this reaction is quickly re-reduced by dithionite. Note, that the rate of the second step in curve 2 is found to be proportional to the square of the viologen local concentration in the membrane, as expected for reaction (42).

Hurst et al. [172, 180–185] in a series of experiments on the reduction of alkylmethylviologens located in DHP vesicles, similar to those described above, confirmed that the viologen dications cannot diffuse across the membrane. They also found out that the number of electrons transported across the membrane can exceed the number of transferred C_nV^+ radical cations. This confirms the existence of the second channel of the type of reaction (42) for electron transfer. The existence of two channels of electron transfer across membranes was suggested to arise from two types of alkylmethylviologens embedding in DHP membranes, which differ in orientation of bipyridine ring in the viologen molecule, namely along or across the membrane surface [181].

4.2.5 Electron Tunneling Across the Membrane Core

The appearance of electron transfer across membranes via electron exchange reactions seems to result from the necessity of overcoming the difficulties for an ion to pass through the highly hydrophobic region of the boundary which separates the two membrane monolayers. This boundary corresponds to the maximum of potential energy profile for the ion motion in the membrane (see Fig. 6b). If the ion could reach the top of the potential barrier, it would be able to diffuse with

equal probabilities in both directions and hence to migrate from one monolayer to the other. Since the partners in the electron exchange reaction do not reach the boundary between the membrane monolayers, one can consider the possibility of them being separated by a certain distance at the moment of electron exchange. In this case reactions of the (8), (12), (14), (41) or (42) type may proceed via electron tunneling. Following the data presented in this book in the Chapter by Zamaraev and Khairutdinov, let us estimate how long the tunneling distance can be in the systems under discussion. The tunneling probability, W , is known to fall off exponentially with the distance R between the electron donor and electron acceptor [227]:

$$W = v \exp (-2R/a) . \quad (43)$$

Parameters v and a depend strongly on the properties of reactants and the environment and can vary over wide ranges. Unfortunately the present status of the theory does not provide the possibility of predicting the values of v and a *a priori*, so let us look at the corresponding experimental data. For electron transfer from the photoexcited copper porphyrins to acceptors in vitreous ethanol the values have been obtained of $v = 10^7$ – 10^9 s⁻¹ and $a = 1.8$ – 2.2 Å [228], while for similar reactions of zinc and magnesium porphyrins in organic solvents it was found that $v = 10^9$ – 10^{11} s⁻¹ and $a = 5$ – 7 Å [229]. From the data of Mobius [230] one can obtain $a = 6.8$ Å for electron tunneling across the layer of organic molecules from the photoexcited cyanine dye to viologen (see Fig. 23 from the Chapter by Zamaraev and Khairutdinov). Using these values of v and a , one obtains for the most optimistic estimate of the characteristic time of electron tunneling $\tau = 10^{-6}$ and 10^{-4} s for $R = 25$ and 45 Å, respectively, while the pessimistic estimate gives $\tau = 10^2$ and 10^{12} s for the same distances. The characteristic times for the transmembrane electron exchange reactions were shown above to vary over a very wide range from 10^{-5} s to 10^3 s, i.e. they fall within the range of the estimated characteristic times for electron tunneling at distances $d = 25$ – 45 Å. Note, that in the case of the tunneling mechanism for electron exchange reactions in the membrane, the experimentally measured values of τ may refer either to the electron tunneling process itself or to the diffusion process providing the approach of the reacting particles at the distance from which the tunneling starts, depending on which of these stages controls the overall rate (see the Chapter by Zamaraev and Khairutdinov for more details).

Unfortunately, the experimental data concerning the distances at which electron exchange reactions in the membranes take place are very scarce. Tsuchida et al. have shown [147], that even when the photoexcited Zn porphyrin embedded in the membrane cannot approach the membrane // water interface closer than 12 Å, the electron transfer is still possible to MV^{2+} located in the water phase outside the membrane. However, when the distance of the closest approach of these reactants is increased up to 17 Å, the electron transfer is totally stopped. Examples of electron transfer proceeding presumably via electron tunneling across molecular layers about 20 Å thick, which separate electron donor and acceptor molecules, can be found in papers by Mobius [230, 231] and Kuhn [232, 233]. Note, that in

these systems, similarly to the previous one, electron transfer takes place during the lifetime of the excited electron donor, i.e. in times much less than 10^{-3} s.

According to the data from Smalley [234] the quenching of the fluorescence of magnesium octaethylporphyrin proceeds via electron tunneling in statistical pairs. The distances between the reactants and the characteristic time of electron transfer in the pairs are 10–18 Å and 5 ns, respectively.

Guarr et al. [235] reported the long distance (up to 12 Å from edge to edge) electron tunneling from the excited polypyridine Ru complexes (with lifetime about 2 μs) to aromatic amines fixed in a rigid polymer.

Thus, the available experimental data on transmembrane electron transfer via electron exchange reactions can be described in terms of the model of electron tunneling at large distances. On the other hand, at least for some reactions, it seems that one cannot completely rule out the possibility for the partners having extended π -orbitals to contact each other rather closely but still remaining in different monolayers. Danhauser et al. [236] controlled the maximum depth of a manganese porphyrin embedding into the membrane by linking it to the hydrophilic polyethyleneimine. It has been shown that the electron exchange reaction of the type (41) proceeds only when the edge-to-edge distance between Mn(II) and Mn(III) porphyrins becomes less than 4 Å. Taking into account the uncertainty of the distance estimation, it seems difficult to reject the possibility for this reaction proceeding via direct contact of the two porphyrin molecules, each of them remaining, however, in its lipid monolayer.

Thus, there is no doubt that in principle electron tunneling at large distances is capable of producing electron transfer across the hydrophobic core of the membrane. However, in order to obtain more definite evidence that transmembrane electron transfer via bimolecular exchange reactions actually proceeds via electron tunneling at large distances, more detailed studies of this reaction are needed. Such studies are important both for the problems discussed here and for a better understanding of the role of electron tunneling processes in photosynthesis.

4.3 Electron Transfer Along Bridging Molecules, Molecular Wires and Semiconductor Particles Embedded in Membranes

When developing the chemical models of photosynthesis, an approach is intensely explored which is based on synthesis of the molecules containing a photosensitizer and electron acceptor or/and donor bridged by covalent bonds. Both bifunctional, i.e. containing two redox active fragments, and triad, i.e. containing three redox active fragments, molecules were synthesized. A comprehensive review of work in this field was recently published by Connolly and Bolton [237].

As a result of intramolecular PET between the structural units of such bridging molecules one can obtain within 10^{-9} s spatially separated charges, localized at different ends of the molecule. Due to the rigidity and large size of the molecules used and also to a higher potential barrier for back electron tunneling, the reverse intramolecular recombination proceeds relatively slowly. For the best triad molecules the characteristic time of the intramolecular charge recombination

ranges within the microsecond scale. However, we would point out that for further use of separated charges in, e.g. the process of light-to-chemical energy conversion or artificial photosynthesis, one should involve them in the secondary processes leading to the formation of more stable chemical compounds. To our knowledge, this has not been done so far. Note also that in homogeneous solutions, the charges separated via intramolecular PET are still expected to recombine rapidly via collisions of the oxidized and reduced fragments belonging to different molecules.

One may try to overcome these difficulties by embedding the bridging molecules into bilayer membranes. If their redox active terminal groups are able to undergo reactions with the electron donors and acceptors from aqueous phases, an efficient transmembrane PET will be possible.

Tien and co-workers [100, 238] observed a photopotential and photocurrent arising in the planar BLM containing bridging molecules with a porphyrin bound covalently to a quinone (see System 44 of Table 1). The size of this porphyrin-quinone complex was not large enough to span across the whole of the membrane, therefore the mechanism of the arising photoeffect is most likely to be similar to those discussed in Sect. 2.4 for other BLMs doped with photosensitizers.

To our knowledge, the only system, where PET across membranes involves the intramolecular photoinduced electron transfer is System 45 of Table 1 which was also discussed in Sect. 2.4 (see Fig. 4e). The time of the transmembrane electron transfer via reaction (33) is only about 10^{-10} s [239, 240], that is many orders of magnitude less than the time of electron transfer via a diffusion mechanism and via electron exchange. The lifetime of the triad molecule in the $\text{Car}^+ \text{-P-Q}^-$ state reaches several microseconds, i.e. it is long enough for Car^+ and Q^- fragments to be able to undergo redox reactions with the water soluble donor and acceptor, respectively. Provided the concentrations of the latter is high enough, the overall quantum yield of the transmembrane PET in the system will be equal to the quantum yield of reaction (33), i.e. about 10%. Note also, that in this system the triad molecules are embedded in the membrane in a non-oriented fashion, i.e. one half of the molecules are located with Car fragments near the inner and Q fragments near the outer membrane // water interface, while the other half is located in the opposite manner. As a result, only half of the Car-P-Q molecules can participate in vectorial PET in the desired direction.

Another way of arranging the intramolecular transmembrane electron transfer is to use the so called molecular wires, i.e. molecules with the electron conduction chain of conjugated bonds, redox active polar terminal groups and the length sufficient to span across the membrane. Such molecules can in principle provide for electron transfer from the externally added or photogenerated reductant across the membrane to the oxidant. This mechanism was suggested [41, 94] to explain the action of carotene-containing System 1 and 38 of Table 1. However, as it was shown later, the transmembrane PET in these systems proceeded also without carotene.

The promoting influence of molecules, containing long electron conducting polyene chains has also been observed for electron phototransfer across molecular monolayers [241]. Lehn and co-workers [242] have synthesized a series of molecular wires which are quite interesting from the point of view of transmembrane electron

transfer. These are bispyridinium polyenes which combine the properties of carotenoids and viologens.

As shown by Nango et al. [243] for the porphyrin-quinone complex as an example, even when an electron travels via intramolecular transfer only a part of its way across the membrane, the observed overall rate of transmembrane electron transport can be notably increased as compared to transport via diffusion only.

In the photosynthetic and mitochondrial membranes the components of the transmembrane electron transport chain are not linked with covalent bonds, but fixed in a protein matrix. An example of such an arrangement of the electron transport chain in an artificial system can be found in papers by Tabushi et al. [244, 245], which deal with the dark electron transfer across the lipid membranes containing the dimers of cytochrome c_3 from *Desulfovibrio vulgaris*. The dimer size is about 60 Å, i.e. it somewhat exceeds the membrane thickness. This enables electron to move across the membrane via the cytochrome along the chain of hem fragments embedded in the protein. However, the characteristic time of the transmembrane electron transfer by this method is rather long (about 10 s).

Colloids of semiconductors are also quite interesting for the transmembrane PET, as they possess both the properties of photosensitizers and electron conductors. Fendler and co-workers [246–250] have shown that it is possible to fix the cadmium sulfide colloid particles onto the membranes of surfactant vesicles and have investigated the photochemical and photocatalytic reactions of the fixed CdS in the presence of various electron donors and acceptors. Note, that there is no vectorial transmembrane PET in these systems. The vesicle serves only as the carrier of CdS particles which are selectively fixed either on the inner or on the outer vesicle surface and are partly embedded into the membrane. However, the size of the CdS particle is 20–50 Å, i.e. this particle can perhaps span across the notable part of the membrane wall. Therefore it seems attractive to use the photoconductivity of CdS for the transmembrane PET. Recently Tricot and Manassen [86] have reported the observation of PET across CdS-containing membranes (see System 32 of Table 1), but the mechanism of this process has not been elucidated. Note, that metal sulfide semiconductor photosensitizers can be deposited also onto planar BLMs [251].

In conclusion of the discussion concerning intramolecular and intraparticle transmembrane electron transfer, it should be stressed that this sort of PET may occur rather efficiently due to the possibility for this process to attain very high rates. The studies in this direction are still at the beginning. A challenge for chemists here is the synthesis of molecules of the specified structure and length to span the bilayer with appropriate photo- and electrochemical properties and able to be oriented when embedded into the membranes.

5 Conjugation of Transmembrane PET with Redox Reactions

As shown in the previous Sections, the transmembrane PET may lead to the generation of energy-rich one-electron reductant and oxidant separated by the membrane (see example in Fig. 3). The final goal in designing the membrane

systems is usually to accomplish a certain photocatalytic process with a high quantum yield. The discussion of photocatalytic reactions of potential interest, mostly endoergonic ones, can be found elsewhere [4, 5, 252]. In this section we shall restrict ourselves to the discussions of the data obtained when using the charges that are photochemically separated in membrane systems, for performing the redox reaction of water cleavage. The approaches used here illustrate well the potentialities of membrane systems in photocatalysis and can apparently be of help also for the accomplishment of other redox reactions, which provide the lightenergy storage via production of the carbon- and nitrogen-containing fuels from water and atmospheric gases.

For the membrane-separated oxidant and reductant to be involved in the water cleavage process, several thermodynamic, kinetic, steric, etc. conditions should be simultaneously satisfied.

First, the reductant and the oxidant generated via transmembrane PET must have standard redox potentials close to the relevant electrochemical potentials of water reduction to dihydrogen $E_m^{H_2} = (-0.059 \text{ pH}) \text{ V}$ and of water oxidation to dioxygen $E_m^{O_2} = (1.23 - 0.059 \text{ pH}) \text{ V}$, respectively (vs NHE). Unfortunately these requirements are met only for few of the systems listed in Table 1. For example, in Fig. 3 the redox potentials of intermediate particles generated by PET in Systems 12 and 21 are compared with the redox potentials of dihydrogen and dioxygen evolution from water at pH 7. One can see that transmembrane PET in these systems generates particles which are thermodynamically capable of reducing water to dihydrogen (MV^+ and $C_{16}V^+$ radical cations) as well as oxidizing water to dioxygen (Chl^+ and $Ru(bpy)_3^{3+}$).

Second, in order to involve the oxidant and reductant in the multielectron reactions of water oxidation and reduction, one has to introduce appropriate catalysts into the aqueous phases separated by the membrane.

Third, to provide sufficient rates of water photodecomposition, the high specific rates of the transmembrane PET are needed. In this respect the suspensions of vesicles with a more developed membrane surface are preferable as compared to planar BLMS.

Fourth, the oxidant and the reductant resulting from the transmembrane PET should not react with the gaseous products of water cleavage (dihydrogen and dioxygen) which can readily permeate through lipid membranes.

To our knowledge, at present there are no bilayer membrane systems which simultaneously satisfy all the requirements listed. Nevertheless, notable achievements have been made on the way towards their developments. Introducing appropriate catalysts in the vesicles it was possible to accomplish separately both water reduction to dihydrogen and its oxidation to dioxygen at the expense of irreversible consumption of sacrificial electron donors and acceptors, respectively.

5.1 Photocatalytic Reduction of Water

Among the numerous catalysts of dihydrogen evolution known at present (see e.g. the reviews [253–257]) the most promising for application in the vesicle systems

seem to be colloids of noble metals and enzymes. These catalysts can be rather easily placed both inside and outside vesicles depending on the design of the vesicular PET system for H_2 evolution.

For example Kurihara and Fendler [258] succeeded in forming colloid platinum particles, Pt_{in} , inside the vesicle cavities. An analogous catalyst was proposed also by Maier and Shafirovich [164, 259–261]. The latter catalyst was prepared via sonification of the lipid in the solution of a platinum complex. During the formation of the vesicles platinum was reduced and the tiny particles of metal platinum were adsorbed onto the membranes. Electron microscopy has shown a size of 10–20 Å for these particles. With the Pt_{in} -catalyst the most suitable reductant proved to be a $Rh(bpy)_3^{2+}$ complex generated photochemically in the inner cavity of the vesicle (see Fig. 8a). With this reductant the quantum yield for H_2 evolution of 3% was achieved. Addition of the oxidant $Fe(CN)_6^{3-}$, in the bulk solution outside vesicles has practically no effect on the rate of dihydrogen evolution in the system. Note that the redox potential of the bulk solution remains positive during the H_2 evolution in the vesicle inner cavities, i.e. the inner redox reaction does not depend on the redox potential of the environment. Thus redox processes in the inner cavities of the vesicles can proceed independently of the redox potential in the bulk solution.

Now let us discuss how one can conjugate the process of H_2 evolution on the catalyst anchored to the membrane or located in a water phase with the vectorial PET across this membrane.

Dihydrogen can be rather easily evolved with Systems 10–15 of Table 1, where, with PET across the membrane, the water-soluble radical cation MV^+ is produced outside the vesicle. This radical cation can evolve dihydrogen from water in the presence of various catalysts. This was demonstrated by Tsvetkov et al. [262] for System 12 of Table 1. As a catalyst, the $\square$ water soluble hydrogenase from *Thiocapsa roseopersicina* was used or a heterogeneous rhodium-polymer catalyst [263]. The quantum yield of H_2 production was comparable with the quantum yield of MV^+ generation.

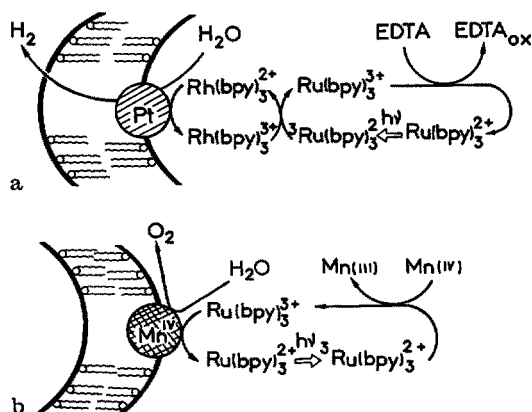


Fig. 8. The application of vesicles for photocatalytic water decomposition in sacrificial systems: (a) — dihydrogen evolution in the vesicle cavity. Pt metal catalyst is anchored to the inner membrane // water interface; (b) — dioxygen evolution in the bulk solution. Manganese oxide catalyst is anchored to the outer membrane // water interface of the vesicle

Much more complicated is the situation with dihydrogen evolution in such Systems as those 21–23 of Table 1. The ultimate electron acceptor used in these systems does not possess the redox potential negative enough to reduce water. However, the redox potentials of the intermediate electron carriers, namely the radical cations of membrane-bound viologens, are sufficient to reduce water. Hence it looks tempting to use these carriers for water reduction on catalysts anchored to the outer surface of vesicles. Here in the photocatalytic system the secondary electron acceptor outside vesicles is no longer needed, because the catalyst particle itself can act as such acceptor. Maier et al. [261] demonstrated the possibility of using the platinum catalyst Pt_{out} anchored to the outer vesicle surface for dihydrogen evolution via photochemical generation of MV^+ radical cations inside the vesicle inner cavity. The evolution of H_2 is possible here due to the MV^+ capability of passing slowly through the membranes. An attempt to use in a similar way the hydrophobic viologens embedded in the membranes, which transfer electrons across the membranes much faster, faces difficulties of another character. It turned out that the strong hydrophobic interactions of the viologen radical cations with the membranes (discussed in Sect. 3.2.2) in addition to the positive effect, viz. slowing down the recombination of the radical cations with the oxidized photosensitizer, also exert an effect which is harmful for dihydrogen evolution. Namely they increase the reduction potential of the viologen radical cations from about -0.4 V up to approx. -0.2 V (vs NHE) [264]. As a result, the evolution of H_2 becomes thermodynamically possible only at $\text{pH} < 4$. Efimova et al. reported [265] data on dihydrogen evolution by the radical cations of the above mentioned hydrophobic viologens embedded in the vesicle membrane with the finely dispersed (particle size of about $20\text{ \AA}$) metallic palladium catalyst anchored to the outer surface of the vesicle membranes.

Thus the data presented in this Section prove that vectorial PET across membranes in vesicle systems indeed can be conjugated with the catalytic process of water reduction to dihydrogen.

5.2 Photocatalytic Oxidation of Water

Among known reversible one-electron oxidants capable of oxidizing water to O_2 , a $\text{Ru}(\text{bpy})_3^{3+}$ complex is considered to be the most promising one, because it can be rather easily generated photochemically on illumination with visible light [110]. In the late 1970s a series of both homogeneous and heterogeneous catalysts for water oxidation was suggested, including hydroxocomplexes or colloid oxides of iron, cobalt, nickel, copper, ruthenium and manganese (see comprehensive review articles [266, 267]).

To employ the catalysts for O_2 evolution in the vesicle systems, it was essential to check whether their selectivity towards evolution of O_2 remains high enough after immobilization on the lipid membrane. Shilov, Shafirovich and co-workers prepared [268–271] a membrane-bound catalyst for water oxidation by oxidation of Mn(II) salts in the presence of lipid vesicles. The Mn(IV) hydroxide catalyst

formed was found to be strongly bound to the lipid membrane. Under optimal conditions this membrane-bound Mn(IV) catalyst exhibits the selectivity which is close to the selectivity obtained with Mn(IV) hydroxide catalyst in the absence of the vesicles. Thus the immobilization of the manganese hydroxide catalyst on the membrane promotes rather than inhibits the water oxidation process, despite the fact that the membrane is formed by rather easily oxidized lipid compounds.

The membrane-bound catalysts for water oxidation can also be obtained with other transition metal hydroxides. Gerasimov et al. [272] have shown that illumination of a $\text{Ru}(\text{bpy})_3^{2+}$ – persulfate system in the presence of Co(II) and lipid vesicles results in the formation of a colloid catalyst for water oxidation, viz. Co(III) hydroxide, immobilized on the lipid membranes. The same catalyst can be obtained without illumination by Co(II) oxidation with a $\text{Ru}(\text{bpy})_3^{3+}$ complex in the vesicle suspension. The selectivity of water oxidation with the catalysts thus obtained depends on the nature of the membrane-forming lipid. Switching from the synthetic DPL to the natural eggL the process selectivity decreases by about two orders of magnitude due to consumption of the oxidant for oxidation of organic impurities contained in lipids of natural origin [113].

Unfortunately, the oxidation of water in the systems discussed was not conjugated with PET across the membranes.

The first communication about the Chl-sensitized water oxidation to O_2 on the outer vesicle interface conjugated with $\text{Fe}(\text{CN})_6^{3-}$ reduction at the inner interface appeared in 1977 [42] (see System 2 in Table 1). However an attempt to reproduce this result was a failure [273]. Thus the possibility of water photooxidation in vesicular systems which contain either only Chl molecules or Chl molecules in combination with other photosynthetic pigments is still under discussion. However, embedding of the intact fragments of thylakoids in the vesicle membranes was found to provide the evolution of O_2 from water upon illumination [273]. But again this process was not conjugated with PET across the membranes.

5.3 Simultaneous Accomplishment of Water Reduction and Oxidation

The development of the appropriate technique for the preparation of catalysts for water oxidation and reduction, which are immobilized on the membranes, offers the possibility of constructing photochemical systems containing vesicles of different types capable of performing various redox functions simultaneously. The first system of this kind, where the simultaneous photocatalytic evolution of dioxygen and dihydrogen was observed was suggested by Luneva et al. [274]. The photocatalytic system for dihydrogen evolution was incorporated into the inner volume of lipid vesicles (Fig. 8a), while the photocatalytic system for dioxygen evolution was located in the outer bulk solution (Fig. 8b). Upon illumination of the suspension obtained by mixing both systems shown in Fig. 8, one could observe a simultaneous evolution of H_2 and O_2 . Note, however, that no conjugation of these processes with electron transfer across the membranes was carried out in this system.

In the vesicle suspension of Fig. 8 it was possible to isolate the centers for dihydrogen and dioxygen evolution and thus to avoid cross reactions of S^+ and A^- with the catalysts for H_2 and O_2 evolution, respectively. However, it turned out that O_2 evolution gradually inhibits the H_2 evolution, because oxygen evolved in the outer volume permeates across the membranes and destroys the apparatus for dihydrogen evolution located inside the vesicles. Note, that such a problem also arises for biological systems adapted to provide simultaneous evolution of H_2 and O_2 [275, 276].

The difficulties arising from the penetration of O_2 through the membrane which separates the oxidative and reductive parts of the photocatalytic system are unlikely to be solved with the use of microscopic mono- or bilayer membranes for photoinduced charge separation. In fact, it seems rather difficult to prevent the diffusion of a small non-polar oxygen molecule across a lipid or surfactant membrane with a thickness of 30–40 Å. Better isolation between the oxidative and reductive parts of the photochemical system, perhaps, may be provided by macroscopic porous or ion-exchange membranes separating the solutions with systems a and b of the type presented in Fig. 8, the way it is usually done in water electrolysis. It might also be possible to avoid the inhibiting influence of O_2 on the molecular apparatus for H_2 production, by means of evolving dihydrogen and dioxygen from water consecutively rather than simultaneously. In this case one may benefit from the technique suggested by Gerasimov et al. [277], which gives the separation in two steps: (i) photogeneration of a strong oxidant, which in this case is conjugated with the simultaneous process of dihydrogen evolution, and (ii) subsequent oxidation of water with this oxidant.

Thus the techniques have already been developed which allow us to introduce the catalysts for H_2 and O_2 evolution into appropriate places of the membrane system: inside or outside vesicles, on the inner or outer surface of the membranes. However, the problem of efficient conjugation of the catalytic processes of H_2 and O_2 evolution with the PET across the membranes is still to be solved.

6 Conclusion

The data presented in this Chapter show that during the past 10–15 years numerous systems providing vectorial PET across bilayer membranes have been developed. The key-steps of PET across the membranes are: (i) primary photochemical separation of charges, (ii) their recombination and (iii) electron transfer across the membrane. As found, the first two processes are substantially influenced by electrostatic and hydrophobic interactions of reagents with the membrane. The process of electron transfer across the membrane can be performed by three mechanisms: (1) via the diffusion of an electron (or hole) carrier through the membrane, (2) via reactions of electron exchange between molecule located in different monolayers of a bilayer membrane, and (3) via intramolecular electron transfer along specially designed bridging molecules, and molecular wires or intraparticle electron transfer along ultrafine semiconductor particles embedded

in the membrane. The kinetics of transmembrane electron transfer is substantially influenced by electric polarization of the membrane and the gel-liquid crystal phase transition.

Despite the fact that at present many important regularities of PET processes across the membranes seem to be understood at a qualitative level, this turns out to be insufficient for PET across membranes to be controlled purposefully. For this, more detailed quantitative mechanistic studies are needed. In particular, more data are needed concerning the location of the photosensitizer and electron carriers inside the membrane, dynamics and spatial limits of their diffusion in the membrane, the actual role of electron tunneling in providing electron transfer across the hydrophobic core of the membrane.

One of the main fields of application of PET across membranes is expected to be the functional modelling of plant photosynthesis, and in particular, accomplishment of light-to-chemical energy conversion processes. An attractive process of this type is water cleavage into dihydrogen and dioxygen under the action of visible light. For the time being this process has not been accomplished yet, since nobody has succeeded in creating a system based on the transmembrane PET that would demonstrate simultaneously all the properties enumerated in the first paragraphs of Sect. 5. At present membrane systems are available that match only one of such necessary properties as: (i) a high quantum yield of PET across the membrane, (ii) the ultimate electron donor formed upon PET has the redox potential sufficient for water oxidation, and (iii) the ultimate electron acceptor formed upon PET has the redox potential sufficient for water reduction. To construct a system demonstrating all the indicated properties simultaneously, is still a problem to be solved.

Once such system is created, the second task will be to combine it with the catalysts of H_2 and O_2 evolution. As shown in Sect. 5.1 and 5.2, the techniques have already been developed which provide the possibility of introducing such catalysts selectively into appropriate places of the membrane systems: inside or outside vesicles, on the inner or outer surface of the membrane.

Once this second task is solved, the next problem will be how to protect the sites for H_2 evolution from poisoning with O_2 . Possible ways for solving this problem have been indicated in Sect. 5.3.

We should remember that it took Mother Nature billions of years to invent photosynthesis and to make it as perfect as it is today, and it would be naive to expect a simple and rapid creation of its artificial functional analog. Nevertheless, from what we know today about PET in the membrane systems, we may expect that an artificial apparatus providing efficient charge separation via transmembrane PET is likely to be developed in a rather universal way and may be expected to accomplish not only water reduction and oxidation but also various other redox reactions which provide the storage of light energy.

Another possible field of application of PET across membranes may be molecular electronics (see the recent monographs [278–280]). So far little information is available on the application of bilayer membranes to this field. However it cannot be ruled out that in the future electrogenic membranes including light-controlled ones may be used as the components of molecular electronics.

7 Acknowledgements

The authors express their deep thanks to Dr. E. Efimova and Mrs. K. Talysheva from the Institute of Catalysis, Novosibirsk, for their assistance in the preparation of the manuscript. We wish also to thank Drs. M. Khramov and I. Tsvetkov from the Institute of Catalysis, Novosibirsk, and Drs. V. Shafirovich and V. Nadtochenko from the Institute of Chemical Physics, Chernogolovka, for stimulating discussions. This work was supported by the Academy of Sciences of the USSR and the State Committee for Science and Technology of the USSR.

8 List of Abbreviations

General Notations

PET — photoinduced electron transfer

BLM — planar bilayer lipid membranes

P — porphyrin

Car — carotene

P-Q — porphyrin-quinone bridging molecule

Car-P — carotene-porphyrin bridging molecule

Car-P-Q — carotene-porphyrin-quinone triad (see Fig. 21a in the Chapter by Zamaraev and Khairutdinov)

Membrane Materials (see also Fig. 1)

eggL — lecithin from egg yolk

DPL — dipalmitoyl lecithin, $R_1 = R_2 = \text{CH}_3(\text{CH}_2)_{14}-$

DML — dimyristoyl lecithin, $R_1 = R_2 = \text{CH}_3(\text{CH}_2)_{12}-$

DFL — diphytanoyl lecithin, $R_1 = R_2 = \text{CH}_3[\text{CH}(\text{CH}_3)-(\text{CH}_2)_3]\text{CH}(\text{CH}_3)\text{CH}_2-$

DOL — dioleoyl lecithin, $R_1 = R_2 = \text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_8-$

PE — phosphatidylethanolamine

PS — phosphatidylserine

GMO — glycerol monooleate

Chol — cholesterol

DHP — dihexadecylphosphate

Photosensitizers

Chl — chlorophyll

Chln — chlorophyllin

Phe — pheophytin

$\text{Ru}(\text{bpy})_3^{2+}$ — trisbipyridylruthenium(II)

$(bpy)_2Ru(2\ C_nbpy)^{2+}$ — surfactant analogues of $Ru(bpy)_3^{2+}$, having two alkyl
($n = 12, 16$ or 17) substituents in one bpy ligand

H_2TPP — *meso*-tetraphenylporphin

$ZnTPP$ and $ZnTPP-Ac$ — tetraphenylporphyrinatozinc(II)
and its $1-(CH_2)_2CO_2H$ derivative

H_2MP^{2-} — diglycilamide of mesoporphyrin-IX

$MgOEP$ — octaethylporphyrinatomagnesium(II)

$ZnTPPS^{4-}$ — *meso*-tetra(*p*-sulfonatophenyl)porphyrinatozinc(II)

$ZnMPyP^{4+}$ — *meso*-tetra(*N*-methyl-4-pyridinium)porphyrinatozinc(II)

$ZnC_{18}TMPyP^{3+}$ and $MgC_{18}TMPyP^{3+}$ — *meso*-tris(*N*-methyl-4-pyridil)
-(4-octadecyl)porphyrinatozinc(II)
and magnesium(II)

$ZnC_{12}TPP^+$ — *meso*-tris(4-Pyridyl)-*N*-dodecyl-4-pyridinium)-porphyrinato-
zinc(II)

HCD — heterocyclic dyes

AF — acriflavine

TCNQ — tetracyanoquinodimethane

Electron Donors

Asc — ascorbate

EDTA — ethylenediaminetetraacetate

GSH — glutathione (reduced form)

NADH — nicotinateadenine dinucleotide (reduced form)

$Os(bpy)_3^{2+}$ — trisbipyridylosmium(II)

$(bpy)_2Os(2\ C_{17}bpy)^{2+}$ — surfactant analog of $Os(bpy)_3^{2+}$, having two C_{17} sub-
stituents in one bpy ligand

Electron Acceptors (see also Fig. 1)

MV^{2+} — methylviologen dication, $R_1 = R_2 = CH_3$ —

C_nV^{2+} — alkylviologen dication, $R_1 = R_2 = C_nH_{2n+1}$ —

PVS — propylviologensulfonate, $R_1 = R_2 = ^-O_3S-(CH_2)-CH_2-$

EVS — ethylviologensulfonate, $R_1 = R_2 = ^-O_3S-CH_2-CH_2-$

MB^- — methylene blue anion

Q — quinone

BQ — *p*-benzoquinone

UQ_{10} — ubiquinone-10

NQS^- — naphthaquinonesulfonate

$AQDS^{2-}$ — anthraquinonedisulfonate

MGNQ — S-(2-methyl-1,4-naphthoquinoyl-3)-glutathione

Cyt — cytochrome

$Rh(bpy)_3^{3+}$ — trisbipyridylrhodium(III)

FMN — flavin mononucleotide

$MnC_{16}TPyP^{2+}$ — *meso*-tris(4-pyridyl)-(*N*-hexadecyl-4-pyridinium)-
porphyrinatomanganese(III)

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Photoinduced Electron Transfer in Arranged Media

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1 Introduction

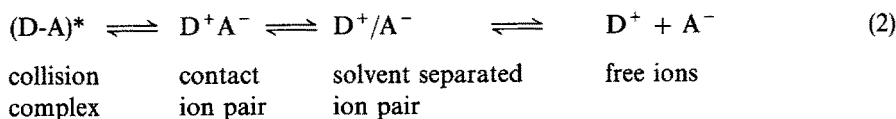
Photoinduced electron transfer [1, 2] represents the simplest way of achieving charge reversal in chemical reagents. As shown in Eq. 1, an electron-rich reagent D can interact



with an electron-deficient reagent A to generate, via electron transfer, the corresponding radical ion pair D^+A^- . This electron transfer inverts normal chemical electron demand, and hence chemical reactivity, with the electron-rich reagent becoming a cation and the electron-deficient reagent becoming an anion.

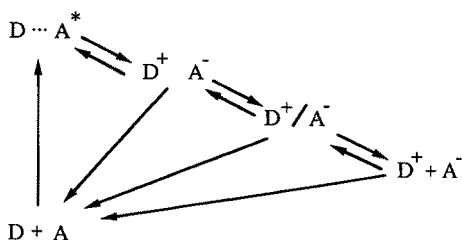
Although Eq. 1 is written as an equilibrium, full exploitation of this inverted charge demand requires that the equilibrium be shifted far to the right, at least on a timescale consistent with kinetic exploitation of the altered chemical properties of the components of the radical ion pair. If the reagents from which this radical ion pair are to be derived are to be chemically stable, however, it is clear that under thermodynamically dictated conditions the equilibrium will lie to the left in most cases. Photochemical and electrochemical methods can be used to activate this donor-acceptor pair, causing the requisite electron transfer to occur to generate the radical ion pair shown at the right. The driving force for reestablishment of the original equilibrium, however, rapidly causes the photoinduced radical ion pair to relax via back electron transfer, regenerating starting materials. Thus, any energy storage or chemical activation achieved with these photochemical or electrochemical methods will be lost.

The initial photoinduced radical ion pair equilibrium is further complicated by competing solvation equilibria. As shown in Eq. 2, the electron transfer typically occurs



within a collision complex in which the donor and acceptor are brought to within close contact. Photoinduced electron transfer within this collision complex gives rise to a radical ion pair in intimate contact, referred to as a geminate radical ion pair, or contact ion pair. The charge separation induced upon formation of this geminate radical ion pair enhances the tendency of solvent to associate with the individual components. If a small number of solvent molecules intervene between the positively and negatively charged ions, electrostatic interactions between these species will occur so that spin correlation and electrostatic attraction between these ions remain. The resulting ion pair thus differs from the contact ion pair in terms of orbital overlap and donor-acceptor interactions, but the solvent-separated ion pair has strong interaction between the component ions. If enough solvent molecules interact with the oxidized and reduced species formed from the

photoinduced electron transfer, eventually the component ions become fully solvated and the electrostatic interaction between them becomes negligible. At this point we have free ions, and to the extent that such ions are completely solvated, the tendency for back electron transfer is significantly diminished.



Scheme 1. Back electron transfer from several types of ion pairs

A kinetic scheme can be written, Scheme 1, in which the rates of back electron transfer from the contact, solvent-separated, and free ions must each be individually considered. Clearly, the greater the tendency of a given solvent to separate the ions, the less significant will be the electrostatic interaction between them, and the greater tendency to suppress back electron transfer for a period sufficiently long to allow radical ion chemistry to ensue. A major concern of this article will be in defining the efficacy of supramolecular assemblies which create inhomogeneous arrays to control the secondary chemistry of radical ions formed via photoinduced electron transfer.

2 Control of Back Electron Transfer

The problem of differentiating the rates of back electron transfer and of chemical reaction of radical ions can be addressed in one of two ways: either the rate of reaction of the radical ions can be increased, or the rate of back electron transfer between the components of the radical ion pair can be suppressed. Although the reactivity of the component radical ions can be manipulated by standard physical organic techniques (which alter the electron density and steric access to sites of electron sufficiency or deficiency), it is very difficult to change the chemical reactivity of fixed members of a donor-acceptor pair. Yet the rate of chemical reaction, rearrangement, or trapping of the individual radical ions must be competitive with the rate of back electron transfer (the reverse of Eq. 1) if net chemistry is to be observed. Obviously, if the rate of reaction of these radical ions is extremely fast, the relative rate of back electron transfer may be slow enough to obviate this problem.

The factors instrumental in influencing the rate of back electron transfer [3] are similar to those which have been demonstrated to influence forward electron transfer [2]: the relationship between rate and energetics, the dependence of the rate of electron transfer on the distance separating the donor and acceptor, the

solvation of the components of the radical ion pair, and the mode and identity of solvent or spacers separating the participants in the electron transfer reaction.

Electron transfer rates have been described using both classical and quantum mechanical approximations. If one considers first a classical approximation, one writes a potential energy surface for the reactants and products and considers changes in energy induced by perturbing the structure of the molecule or its environment. A potential energy barrier, and hence kinetic retardation, is encountered as one passes from the reactant to the product surface, and the magnitude of the barrier will depend not only on the overall thermicity of the relevant electron transfer but also on the degree of reorganization of the redox participants (and their solvation shells) which must occur as the transition state for surface crossing is approached. Marcus theory predicts that for modestly exothermic reactions the rate will increase with the driving force, but if an electron transfer reaction becomes too highly exothermic, the accompanying barrier may increase so appreciably that the observed rate will actually decrease.

From a quantum mechanical perspective, the rates of electron transfer will depend on the product of the frequency of motion along the reaction coordinate, the magnitude of electronic coupling between donor and acceptor, and a factor describing nuclear reorganization. An alternative approach, which handles non-adiabaticity, describes electron transfer rates as a product of an electronic coupling term and the Franck-Condon weighted density of states. Clearly, electronic coupling between two redox sites will depend on the distance separating the sites and the ability of the intervening medium to permit electronic interaction. Thus, distance, orientation, and matrix coupling elements will figure significantly in describing rates of electron transfer in both the forward and reverse reactions. In turn, this means that the medium in which a desired electron transfer reaction is conducted will significantly influence the rates of both the forward and back electron transfer in Eq. 1 and, hence, the position of the electron transfer equilibrium.

In most cases, back electron transfer has an appreciable thermodynamic driving force and is fast indeed (rates exceeding that of diffusion control) so that kinetic suppression of back electron transfer often becomes the limiting factor in the ability of the chemist to observe well-defined chemistry derived from photoinduced electron transfer. In order to control the relative rates for a given set of reagents, the most profitable approach often involves addressing the decreasing of the rate of back electron transfer by controlling the polarity and spatial inhomogeneity of the medium [3]. To see how electron transfer reactions might be controlled by the reaction medium, we can look to nature. Dramatic progress in the last several years in characterizing the components and spatial arrangement of the bacterial photosynthetic reaction center, for example, has shown that the rate of electron transfer is controlled at the molecular level by a cascade of redox-active reagents which act as electron shuttles to the final site for redox catalysis and, at the supramolecular level, by the highly organized membrane-bound protein units in which this redox cascade is imbedded [4]. This matrix holds the individual components at a fixed distance and orientation for optimal efficiency for electron motion.

The photoinduced electron transfer accomplished in this system is initiated by absorption of a photon by the active chromophore. The resulting excited state lies at a higher energy than the ground state and a high energy electron occupies a molecular orbital which was originally not populated in the ground state. The excited donor can then transfer an electron to an appropriate acceptor, i.e., one which has a vacant orbital at an energy level below that of the excited state. The energetics of this transfer can be approximated by the Rehm-Weller equation [5], Eq. 3, in which the excited state singlet energy is compared with

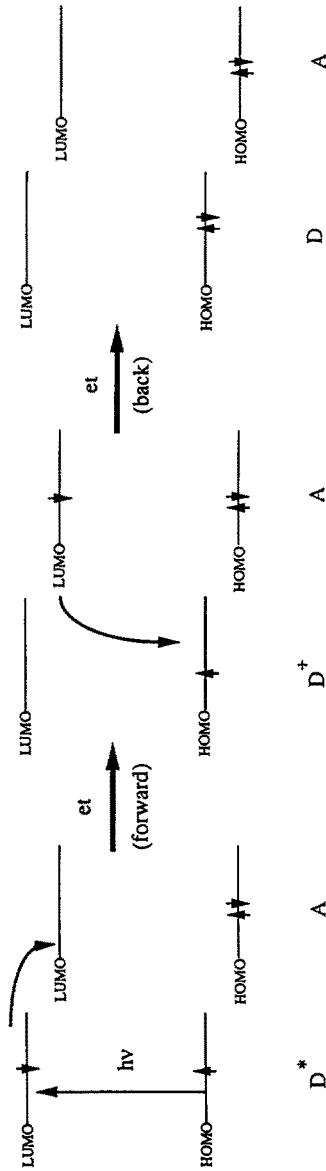
$$\Delta G^0 = E_{A/A^-}^0 - E_{D/D^+}^0 - \Delta E_{0,0} - e^2/\epsilon_a \quad (3)$$

the oxidation potential of the donor and the reduction potential of the acceptor. The final term in this expression is a work term which corrects for charge separation in a solvent medium of varying dielectric. If the free energy for the electron transfer is negative, the transfer will occur at a diffusion-controlled rate.

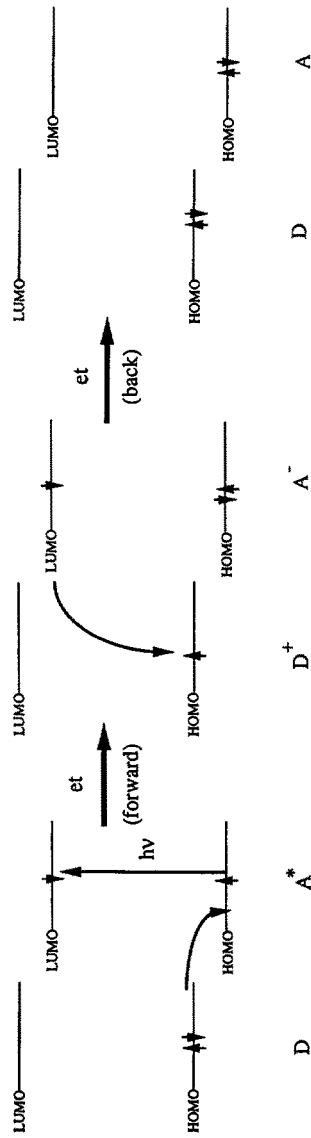
Back electron transfer, in general, will have a different driving force than forward photoinduced electron transfer, since the back reaction often does not involve the excited state of either the donor or the acceptor and because the charge types for the forward and reverse electron transfers may differ. The energetics for this transfer can be seen conceptually in Scheme 2. By definition, a donor will have a high lying occupied orbital and an acceptor will have a low lying orbital vacancy. Photoexcitation promotes an electron from the donor's highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO). Forward electron transfer to the acceptor depletes the donor excited state while populating the acceptor's LUMO, whereas back electron transfer depletes the acceptor LUMO by re-populating the donor's HOMO. Very roughly then, the energy difference between the donor LUMO and the acceptor HOMO governs the forward transfer, while the difference between the acceptor LUMO and the donor HOMO controls back electron transfer. Both of these transfers will be exothermic, but since the acceptor LUMO will not bisect energetically the donor's HOMO-LUMO gap, there will be a difference in driving force for the two transfers. A similar analysis can be applied to photoinduced electron transfer from the excited acceptor, Scheme 3.

The chemical structures of the respective radical ions obviously permit different degrees of charge localization in each ion and, hence, the response of the ion to dielectric change in the surrounding medium. A more polar medium will therefore shift energies of the donor and acceptor orbitals to different extents and hence will provide differential driving forces for forward and back electron transfers. Solvent polarity will also influence the importance of the work term descriptive of charge separation consequent to the primary electron transfer. Alteration of the chemical structure by tight solvation or complexation with a partner which perturbs solvation will thus sensitively influence the relative stabilities of the component ion radicals. Nonhomogeneous media allow for just this sort of coupled spatial and electronic interaction [6].

Nature teaches us, then, that organized media can be used effectively to control the facility of back electron transfer, in that electrostatic and spatial effects can



Scheme 2. Energetics for forward and back electron transfer from an excited electron donor



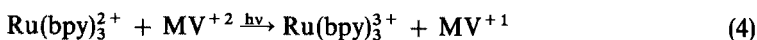
Scheme 3. Energetics for forward and back electron transfer from an excited electron acceptor

be exploited to either favor or disfavor reaction within radical ion pairs. This chapter seeks to define those features inherent in various pre-arranged heterogeneous media which allow for preferential kinetic control of reactions of the photogenerated radical ion pair.

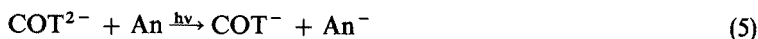
3 Non-homogeneous Media for Enhanced Charge Separation

3.1 Electrostatic Effects

One of the principal reasons that the reversal of Eq. 1 is so facile is that neutral donor-acceptor substrates form oppositely charged paramagnetic ions in which both electrostatic considerations as well as electron pairing effects would dictate appreciable driving force for charge recombination. One simple way of subverting this strong electrostatic attraction is to employ multiply- and like-charged reagents. For example, if cationic donors and acceptors are employed, the electrostatic attraction between the redox pair will be diminished. In one of the classical reactions of this field, $\text{Ru}(\text{bpy})_3^{2+}$ transfers an electron to dicationic methyl viologen, Eq. 4 [7], the products formed after the electron transfer remain as cations which will



be repelled rather than attracted by electrostatic factors. Similarly, photoinduced electron transfer from an excited dianion, e.g. cyclooctatetraenyl dianion (COT^{2-}), to a neutral acceptor, e.g., anthracene (An) generates a pair of radical anions [8] with analogous electron repulsion, Eq. 5.



Such charge repulsion effects can operate either in homogeneous solution or in anisotropic media where appreciable centers of charge density develop. Two important classes of media in which these electrostatic effects appreciably influence chemical reactivity (in self-organizing assemblies and polymers) are treated in the following sections.

3.2 Self-Assembling Aggregates

Non-homogeneous media provide similar opportunities for control of electrostatic factors operative in electron transfer. Amphiphilic molecules simultaneously exhibit regions of high and low charge density and can thus associate with a like molecule to form a spatially organized pocket of appreciably different polarity. Shown in Fig. 1 are conceptual representations of several types of self-assembling aggregates employing surfactants as major components. The surfactant molecule is represented by a circular head group (which is usually highly acidic or basic and is always polar) connected to a long chain, low dielectric, non-polar tail. The different modes of aggregation are determined by temperature, the surrounding medium, and the

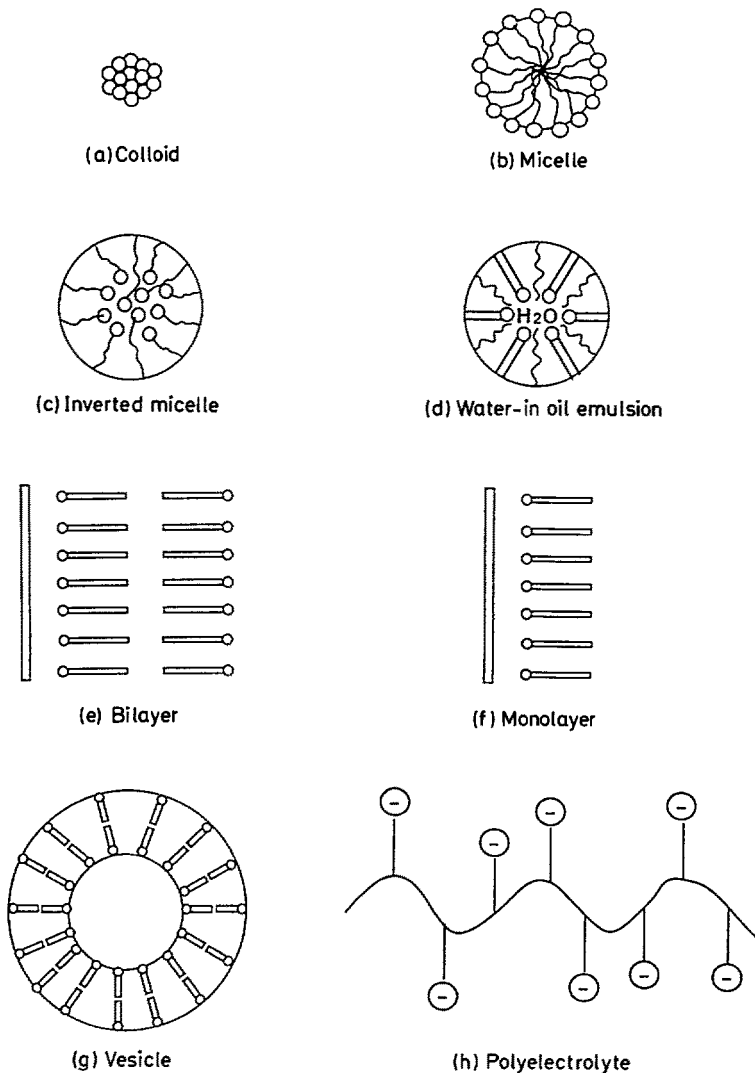


Fig. 1. Schematic representations of some self-assembling structures

relative concentrations of the various components. At low concentrations, the surfactant remains effectively dissolved, but above a certain concentration characteristic of each specific surfactant molecule, the surfactant molecules begin to associate to form the aggregate shown, with a micelle typically containing fifty to several hundred surfactant molecules.

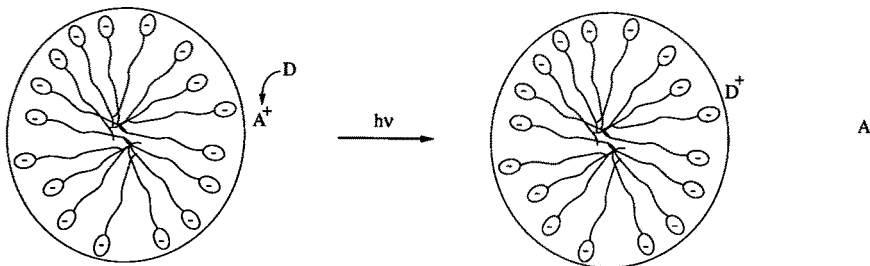
A micelle typically forms as an approximately spherical structure in which a hydrophobic inner core is separated from the surrounding polar solution by a shell comprising of the head groups and their accompanying solvation shells [9].

A hydrophobic probe molecule can thus dissolve in the core of this structure even when it is itself insoluble in the dominant polar solvent. An anionic micelle will display a negatively charged surface to the dispersing solvent, while a cationic micelle will form a positively charged spherical surface. Neutral surfactants can also be used to form biphasic aggregates which lack surface charge. This surface charge can play a role similar to the multicharged ions discussed in the previous section.

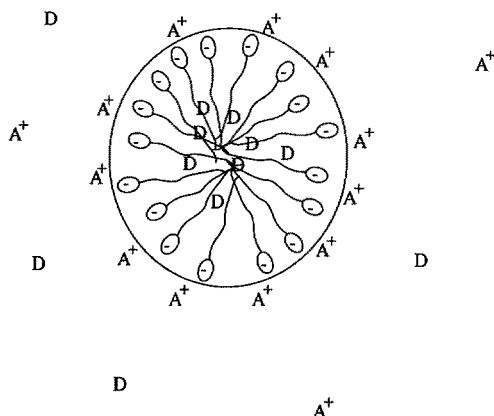
An inverse (or reverse) micelle, which forms in a non-polar solvent, will have the hydrophilic head groups oriented toward the inside of the sphere, where a water pool is formed and a hydrophilic probe can become associated [10]. Some surfactants commonly employed to stabilize reverse micelles include sodium diisooctylsulfosuccinate (AOT), benzylhexadecyldimethylammonium chloride (BHDC), and dodecylammonium propionate (DAP). Ionic surfactants induce formation of a larger water pool than non-ionic surfactants, but the size of the hydrophilic core also depends on temperature and on the ratio of water to surfactant.

The inhomogeneous structure of a micelle (or inverse micelle) can influence the course of a photoinduced electron transfer. Such a micelle is biphasic, containing a hydrocarbon-like core and a water-like surface. If the photoinduced electron transfer produces a product which has lower solubility in the aqueous phase (a situation which might obtain if a cationic acceptor is reduced to a neutral product), this product will be directed by solubility considerations to move toward the hydrophobic center of the micelle, i.e., remote from the site of the forward electron transfer. This spatial separation, shown conceptually in Scheme 4, in turn will retard the rate of the back reaction compared with that of the forward reaction.

The existence of these dielectrically different phases can also cause concentration gradients within the micelle so that effective concentrations of reagents substantially different from the bulk concentrations can be attained, Scheme 5. This concentration effect can be utilized to control bimolecular quenching events, especially when short-lived intermediates are involved. In an anionic micelle, for example, a neutral donor may dissolve in the hydrophobic core, while the electron deficient acceptor (either as a neutral molecule or as a cation) may associate with the surface head



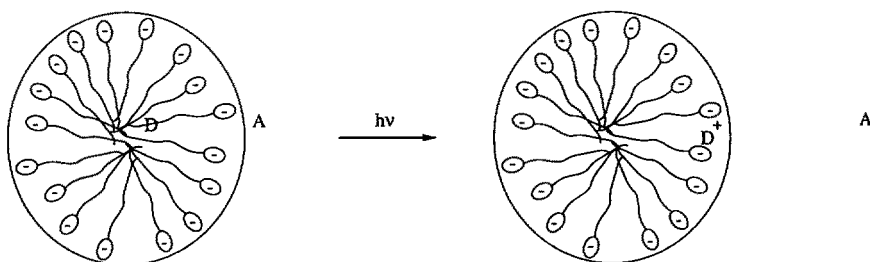
Scheme 4. Spatial separation of a donor cation and neutral acceptor at the surface of an anionic micelle after photoinduced electron transfer



Scheme 5. Concentration effects within a micelle

groups. Upon photoexcitation, this donor may transfer an electron to an acceptor electrostatically bound to the exterior surface of the aggregate, generating a donor cation/acceptor anion pair. The reduced acceptor will then be repelled from its original surface-associated site, while the donor moves from the interior core to a position closer to the charged head groups. An example of such a system is shown in Scheme 6. Electrostatic repulsion, in parallel to the effects seen in homogeneous solutions in Eqs. 4 and 5, will cause a further physical separation of the radical ion pair and thus inhibit back electron transfer.

The presence of two phases at the boundary of a micelle also induces an interfacial potential not unlike that encountered at a solid-liquid interface or at the surface of a charged electrode. This partial charge can further cause separation of oppositely charged components of the radical ion pair and can influence the energetics for the primary photoinduced electron transfer. The solution layer surrounding the aggregate is usually described as a combination of a compact layer and a diffuse layer. The former, called the Stern or the Stern-Graham layer, consists of order introduced by close approach of counterions and is usually about 1 to 5 Å in width. The latter, called the Gouy-Chapman layer, has a much larger



Scheme 6. Interfacial charge transfer at a micelle surface

width (as much as several hundred nanometers) and will significantly influence diffusion and mass transport of solution phase species to the surface of the aggregate.

The biphasic character of a micelle also makes possible the operation of cage effects in which reactive intermediates incapable of crossing the interface between the hydrophobic and hydrophilic regions cannot freely diffuse from the site of their generation, leading to recombination products reflective of this cage trapping. The differing viscosities of the two phases can also influence migration of excited states and reactive intermediates formed within the micelle or near its surface.

A microemulsion, Fig. 1, has a similar organization to that characteristic of a micelle but employs, rather than one, multiple surfactant components, allowing for introduction of other additives into the hydrophobic core [11]. As with micelles, microemulsions are optically transparent and can be easily studied by standard spectroscopic methods. One important use of such microemulsions is in the photoinduced initiation of polymerization of monomers with low water solubility: many such reactions involve a mechanism occurring through photoinduced interfacial electron transfer.

Monolayers, Fig. 1, are formed by strong association between surfactant molecules (both by electrostatic interaction between the functionalized head groups and their solvation spheres and by hydrophobic packing of the long-chain hydrocarbon tails) with each other and with either a solid or liquid phase. Alkyl thiols chemisorbed to gold [12] or Langmuir-Blodgett films [13], obtained by compressing a surfactant at a liquid-gas interface or by dipping a solid support surface (to which the ordered surfactants adsorb via either hydrophobic or hydrophilic interactions) through such an ordered layer, represent two such monolayers. Amphiphilic molecules are oriented in the preparation of monolayers by evaporating solvent from a dilute solution of the molecule spread at the surface of a polar liquid. Originally present as quite dilute components, the molecules are compressed by reducing the available surface area, inducing order similar to that found during phase changes from gas to liquid to solid state. The surface area will then be roughly equivalent to the sum of the areas occupied by the polar head groups (about $20 \text{ \AA}^2/\text{molecule}$). This, in turn, requires that the aligned tails will project at a fixed angle from the surface. If surface pressure is increased substantially beyond that needed to form the monolayer, bilayer or multilayer arrays will be formed. By altering the order of the dipping or the polarity of the original surface to be coated, it is possible to form layered Langmuir-Blodgett films with the different orientations shown in Fig. 2.

In more controlled fashion, sequential deposition of two such monolayers forms a bilayer structure with sheet-like dimensionality, Fig. 1, in which both faces display hydrophilic head groups [14]. Such arrays are major components of complex membrane systems which allow for compartmentalization of reagents needed for kinetic control of chemical reactions with simultaneous dispersion in aqueous media. Alternatively, a bilayer membrane (or BLM — black lipid membrane) can be formed by painting an organic lipid solution across a small opening separating two aqueous solutions or by pulling a small loop through a lipid monolayer. The resulting structure is sometimes unstable and difficult to work with and its principal

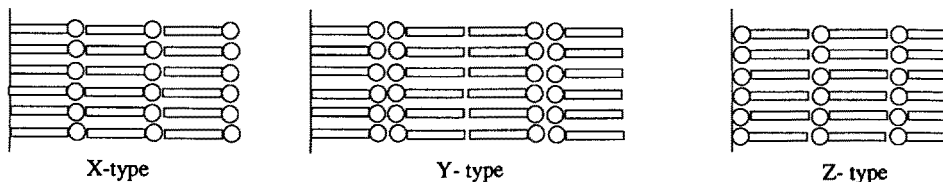


Fig. 2. Schematic representations of several types of order possible in Langmuir-Blodgett films

advantage is in mimicking the separation function of ordered membranes in biological systems. As in biological membranes, these arrays permit the characterization of ion transport consequent to the development of a photopotential. The name BLM reflects the black color caused by the appreciable light reflection of such membranes. Resistance and electrical capacitance measurements are generally used to define the thickness of such systems.

Irradiation of a membrane containing a photoactive electron donor in the presence of an electron acceptor held in the solution outside the membrane induces an electrical potential as shown schematically in Fig. 3. The attainable potential difference can be described as analogous so that attained by band bending of at a semiconductor surface (see below), which in turn depends on Fermi level equilibration of the electrochemical potentials of the solid and the standard A/A^- electrochemical potential of the couple. This electrical gradient, in providing a driving force for electron migration to reestablish dark equilibrium conditions, effectively rationalizes photoinduced charge separation across bilayer or liposome membranes.

A spherical three-dimensional dispersion of such bilayers forms a vesicle, Fig. 1, in which a water pool can be formed both inside and outside the ordered array [15]. Synthetic vesicles often have dimensions between 500 and 1000 Å. The component surfactants employed in forming vesicles (rather than bilayers) usually

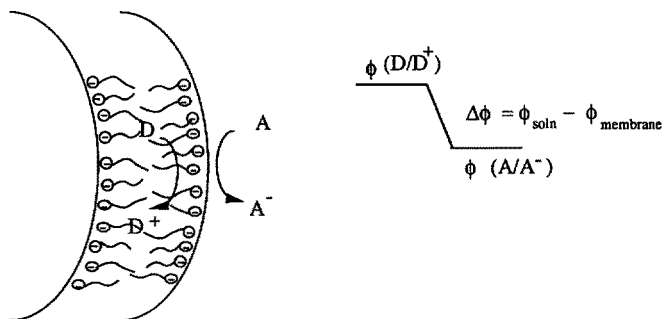
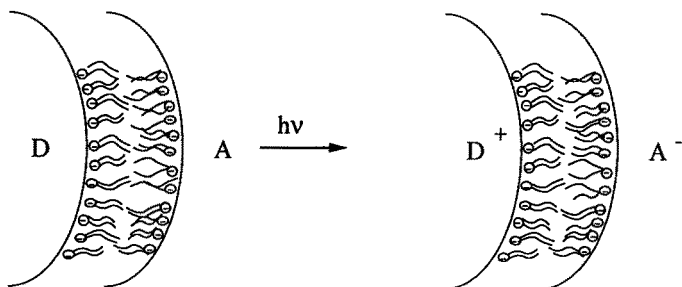


Fig. 3. Electrical potentials at the surface of a vesicle immersed in a solution containing a poised redox couple

have two long alkyl chains attached to a polar head group. The resulting structure is analogous to a liposome formed from similar orientation of naturally occurring phospholipids. The membrane separating the core of the vesicle from the outside reagents thus provide a physical barrier for the products generated in the photoinduced electron transfer, Scheme 7. This barrier also allows for different concentrations of reagents or separate locations for operative catalysts to be placed inside and outside of the vesicle.



Scheme 7. Spatial separation of the radical ion pair formed via photoinduced electron transfer across a bilayer membrane

Depending on the thickness of the vesicle-enclosing membrane, photoexcitation can either permit direct or mediated electron transfer through this insulating wall. Dissolved electroactive mediators or electron carriers contained within the membrane itself can thus be examined as models for biological redox mediators. The restricted volume of the inner core of the vesicle may also allow for controlled growth of reagents or catalysts to a desired size. Where size effects cause perturbation of the electronic properties of a thermal- or photocatalyst (see Sect. 4), this constrained environment will obviously influence the course of reactions involving such catalysts as either photosensitizers or as media for influencing subsequent dark transformations.

Polyelectrolytes represent the polymeric analogs of charged surfactants bound to a common insulating backbone [16]. The coiling of the polymer backbone can provide an environment in which the charged side chain groups remain either randomly oriented (in a well-solvated system) or intramolecularly aggregated to form inverse micelle-like islands. These microscopic regions represent pools for spatial ordering with differential microviscosity and electrical fields than are experienced within the bulk solution. Such coiling can sometimes be altered by pH changes or by the presence of inert counterions. These reagents thus induce altered surface charge and hence gradients in the effective electrical field. Parallel reaction control to that attained in micelles can thus be accomplished. Non-charged polymers can also influence photoinduced electron transfer by providing microscopic domains in an otherwise homogeneous solution or by acting as solid matrices in which diffusional effects can be separated by other perturbations.

3.3 Semiconductor Surfaces

Inhomogeneity can also be attained by dispersal of photoactive solids within a liquid support medium or by conducting the photoreactions at the surface of a semiconductor particle. Although the use of semiconductors themselves as vehicles for photoinduced electron transfer is an important area per se, we will discuss in this article (for reasons of space) only those reactions of semiconductors occurring when these photocatalysts are contained within a support which itself is inhomogeneous. In this section we present a brief overview of photoinduced electron transfer occurring on semiconductor surfaces. The interested reader should consult any of several excellent review articles on this topic for more extensive coverage [17, 21, 22].

Particles can be broadly classified as either colloids or as macroparticulate powders. Colloids typically have dimensions smaller than 1000 Å and are optically transparent, while dispersed powders are generally larger and form turbid suspensions. Neither colloidal dispersions nor powder suspensions are usually monodisperse, and to the extent that particle size can influence attainable surface charge and area, many such systems will typically reflect a distribution of properties as a function of preparation method. Recent advances in synthetic techniques for providing materials with reduced polydispersity are likely to allow for better characterization of these effects in the near future.

The colloidal or powder particle can be composed of either insulating, semiconductive, or conductive molecules. While only semiconductor particles are likely to be photoactive per se (by virtue of the energy gap between the filled valence band and the vacant conduction band), photoactivity of adsorbates can be mediated at the surface of other solids [18] which are often used themselves, or in conjunction with an irradiated semiconductor, as catalytic sites for alteration of kinetics of dark reactions initiated by photoexcitation.

Irrespective of the nature of the component molecule of the solid particle, surface charge is induced by bringing a polarizable solid into contact with a polar liquid, and the magnitude of the surface effect will depend on the surface area. Fractal geometry can be effectively employed to describe surface irregularity and molecular accessibility to the surface [19]. Since a large number of experimental variables (e.g., particle size, distance between adsorbates, diffusional distance, etc.) can be used in a power law expression to relate an observable to surface characteristics, an accessible model for employing surface charge for controlling photoinduced charge separation is available. Adsorption onto photochemically inactive supports is often governed by a Langmuir adsorption isotherm [20], and since such effects are also quite sensitive to surface charge, the same experimental variables which proved to be useful in manipulating micellar surface charge will also be operative with solids. Charge transfer reactions occurring in the vicinity of this highly polarized surface will be similarly affected.

An appreciable space-charge layer also develops upon dispersion of a semiconductor into an electrochemically poised redox solution [21, 22]. The valence and conduction band edges of a given semiconductor will be characteristic of the individual material. Shown in Table 1 is a summary of the band edge positions

of a number of common semiconductors in contact with aqueous inert electrolyte at pH 1 [23]. In general, these values are obtained from flat band potentials derived from capacitance measurements. Of the materials shown, the metal oxides are most stable under continuous illumination, but their wide band gaps preclude excitation with incident wavelengths longer than the long wavelength end of the ultraviolet spectrum. Smaller band gap materials tend to photocorrode, a reactivity which mitigates against their long term stability and complicates their photocatalytic activity.

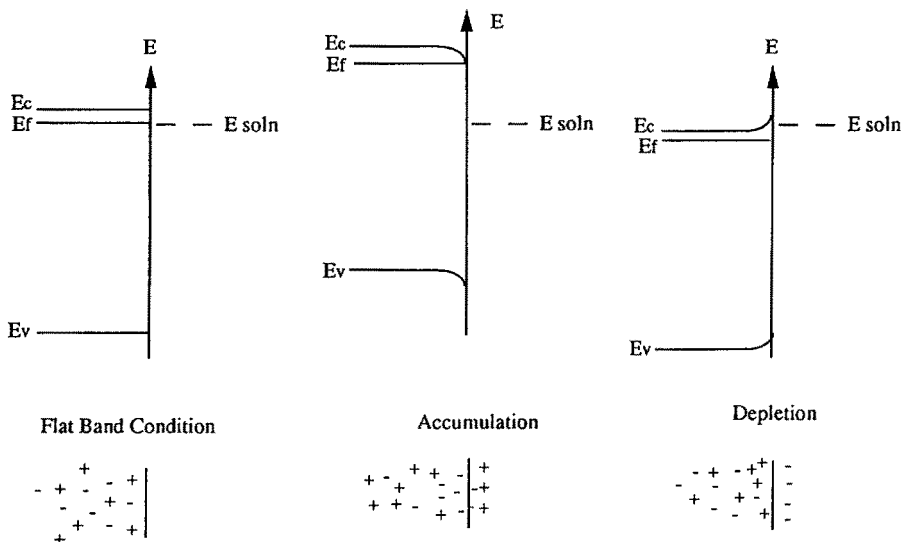
Table 1. Band Positions [23] for Some Common Semiconductor Photocatalysts^a

Semiconductor	Valence Band (V vs SCE)	Conduction Band (V vs SCE)
TiO ₂	3.1	-0.1
SnO ₂	4.1	+0.3
ZnO	3.0	-0.2
WO ₃	3.0	+0.2
CdS	2.1	-0.4
CdSe	1.6	-0.1
GaAs	1.0	-0.4
GaP	2.2	-1.0
SiC	1.6	-1.4

^a In water at pH 1

In an undoped (intrinsic) semiconductor, the Fermi level can be described as equidistant between the flat bands. In an n-type (negatively doped) semiconductor, the Fermi level moves to a position quite close energetically to the conduction band edge, and in a p-type (positively doped) material, the Fermi level can be approximated by the top of the valence band edge. The flat band condition of a doped semiconductor will be altered by bringing it into contact with a poised redox couple dissolved in a contacting electrolyte solution, which induces band bending to form an excess of either negative or positive charge at the surface of the semiconductor (an accumulation or depletion layer), Scheme 8. Band bending at the surface, via interfacial equilibration of the semiconductor bulk and the electrolyte, induces electrical surface charge by the motion of mobile charge carriers across the interface.

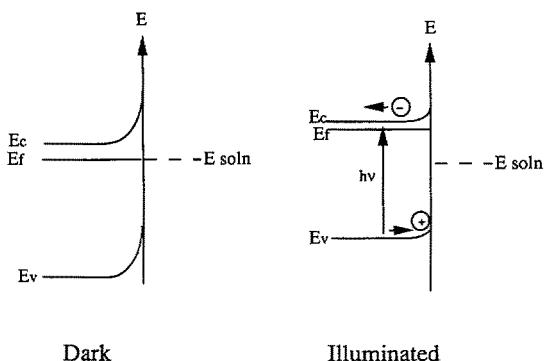
Band gap photochemical excitation of a semiconductor particle promotes an electron from the valence band to the conduction band, thus forming an electron-hole pair. Under illumination, the bands shift from their dark equilibrium positions to ones closer to the flat band condition, Scheme 9. Here the chemical potential of the electrons becomes different from that of the holes and a photovoltage develops. The concentration of free carriers, and hence of the number of available redox equivalents, will depend linearly on the incident light intensity. The free energy of these charge carriers will be related to



Scheme 8. Space-charge layer formation at a semiconductor-electrolyte interface

the chemical potential of the band edges, in that the band edges define thermodynamic limitations of the available photoinduced redox activity. These values represent internal potentials rather than free energy as a result of configurational entropy caused by the large number of translational states available to the mobile charge carriers.

Although the free energies of the electron-hole pair will therefore be slightly lower than the band gap energies, the band positions can nonetheless be used as crude descriptors of permissible redox reactions. Thus, on an irradiated semiconductor suspension, the valence band edge will establish the photogenerated hole's oxidizing potential and the conduction band edge will dictate the reducing power of a photogenerated electron. Thus, oxidative trapping of the photo-



Scheme 9. Band bending in the dark and under illumination in an n-type semiconductor immersed in a poised electrolyte

generated hole effects oxidation of an adsorbed donor and reductive trapping of the photogenerated electron induces reduction of an adsorbed acceptor, Fig. 4 [21]. This description is equivalent to one describing the respective half reactions as electron and hole injection into the irradiated semiconductor. This picture for describing interfacial electron transfer derives from electrochemical potentials maintained within an electrochemical cell, but an analogy between the space-charge layer developed upon irradiation of a poised semiconductor electrode can be extended to the "short-circuited" cell formed by depositing a metal island (parallel to the dark counterelectrode in a two compartment cell) on a semiconductor powder or colloid [24]. Even here a further simplification allows parallel photoelectrochemical activation on a non-metallized powder so long as the rates for electron and hole trapping can be kinetically distinguished.

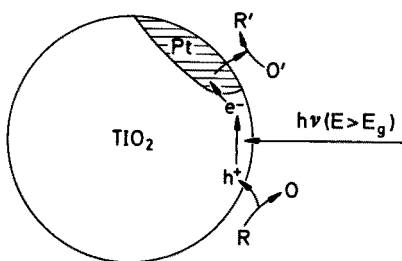


Fig. 4. A semiconductor powder as a short-circuited photoelectrochemical cell [21]

The efficiency of such photocatalysts in influencing charge separation will depend sensitively on the dynamics of interfacial charge transfer, particularly as compared with the rate of electron-hole recombination. The presence of trap sites and dopants will profoundly influence the latter rates, and quantum yields attainable on such heterogeneous suspensions will clearly reflect such structural variants. A trapped carrier will possess a longer lifetime consistent with an enhanced ability to participate in charge transfer with a desired adsorbate.

We see therefore that photoactive semiconductor particles provide ideal environments for control of interfacial electron transfer. Photoinduced electron-hole pairs formed on irradiated semiconductor suspensions, as in photoelectrochemical cells, allow for reactivity control not available in homogeneous solution. This altered activity derives from controlled adsorption on a chemically manipulable surface, controlled potential afforded by the valence band edge positions, controlled kinetics by virtue of band bending effects, and controlled current flow by judicious choice of incident light intensity.

In subsequent sections, we shall see examples of how organized media, with or without suspended semiconductor photocatalysts, can be used to influence the efficiency of charge separation and hence the observable chemistry occurring consequent to photoinduced electron transfer.

4 Charge Separation in Micelles

We can now consider specific examples of micellar influence on the course of photoinduced electron transfer [25, 26]. The simplest photoinduced electron transfer involves photoionization, i.e., the transfer of an electron from the excited state of a solute to the solvent. The next level of complexity involves electron transfer from an excited donor to an acceptor or from an excited acceptor to a donor. Such reactions can occur either within a photoinert micelle, in a functionalized assembly, or through multicomponent arrays.

4.1 Normal Micelles (Oil-in-Water)

4.1.1 Photoionization

If a photoactive probe molecule is buried in the core of an anionic micelle, biphotonic excitation generates an upper excited state from which electron ejection to solvent can occur. With pyrene (Py) imbedded within a sodium lauryl sulfate micelle (NaLS), for example, electron ejection to form a hydrated electron occurs, Eq. 6 [27].



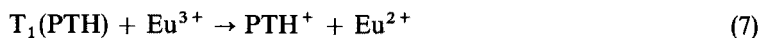
The back reaction in which the electron recombines with the pyrene cation radical is retarded by the negative surface charge of the micelle, while it occurs readily if the same reaction is conducted in neutral or cationic micelles. Parallel results are also observed with monophotonic ionization. *N,N,N',N'*-Tetramethylbenzidine [28] and chlorophyll [29] can be ionized in NaLS by sunlight: the slower back reaction permits the hydrated electrons to split water in the former case, evolving hydrogen. In the parallel ionization of perylene, a much steeper photoionization yield at energies above threshold was observed in anionic micelles than in neutral or cationic ones [30]. Similar electron transfer to solution can also be induced by irradiation of metal ions contained within surface-charged micelles [31]. Since the reactive excited states involved in photoionization are so short-lived, it is quite likely (and in some cases mandatory) that the requisite electron ejection involve long range tunnelling.

The solubilization site in the micelle can also influence the ionization efficiency. Kevan et al. have shown, for example, that in frozen solutions (where mobility is restricted) the ionization efficiency of several benzidine derivatives was greater in cationic than anionic micelles since the position of the electron rich neutral starting material was closer to the positively charged interface [32]. The yield in anionic micelles could be improved by counterion exchange: with larger, more charge diffuse tetraalkylammonium ions bound at the surface of the negatively charged micelle, greater water penetration was thought to occur, thus shortening the distance which the ejected electron would have to traverse before being solvated. Electron spin resonance and electron spin echo modulation studies have shown that the inclusion of 1-butanol in such micelles can alter the micelle's hydration

and the efficiency of charge separation as a function of surfactant head group density [33]. That interfacial solvation in such ionization processes can be followed by time-resolved Raman scattering has been demonstrated by Brus and coworkers in a study of the photoionization of tetrathiafulvene in micellar solution [34].

4.1.2 Transfer Between Donors and Acceptors

A more general case for describing micellar effects on photoinduced electron transfer involves a micelle-included donor (or acceptor) interacting with an acceptor (or donor) held in the Stern or Gouy-Chapman layers surrounding the micellar aggregate. A time-resolved investigation of the reaction of phenothiazine (PTH) included within the core of a sodium dodecyl sulfate (SDS) micelle revealed that, upon excitation and after intersystem crossing, triplet PTH transferred an electron to surface-associated Eu^{3+} , Eq. 7, in a process



which followed neither straightforward first nor second order kinetics [35]. The first order process was greatly accelerated by virtue of the close proximity of the reagents caused by the micellar order. Since both products remained associated with the micelle, a rapid back reaction also occurred. The proper kinetic analysis of the data required inclusion of a term describing average micelle occupancy, a situation frequently encountered in analogous systems [36]. No unambiguous evidence for long range electron tunnelling has yet emerged.

Sustained charge separation requires more significant differentiation of the rates of the forward and back electron transfers, rather than a mere parallel acceleration [37]. As in homogeneous solution, one method for differentiating these rates is to allow a competing dark chemical reaction to destroy the product of the electron transfer. In the debromination of 2,3-dibromo-3-phenylpropionic acid, for example, a micelle can amplify differences in the rates seen in homogeneous solution [38]. A route which exploits the surface potential of the micelle, however, uses the surface to separate the photogenerated ion pair [39]. For example, solubility differences of the redox participants before and after electron transfer can be used to separate the products, as in a water-soluble porphyrin and a reduced viologen [40]. Viologens [41] and quinones [42] have been especially extensively studied in such systems, and to a lesser extent aromatic hydrocarbons [43], biologically important molecules (such as chlorophyll [30, 44] and NADH [45]), and metal ions [46] have been similarly employed. With the latter substrates, micellar complexation even allows for stereoselectivity in the electron transfer [47].

The inhomogeneity of the micellar aggregate also affords assisted spin trapping and the exploitation of magnetic field effects on the charge separated ion pairs [48]. Optical modulation spectroscopy can be used, for example, to follow the decay of radicals formed in homogeneous solution and in SDS micelles. Enhancements of a factor of about 50 in the lifetimes and the steady state concentrations of the radical were observed in the micelle, and a kinetic analysis led to a value of $2 \times 10^3 \text{ s}^{-1}$ for the exit rate constant from the micelle [49].

Spectroscopic methods can be used to specify the position of donors and acceptors before photoexcitation [50]. This spatial arrangement can obviously influence the equilibrium complexation in charge transfer complexes, and hence, the optical transitions accessible to such species [51]. This ordered environment also allows for effective separation of a sensitizing dye from the location of subsequent chemical reactions [52]. For example, the efficiency of *cis-trans* isomerization of *N*-methyl-4-(β -styryl)pyridinium halides via electron transfer sensitization by $\text{Ru}(\text{bpy})_3^{2+}$ was markedly enhanced in the presence of anionic surfactants (about 100-fold) [53]. The authors postulate the operation of an electron-relay chain on the anionic surface for the sensitization of ions attached electrostatically. High adsorptivity of the salt on the anionic micelle could also be adduced from salt effects [53, 54]. The micellar order also influenced the attainable electron transfer rates for intramolecular and intermolecular reactions of analogous molecules (pyrene-viologen and pyrene-ferrocene) solubilized within a cationic micelle because the difference in location of the solubilized substances affects the effective distance separating the units [55].

Among the practical consequences of micellar-contained electron transfer systems are the photocatalytic evolution of hydrogen [56], the containment of photoactive semiconductors within the protective micellar core [57], and the use of such systems as kinetic models for mechanistic characterization of light-responsive redox herbicides [58].

It should also be noted that the biphasic core of a micelle can also be itself approximately described by the hydrophobic cavity formed at the inside of a cyclodextrin dissolved in aqueous media. As with micelles, cyclodextrins are known to effect dissociation of ground state complexes, rates of electron transfer, the efficiency of charge transfer, and the evolution of hydrogen gas [59] as well as orientational effects in organic photochemistry [60].

4.2 Inverse Micelles (Water-in-Oil)

The organizational structure of inverse micelles would suggest that similar electrostatic and spatial effects should be operative. The existence of a water pocket in these aggregates, however, makes these structures more appropriate models for characterizing the critical features of aqueous microphases in hydrophobic environments such as found within living cells. As might be expected from the preceding considerations, the organization in these structures allows for kinetic differentiation of the forward and back electron transfer rates [61]. For example, the kinetic competition between back electron transfer and escape of radical products from the water pool was shown to depend on the water pool size [62]. Spin systems involving triplets showed slower back electron transfer rates in the presence of a magnetic field, since the field can split the degeneracy of the triplet radical pair, thus inhibiting intersystem crossing. Since recombination is spin-forbidden in the triplet manifold, this in turn will allow for escape to compete more effectively with back electron transfer.

Charge separation again relies on the alteration of hydrophobicity upon electron exchange. For example, if a cationic sensitizer ($\text{Ru}(\text{bpy})_3^{2+}$) is dissolved in the water

pool along with a sacrificial donor, photoexcitation can cause electron migration, via an amphiphilic viologen relay, the ultimate acceptor held outside the inverted micellar aggregate [63]. The key feature for successful operation of this array was the driving force for the reduced viologen to move from the water pool to the outside of the structure. Spatial segregation exerts similar influences on the excited state interactions of porphyrin-quinone systems oriented within reverse micelles [64].

The kinetic complexity seen in oriented micelles persists in inverse micelles. The distribution of electron transfer quenchers within the water pool follows Poisson statistics and enables the kinetic data to describe migration rates to and from the aqueous subphase [65]. These orientation effects also make possible topological control of non-electron transfer photoreactions occurring within AOT micelles [66].

As in normal micelles, practical consequences of photoinduced electron transfer within this environment can be exploited. For example, photoactive semiconductors can be formed in situ within the water pool [67] and radical polymerization can be initiated via photoinduced electron transfer with sensitizers held within the water pool [68].

4.3 Microemulsions

The multicomponent version of an inverse micelle is a water-in-oil microemulsion and that of a normal micelle is an oil-in-water microemulsion. Not unexpectedly, the similarities between such microemulsions and micelles are striking. Their principal advantage over conventional micelles is in their much higher capacity for enhancing solubility of desired substrates. The presence of the additional components, e.g., a co-surfactant, does decrease, however, the attainable surface charge, which in turn makes the dynamic interchange of organizes more facile. Thus, compartmentalization is less secure and sometimes normal kinetics can be observed in microemulsions.

Nonetheless, sensitization by dyes held within the cores of microemulsions can be easily accomplished [69]. Such sensitization is an important component of photogalvanic effects, the magnitude of which are significantly enhanced in the non-homogeneous environment of a microemulsion [70]. The hydrophilic core of an water-in-oil microemulsion can concentrate cation radicals formed via interfacial electron transfer and hence increase the yield of subsequent dimerization: the dimethylnaphthalene cation radical exhibits a dimerization equilibrium constant of nearly 500 in a microemulsion [71]. For similar reasons, hexylviologen acts as a much more efficient relay than methyl viologen in a CTAB/hexanol microemulsion [72].

Dynamics in a microemulsion must differentiate those reactions occurring between donor-acceptor pairs co-included within the core and those in which one redox component is inside and one outside the microemulsion. With duroquinone and diphenylamine, the first situation applies: here electron transfer was found to occur in two steps — a subnanosecond reaction from the singlet state and a slower reaction (requiring microseconds) from the triplet manifold [73]. With methyl viologen and *N*-methylphenothiazine, the second situation applies, and while two

kinetic pathways are again observed, the local separation of radical ions of opposite charge type as a consequence of the difference between the electrostatic potentials prevailing in the droplets and in the bulk solution could be clearly seen. Analogous reasoning has also been applied to explain the picosecond absorption spectra of dyes in microemulsions [74].

Chemical reactions conducted within microemulsions occur with the same modes of control afforded by micelles. Thus, photoactivity of semiconductors [75] and metal colloids [76] formed within microemulsions are maintained, as is the capacity for initiation of photooxidative polymerization [77].

5 Charge Separation in Layered Structures

In Fig. 2 in Sect. 3.2 were shown several complex assembly patterns which can be formed by organizing amphiphilic molecules (bearing long hydrocarbon tails and polar head groups) via appropriate pressure-area isotherms [6b, 78]. In this section is described the use of such organized environments in controlling photoinduced electron transfer.

5.1 Monolayers

Although techniques for forming monolayer assemblies have been known for over fifty years [13], their application in the study of energy and electron transfer in organized media has occurred mainly within the last two decades. Kuhn and coworkers have shown that sequential deposition of ordered monolayers allows for construction of well-defined arrays with fixed structures and geometries [79]. With these assemblies, for example, the distance for electron transfer can be varied by interspersing a defined number of fatty acid layers. Such studies revealed an exponential decrease of the rate of electron transfer with distance between donors and acceptors held on opposite sides of the multilayer assembly with the magnitude of the exponent (the β value) changing only slightly with differing measuring techniques. For example, the dark conductivity through one fatty acid layer of varying chain length gave a β value [80] of $1.5 \text{ \AA}^{-1}$, a value comparable to that seen in covalently bound donor-acceptor molecules separated by an insulating hydrocarbon framework [81]. Driving force dependence similar to that observed in homogeneously dispersed systems has been also noted [82]. Analogous effects have also been seen in characterizing energy transfer in Langmuir-Blodgett films [83].

When amphiphilic dyes are incorporated into such monolayers, their fluorescence properties can be used to characterize the organization of the array [84–87]. An amphiphilic cyanine dye used in this way showed a much lower distance damping factor (β value) between layers containing the donor cyanine and the acceptor viologen ($\beta = 0.3$) than is usually observed in fixed donor-acceptor systems [88]. An even smaller β value was obtained from photocurrent measurements in monolayer assemblies containing amphiphilic porphyrins ($\beta = 0.005$) [89]. The former value was attributed to electron tunnelling occurring in parallel

with dispersive transport of carriers in disordered solids or in sensitized hole injection into organic single crystals [90]. The latter very low value was assigned to superexchange, i.e., orbital mixing of high lying vacant orbitals of the intervening insulator with the coupling matrix elements of the donor and acceptor. Contributions of trans-layer diffusion of excimer-forming amphiphiles [91] was not specifically considered in either model.

The monolayer also provides an environment of variable dielectric so that intermolecular association between photoactive molecules can readily occur. For example, molecular association of pyrene within a Langmuir-Blodgett film is clearly seen through time-resolved fluorescence measurements on the picosecond timescale [92]. Attenuated total reflectance studies of dyes in cast films can similarly reveal their positions and photophysical interactions [93]. Photochromism in a monolayer assembly has been attributed to excitation of ion-pair charge transfer complexes formed within the array [94].

5.2 Bilayers

Bilayers represent the simplest organizational array which can approximate the compartmentalization of the membrane coverage of a cell. Understanding electron transport in bilayer systems is thus of great interest to those interested in biomimetic chemistry. Closed bilayers are called vesicles and are considered in the next section: here we consider planar bilayers. As discussed earlier, planar bilayers are sometimes difficult to work with because of their kinetic instability, and the most fruitful studies employing these arrays have used membranes partitioning two aqueous solutions. These structures are often referred to as BLMs or black bilayer lipid membranes from their intensive refractive color. The key studies which initiated interest in these structures were observations of photocurrents produced upon irradiating BLMs separating two solutions containing substrates of different chemical potentials [95–99]. Substantial photovoltages can be observed in some cases almost equal to the potential differences between the couples on opposite sides of the barrier [14a]. An electrostatic gradient can be established by irradiating to generate charge carriers or by using ionophores [100], such as valinomycin, which can render the membrane permeable to ions so that a direct comparison can be made between chemically and photochemically driven electron transport [101].

A trans-membrane redox process can be stimulated by irradiation of a sensitizer which initiates electron transfer within an appropriate donor-acceptor pair. The efficiency of the charge transport can be improved if an amphiphilic relay molecule is contained within the bilayer to carry electrons from one face to the opposite [102–105], although electron exchange can still occur even in the absence of a relay. The kinetics for charge transfer, for example, correlates with the solubility of viologen acceptors accessible to the bilayer surface [106]. As in the charge repulsion effects described earlier for micelles, the efficiency of charge transfer was predicated on favorable electrostatic interactions between the charged acceptor and the positively or negatively charged surface of the bilayer [107]. Direct electron release from dyes contained within the bilayer have been observed with

carbazole-containing bilayers [108, 109] and from lipids to dye acceptors dissolved outside the bilayer [110].

Photophysical studies allow the measurement of rate constants for trans-membrane electron transfer. The distributed kinetics observed in describing the decay of photovoltage across a BLM is consistent with a highly inhomogeneous disposition of donors and relays within the membrane [111, 112]. A typical value for the rate constant for electron transfer across a BLM (about 10^4 sec^{-1}) would predict a spatial separation of about $10 \text{ \AA}$, whereas the thickness of the bilayer is usually about $40\text{--}50 \text{ \AA}$. This apparent discrepancy can be resolved if transmembrane electron transfer occurs by several sequential steps involving deeply buried redox sites, thus decreasing the operational tunnelling distance [113].

The structure of the BLM can be altered by introducing microcrystalline aggregates or films of inorganic metal sulfide semiconductors in the BLM [114]. The resulting film, which was about $1000 \text{ \AA}$ thick and penetrated the BLM by about $17\text{--}18 \text{ \AA}$, was stable for days and produced stable photovoltages upon band gap excitation. Such semiconductor-loaded films could be polymerized via photochemical sensitization by band gap excitation of the semiconductor [115].

Although the quantum yields for trans-bilayer electron transfer are often low in functionalized BLMs, several cases have been reported in which reasonable efficiencies have been observed. For example, Ford and Tollin report a 20% efficiency for charge separation in a bilayer containing chlorophyll *a* and glutathione [116] and Parmon et al. claim a 57% efficiency in a zinc tetraphenylporphyrin-methyl viologen system [117]. As in other organized media, the interior of a bilayer assembly can influence intermolecular association, with enhanced excimer formation occurring as a function of changes in lipid microviscosity [118]. Magnetic field effects can also modify interfacial electron transfer dynamics [119]. It is also important to realize that trans-membrane electron transfer can be expressed in the generation of chemical redox systems, as in the formation of oxygen from the photosensitized oxidation of water [120]. Here the bilayer not only acts as a vessel for photosensitization but also as a site for accumulation of charge necessary for this multielectron event. An unfortunate complication in such photoinduced electron transfer is the photochemical lysis of the structure of the bilayer, which can introduce leakage and disrupt the interfacial potential [121]. If microcrystalline semiconductor particles are generated on one side of a BLM, however, the resulting array is stable for several days and sustainable photovoltages can be produced [114, 122].

5.3 Vesicles

The three dimensional analogue of a BLM is a vesicle, Fig. 1. Like the bilayer, the wall thickness of a vesicle is typically about $50 \text{ \AA}$ and the vesicle itself may be 300 to $1000 \text{ \AA}$ in diameter. This spatial arrangement makes possible the formation of two phases inside and outside the wall with different chemical compositions. Although the permeability of a typical membrane by water is relatively high (ca. 10^{-2} cm/sec), that of ions and small neutral molecules is much lower (Na^+ :

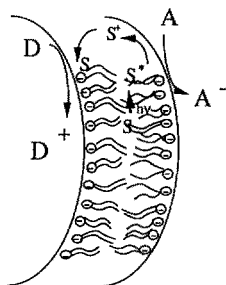
10^{-12} cm/sec; glucose: 10^{-6} cm/sec). Thus, many of the same features of transmembrane electron transfer observed in bilayers will be retained within vesicles, but since the components of the vesicle can be polymerized [123], these three dimensional structures can be prepared in more stable form (shelf lives up to several months). As a result, chemical changes in the solutions inside and outside the vesicle walls can be more readily studied.

Several photoprocesses can be considered operable in functionalized vesicles [124]: reactivity changes caused by orientation of chromophores within the vesicle bilayer itself, those caused by ion transport through the polarized membrane, those induced by photoinduced electron transfer, and those initiated by photoexcitation of semiconductor particles held within the inner core of the vesicle. The first type is exemplified by differences in stereochemistry and quantum efficiency for photodimerization of amphiphilic cinnamic acid derivatives in oriented vesicles [125]. Per se, this orientational effect is not related to photoinduced electron transfer except in so far as orientation influences the relative positions of donors, acceptors, and relays in the assembly.

The photoinduction ion flux derives from the similarity of vesicle systems to the proton flux in halobacterium halobium cell envelopes in the bacteriorhodopsin photocycle [126]. Liposome permeability to glucose can similarly be induced by photoexcitation in vesicles containing polyacetylene or thiophene as ion mediators [127]. As in planar bilayers, the surface charge [128] of the vesicle and the chain length of the component surfactant [129] influence association between the donor-acceptor pairs, and hence the distance of separation of components inside and outside the vesicle walls.

For interests of this article, the most important effect of the vesicular bilayer is in retarding back electron transfer from the components generated by photoinduced electron transfer between donors inside the vesicle to acceptors held in the outside pool, as mediated by relays contained within the walls. In almost all cases, a sacrificial donor is used in conjunction with a photosensitizer and an acceptor. The system's irreversibility derives from the irreversibility of the spatially segregated sacrificial donor, which undergoes a fast chemical dark reaction after charge transfer to the photosensitizer excited state or to the oxidized photosensitizer. A list of common photosensitizers would include chlorophyll a, pheophytin, $\text{Ru}(\text{bpy})_3^{2+}$, metal porphyrins, and phenothiazines; some typical donors are EDTA, water, ascorbate, oxalate, glutathione, amines, and NADH; acceptors include high oxidation state metal ions, quinones, and viologens [48, 62, 63, 65, 69, 70, 72, 73, 74, 114, 130].

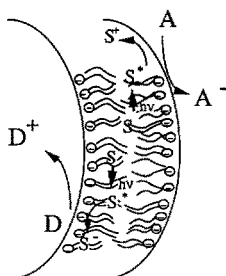
Shown in Schemes 10 and 11 are operational descriptions of photoinduced charge transfer in vesicles. In Scheme 10, the absorption of a single photon generates an oxidized sensitizer which migrates through the bilayer wall to interact with the donor. In Scheme 11 is presented an alternative two photon route in which each redox half reaction is stimulated by light absorption, with a relay molecule carrying charge between the donor and acceptor pair. Distance dependence seen in such systems is analogous to that observed in bilayers, with much smaller effective distances than encountered in the bilayer breadth [131]. Although charge transfer is commonly assumed to occur via electron transfer, rather than via



Scheme 10. Photoinduced electron transfer (one photon) across a vesicle membrane

photosensitizer diffusion, it has been argued that inclusion of the amphiphilic sensitizer may perturb the structure of the vesicular wall, permitting looser membrane interactions and possibly allowing the sensitizer to “flip-flop”, i.e., move within its lifetime from one side to the other.

Clearly the operation of the two photon process exemplifies the possibility of using the non-homogeneous array to induced multiple electron redox processes. For example, the simultaneous formation of gaseous hydrogen and oxygen upon irradiation of a vesicular donor-acceptor system has been reported [132]. The spatial inhomogeneity of the vesicle also allows semiconductor particles and catalysts [133] for charge accumulation to operate in conjunction with the array. The vesicle has been used, for example, to constrain the *in situ* growth [134] of a semiconductor particle so that quantum effects can be observed [135]. These photoactive semiconductors (see Sect. 7.2) can be further modified by deposition of metallic co-catalysts for effective charge accumulation and so permit hydrogen evolution [136]. Metallic colloidal catalysts can themselves be formed inside the vesicle core for use in secondary dark catalytic reactions [137], and the recent demonstration of the synthesis of mixed colloidal suspensions offers an opportunity to fine-tune the band gap of the included semiconductor photocatalyst [138]. This inclusion of electroactive particles also permits simultaneous direct optical and electrochemical determination of diffusion rates of redox couples present during photocatalysis [139].



Scheme 11. Biphotonic electron transfer across a bilayer membrane containing donor and acceptor on opposite sides. The oxidized and reduced sensitizer S can regenerate ground state either by back reaction or by electron exchange with an added relay

5.4 Liquid Crystals

The partial order available in liquid crystalline phases makes them very attractive as media for controlling anisotropic electronic motion. Although liquid crystals have been effectively used as solvents for probing photochemical mechanisms [140], most photochemical and photophysical studies of liquid crystals have involved spectroscopic probes to determine structure and degree of order in the anisotropic phase [141]. The recent observation, however, that applied electric fields can influence fluorescence intensity of chromophores contained within liquid crystals [142] and that directional migration of energy and singlet and triplet excitons occurs in columnar mesophases [143, 144] suggest that directional electron transfer should also be possible. Indeed, more efficient exciton migration is found in liquid crystals than in crystals, and the possibility that exciton path lengths may be controlled by columnar continuity has been considered [143].

The recent description of the construction of a solid state photocell [145] based on order attained via a columnar mesophase of a liquid crystalline porphyrin [146] represents one application of photoinduced electron transfer within organized media which may prove to be fruitful in the future in the burgeoning area of molecular electronics.

6 Charge Separation in Polymers

Polymers represent the single molecule analogues of self-assembled multi-molecule arrays discussed so far. We consider two classes of polymers which have been usefully employed in photoinduced electron transfers: those in which ionized (or ionizable) side groups provide a mechanism for alteration of the environment surrounding a photochemically activated molecule and those in which the polymer is used as a support structure for the photo-redox participants.

6.1 Polyelectrolytes

Polyelectrolytes as polyionic molecules with high charge density which generates a strong electric field, have long been recognized as effective media for controlling light induced electron transfer [16, 147]. Because of the availability of an excellent review [16] on this subject, the salient features operative in controlling electron transfer will be merely summarized here. Most such effects have derived either from compartmentalization of the redox participants [148] or from electrostatic partitioning to retard back electron transfer [149]. For example, the rates of electron transfer between donors and acceptors bearing the same charge can be dramatically enhanced (by as much as five orders of magnitude by polyvinylsulfate for electron transfer between metal cations [150]) by the presence of an oppositely charged polyelectrolyte [151] or a corresponding retardation of the rate for similarly charged electrolytes. This effect has been ascribed to the concentration of the reagents in the small volume in which the polymer's electric field is felt. The polyelectrolyte may also desolvate either of the redox participants, minimizing the reorganization necessary to reach the transition state [152].

Enhanced electron transfer quenching has also been observed in copolymers containing both ionic and hydrophobic segments [153], probably as a consequence of static quenching from preferential binding of the redox participants in electrostatically favorable regions of the polymeric aggregate. The hydrophobic domains in such polymers act as traps for hydrophobic quenchers, while the hydrophilic interactions enhance dispersion and solubility [154].

Electron transfer rates are also significantly enhanced in biopolyelectrolytes such as DNA or proteins. For example, the quenching rate of ethidium by methyl viologen is enhanced by a factor of 5×10^5 by the presence of DNA [155]. The effect has been attributed to several factors including intercalation of the donor, immobilization of the acceptor, and structural features of the backbone by which DNA is likened to a polymerized micelle and a liquid crystalline polymer. The possibility of superexchange interactions in electron transfer reactions mediated by DNA has also been proposed [156]. Biphasic decay in time-resolved measurements has been ascribed to mobile metal ions loosely moving about the DNA helix in equilibrium with ions bound to the DNA phosphate groups [157]. Similarly, studies of electron transfer between metal ions associated with proteins have shown that both through-bond and through-space contributions are important [158].

When photoinduced electron transfer produces products of opposite charge, their physical separation will be enhanced by the presence of a charged polyelectrolyte, with the quantum yield for electron transfer increasing from zero to one in a particular dramatic example [159]. Similar effects will cause inhibition of back electron transfer as well, although the magnitude of these effects is often much smaller than in the photodriven reactions.

One or several redox-active centers can be directly bound to the polymer chain. Charge migration along a polyviologen chain, for example, significantly improves the yield of attainable charge transfer [160]. By synthetically varying the linking group between the viologen units, the viologen content of the polymer, or by attaching the viologen as a pendant group, chain flexibility can be reflected in the properties of the polyelectrolyte and hence in its electron transfer efficiency [161]. Charge transfer relays can also be used in mixtures containing several polymers to form systems with very large retardation of back reaction [162]. Polymers bearing a series of redox active relays can even further improve charge separation by providing an electron cascade to move electron density from the initial site of the donor-acceptor pair to a remote position [163].

6.2 Polymer Supports

We have already seen that photoactive clusters, e.g. CdS, can be introduced into vesicles and BLMs (Sect. 5.2 and 5.3). Similar support interactions are possible with both inorganic and organic polymeric supports. Photoactive colloidal semiconductor clusters can be introduced, for example, into cellulose [164], porous Vycor [165], zeolites [166], or ion exchange resins [167]. The polymer matrix can thus influence the efficiencies of photoinduced electron transfer by controlling access to the included photocatalyst or by limiting the size of the catalytic particle in parallel to the effects observed in polymerized vesicles. As in bilayer systems,

synthetic polymers can also be used as physical barriers between solutions of different compositions. Upon incorporation of a light responsive dye, potential changes similar to those observed in bilayers can be seen [168]. Polymers are also used effectively as means to prevent coagulation of *in situ* generated photocatalyst clusters and to envelop developing semiconductor particles to make possible the formation of ultra-small clusters [17].

7 Conclusions

Although the transfer of an electron is an elementary chemical event, its consequence on the reactivity of the reagents involved in the exchange is profound, inverting the normal electron demand of each participant. Photoinduced electron transfer provides a sensitive probe for excited state dynamics and the influence of the environment of the excited molecule on the course of both the primary photoinduced electron exchange and on the all-important thermal back electron transfer between members of the electron donor-acceptor pair. A non-homogeneous medium provides a unique arena in which sensitive environmental effects can be probed and altered. As practical applications of photoinduced electron transfer come increasingly to the fore, exploitation of these arranged media in providing order at the molecular level will be ever more important. The lessons to be learned from thorough studies of such photoinduced electron transfer reactions will be of significance not only to physical, organic, and inorganic photochemists but also to materials scientists and engineers. This article has provided but a brief summary of how self-assembled systems can be used, either alone or in conjunction with a molecular photosensitizer or semiconductor photocatalyst, as vehicles to enhance supramolecular interactions and observable chemistry. Many fascinating questions still remain.

8 Acknowledgements

This review was prepared as part of our research program on photoinduced electron transfer in functionalized polymers and at irradiated semiconductor surfaces. That research is funded by the Office of Basic Energy Sciences, Fundamental Interactions Branch, of the Chemistry Division of the U.S. Department of Energy.

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Photosynthetic Model Systems

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This review highlights recent studies of synthetic, covalently linked multicomponent molecular devices which mimic aspects of photosynthetic electron transfer. After an introduction to the topic, some of the salient features of natural bacterial photosynthetic reaction centers are described. Elementary electron transfer theory is briefly discussed in order to provide a framework for the discussion which follows. Early work with covalently linked photosynthetic models is then mentioned, with references to recent reviews. The bulk of the discussion concerns current progress with various triad (three-part) molecules. Finally, some even more complex multicomponent molecules are examined. The discussion will endeavor to point out aspects of photoinitiated electron transfer which are unique to the multicomponent species, and some of the considerations important to the design, synthesis and photochemical study of such molecules.

1 Introduction

Considering that photosynthesis is responsible for our oxygenic atmosphere, our fossil fuels and firewood, most of our food, and many of our raw materials, it is not surprising that mankind has long been fascinated by the possibility of mimicking this natural solar energy harvesting technology. Artificial photosynthesis has been the impetus behind much research since the early days of modern photochemistry [1]. For several reasons, significant progress has recently been made in the area. In the first place, great strides have been made in understanding natural photosynthesis. For example, new techniques in time resolved visible and magnetic resonance spectroscopies have allowed researchers to study the very important initial events in photosynthetic energy conversion which occur on the picosecond, or even the femtosecond time scale. In addition, X-ray crystal structure determinations have recently been carried out for several bacterial photosynthetic reaction centers [2], and the structural information provided by these studies is now being used in the design of biomimetic systems.

Paralleling progress in understanding the natural system have been advances in the synthesis of large, complex molecules, their separation using a variety of chromatographic techniques, and their characterization by nuclear magnetic resonance spectroscopy and mass spectrometry, as well as by the fast transient spectroscopic techniques mentioned above. Underpinning experimental work in both natural and artificial photosynthesis has been new knowledge of the theoretical bases of electron and energy transfer processes.

Although there are many valid approaches to mimicry of the natural photosynthetic apparatus in the laboratory, this review will concentrate on molecular systems of covalently linked chromophores, electron donors, and electron acceptors. In particular, molecular devices consisting of three or more such components will be examined. The discussion will be limited mainly to systems in which the pigments employed absorb visible light and are related to the naturally occurring photosynthetic pigments, although a good deal of interesting work with ultraviolet or blue light absorbing chromophores has also been reported. The examples chosen for discussion should help illustrate some of the factors important for the design, preparation and photochemical investigation of artificial photosynthetic materials. It will be seen that in the investigation of complex donor-acceptor systems one often encounters problems which are more severe than with simple monomeric or dimeric models. However, the more intricate molecules allow one to study phenomena which cannot occur in the simple systems. In addition, the examples discussed below will demonstrate the promise of artificial photosynthesis not only with respect to solar energy harvesting, but also from the point of view of the developing field of molecular electronics.

2 Natural Photosynthetic Electron Transfer

The heart of photosynthesis is the absorption of sunlight and the subsequent conversion of singlet excitation energy to chemical potential energy in the form

of long lived transmembrane charge separation. This process occurs in a photosynthetic reaction center, whose structure and function will now be briefly summarized. The reaction center consists mainly of protein, which is embedded in, and spans, a lipid bilayer membrane. Embedded in turn within the protein, but not covalently linked thereto, are a suite of small organic molecules which carry out the photochemistry. Structural information is now available for a class of bacterial reaction centers from several X-ray crystallographic investigations [2]. In these reaction centers, the relevant small organic molecules comprise four bacteriochlorophylls (Bchl), two bacteriopheophytins (Bph), two quinones (Q), and, in wild-type organisms, one carotenoid polyene (C). The spatial distribution of these components within the reaction center is depicted diagrammatically in Fig. 1. This arrangement is very important, because both energy and electron transfer are sensitive functions of donor-acceptor separation and orientation. It will be noted that with the exception of the carotenoid, the small molecules occur in pairs; indeed, the geometry of the reaction center as a whole comes surprisingly close to C_2 symmetry.

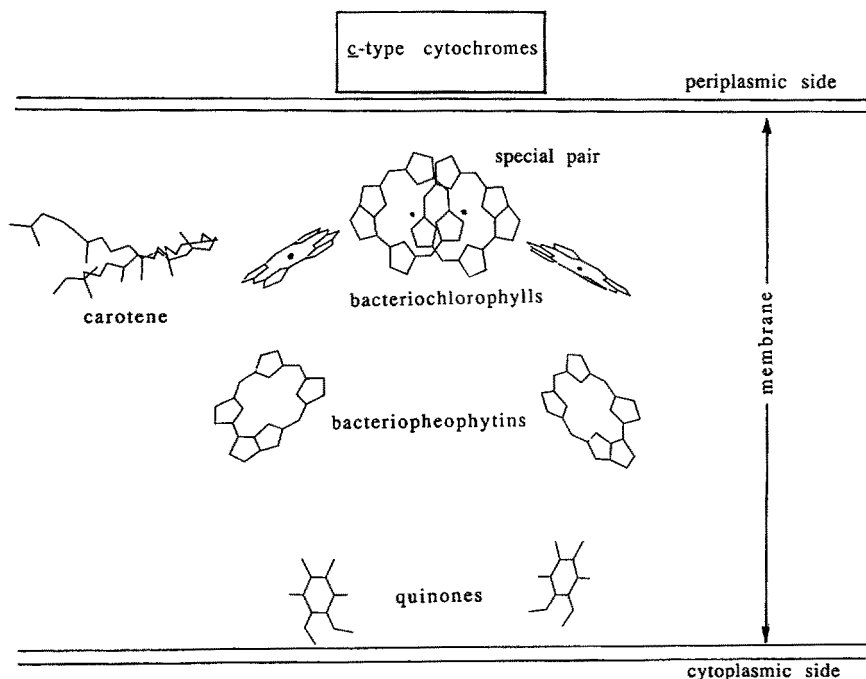


Fig. 1. Arrangement of the chromophores, electron donors, and electron acceptors in the bacterial reaction center of *Rhodobacter sphaeroides* [2f]. The horizontal lines at the top and bottom of the figure represent the approximate location of the surfaces of the lipid bilayer membrane

Within the reaction center, the photosynthetic process begins with excitation of the "special pair" of bacteriochlorophylls, which are located near the outside of the membrane, and are in van der Waals contact with each other. This excitation can be by direct absorption of light, but more usually occurs through singlet-singlet energy transfer from antenna molecules. A variety of these antenna systems exists in different organisms. In each case, the design of the antenna maximizes useful light harvesting under the environmental conditions of the organism in question. Light harvesting molecules employed in these antennas include chlorophylls of various types, other polypyrroles, and carotenoid polyenes. In all cases, the special pair functions as the energy trap for singlet excitation.

The ultimate goal of the reaction center is to use this excitation energy to move an electron across the bilayer membrane. This will produce a membrane potential together with long lived, energetic oxidizing and reducing equivalents; this chemical potential can then be exploited by the organism. However, electron transfer rates are sensitive functions of donor-acceptor separation, and transfer over the entire thickness of the membrane in a single step could not possibly compete effectively with the other processes which depopulate the Bchl excited singlet state. In order to overcome this very basic problem, the reaction center carries out the necessary electron transfer in a series of short-range, rapid steps.

Within 2–4 ps of excitation, the special pair excited singlet state donates an electron to one of the bacteriopheophytin molecules (the one on the right in Fig. 1) with a quantum yield of essentially unity [3–7]. The left-hand branch of the reaction center in Fig. 1 is almost inactive in electron transfer. However, triplet energy transfer occurs down the left branch to yield the triplet state of the carotenoid which then relaxes nonradiatively to the ground state. This process is known as photoprotection and prevents the formation of singlet oxygen by the triplet bacteriochlorophyll species. The accessory Bchl on the right undoubtedly plays some role in the electron transfer process, but the question as to whether it serves as an intermediate acceptor, an electron transfer mediator via superexchange, or in some other capacity has yet to be determined [8]. The Bph radical anion transfers an electron to the nearby quinone in 200 ps, again with a quantum yield of ~ 1 . This quinone subsequently donates an electron to the second quinone on the cytoplasmic side of the membrane. The positive charge remaining on the special pair is neutralized by electron donation from an iron porphyrin component of a c-type cytochrome which resides on the periplasmic (outer) side of the membrane. The net result of this multistep electron transfer sequence is the generation of a transmembrane charge separated state with a quantum yield of essentially unity. This state preserves a significant fraction of the energy of the initial excited state. Because the positive and negative charges are separated by the thickness of the lipid bilayer, rapid charge recombination, which would waste the stored energy as heat, is precluded.

The basic challenge of artificial photosynthesis is to design and prepare synthetic systems which mimic this natural process. We will consider the progress which has been made to date, but first it is desirable to review a little basic electron transfer theory.

3 Basic Principles of Electron Transfer

Recent progress in understanding the theoretical basis of electron transfer has been rapid. Theoretical aspects of electron transfer are addressed in detail in other contributions to this series, and authoritative, up-to-date reviews are available [9–14]. For our purposes, it will be sufficient to review some very basic electron transfer theory which will serve as a framework for the discussion of artificial photosynthetic systems which follows.

In general, for the types of linked donor-acceptor systems to be discussed in this review, electron transfer is assumed to occur in the nonadiabatic regime. That is, the mixing between the electronic state of the donor and acceptor before electron transfer occurs and the corresponding state after electron transfer is weak ($\ll k_B T$) [9]. The actual electron transfer event is assumed to be fast compared to the time scale of nuclear motions. Marcus has proposed [11, 15] that the electron transfer rate constant k_{et} is given by Eq. 1.

$$k_{et} = A \exp [-(\Delta G^0 + \lambda)^2/4\lambda k_B T]. \quad (1)$$

The pre-exponential factor A includes the electronic matrix element that describes the coupling of the reactant state with that of the products, ΔG^0 is the free energy change for the reaction, k_B is Boltzmann's constant, λ is the total reorganization energy for the reaction, which includes both solvent reorganization energy and changes in internal vibrational modes of the molecules in question, and T is the absolute temperature.

The form of Eq. 1 indicates that the electron transfer rate will increase with increasing thermodynamic driving force (as the standard free energy change becomes more negative) up to a maximum, where $-\Delta G^0$ equals λ . This is the "normal" region of the Marcus curve. Additional thermodynamic driving force results in "inverted" behavior: the electron transfer rate constant *decreases* as the standard free energy change becomes more negative. Although experimental verification for inverted behavior was lacking for many years, recent work with small organic molecules has provided evidence for its existence [9, 16–18]. The inverted region has also been probed in covalently linked donor-acceptor systems consisting of porphyrins linked to quinone moieties [19, 20, 21]. As will be seen below, this work has relevance for photosynthetic model systems.

As suggested by Eq. 1, the solvent can affect electron transfer rates strongly via the reorganization energy. It can also have other effects, including an alteration of the magnitude of the free energy change for the reaction. The reviews cited above should be consulted for details.

The pre-exponential factor A in Eq. 1 is a weak function of the temperature and the reorganization energy, and strongly dependent upon the electronic coupling matrix element V . In the simplest case, V may be assumed to be exponentially dependent upon the through-space donor-acceptor separation r . This yields a distance dependence for electron transfer of:

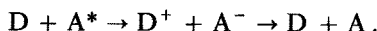
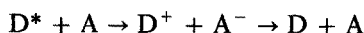
$$k_{et} = v \exp (-\alpha r). \quad (2)$$

When the donors and acceptors lack spherical symmetry, there will also be an orientation dependence. In cases such as those to be discussed below, where the donor and acceptor moieties are linked by covalent bonds, there is considerable evidence that in certain situations the electron transfer occurs through the linkage bonds [22]. Although such linkages are not present in photosynthetic reaction centers, it has been proposed that the accessory Bchl or other intervening material may still take part in electron transfer through a superexchange mechanism [8, 26]. The distance dependence of photoinitiated electron transfer has recently been reviewed [13].

4 Simple Model Systems

4.1 Unlinked Models

One of the simplest kinds of photosynthetic model systems which may be envisaged is a solution of a photochemically active pigment and an additional electron donor or acceptor. The following sorts of reactions can be studied:

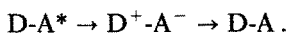
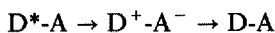


Such studies in solution have revealed much of what we know about the properties of the excited states of the pigments involved in the photosynthetic process and the electrochemical properties of the relevant donor and acceptor moieties. A good deal of fascinating electron transfer chemistry has also been uncovered by such studies. However, as mimics of natural photosynthesis, these simple systems suffer from several problems. For example, reaction kinetics in simple solutions are limited by diffusion controlled rates, with rate constants typically on the order of 10^{10} s^{-1} at most. As mentioned above, the initial events in photosynthesis occur within a few picoseconds of excitation, and the lifetimes of the first excited singlet states of most relevant pigments preclude electron transfer studies in dilute solution. Thus, most studies of bimolecular photoinitiated electron transfer involve the excited triplet state of the donor molecule, which has less direct photosynthetic relevance. In addition, donor-acceptor separations and orientations are not fixed in fluid solution. This is a serious limitation because, as we have seen, electron transfer (as well as energy transfer) rate constants are crucially dependent on these parameters. Thus, the trend has been to construct more sophisticated model systems in which the pigments, donors and acceptors are subject to constraints upon their relative geometries. Although a variety of methods for imposing such constraints exist and have been exploited, we will concentrate here on covalently linked donor-acceptor systems in which the linkage bonds assume the structural role of the protein in the natural reaction center. In addition, we will restrict the bulk of the discussion to models in which the pigments absorb in the visible region

and in general resemble the natural pigments of photosynthesis. Thus, we will be dealing mainly with chlorophyll derivatives, synthetic or naturally occurring porphyrins (P), and a few other metal complexes. Electron donors and acceptors will include quinones (Q), carotenoid polyenes (C), and a few additional organic species.

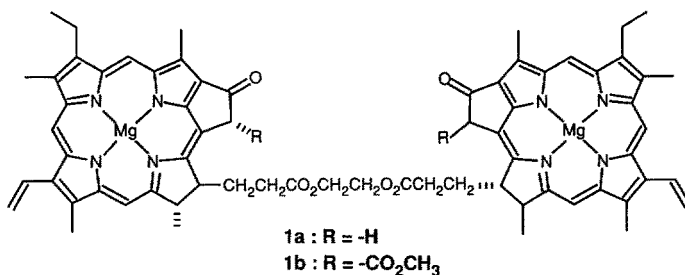
4.2 Dyads

The simplest covalently linked models for photosynthetic electron transfer must consist of a chromophore covalently linked to a donor or acceptor. The following reactions are then observable, in principle.



The first reaction in each sequence is the photoinitiated electron transfer, and can in principle occur from either an excited singlet state, or a triplet state. The second reaction is the charge recombination reaction or "back reaction", as it is sometimes called.

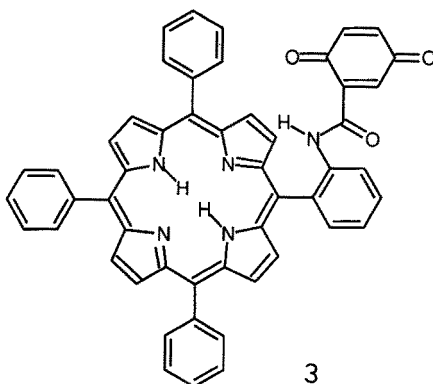
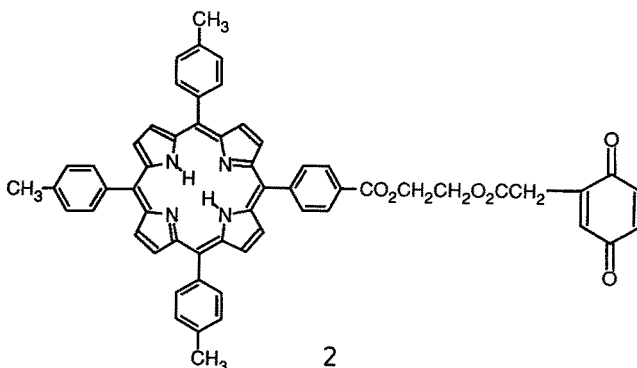
Although covalently linked donor-acceptor systems of small organic chromophores have been studied for some time in order to uncover the basic principles of electron and energy transfer, the first covalently linked cyclic tetrapyrroles were reported by Gouterman, Dolphin and coworkers in 1972 [27]. In 1976 the first dimeric chlorophyll-based models were reported. Structure **1a**, based upon pyropheophorbide-*a*, was prepared by Boxer and Closs [28], whereas the pheophorbide-*a* derivative **1b** was reported by Wasielewski, Studier and Katz [29].



These two molecules were the antecedents of a variety of oligomeric porphyrin and chlorophyll derivatives which were constructed as mimics of the reaction center special pair. Many of these systems exhibit interesting optical properties which allow modelling of the electronic interactions within the special pair and/or the antenna function of chlorophyll, which involves singlet-singlet energy transfer

between the pigments. However, most of the early models have not concentrated on photoinitiated electron transfer. Indeed, in most of these molecules, the charge-separated state lies energetically above the tetrapyrrole first excited singlet state, and electron transfer cannot occur. (This restriction can be lifted by proper substitution of metals into the porphyrin macrocycles.) Several reviews of and literature references to porphyrin and chlorophyll-based dyads are available [30–37]. Some of the more complex oligomeric tetrapyrroles will be discussed in a later section in terms of their possible electron transfer properties.

The vast majority of the dyad models for photosynthetic electron transfer have consisted of synthetic porphyrins covalently linked to quinones. The first such models were reported in the late 1970's. Kong and Loach prepared the ester-linked dyad **2** in 1978 [38], and the amide **3** was reported by Tabushi and coworkers in 1979 [39]. A large number of these P-Q systems have now appeared in the literature. The reader is referred to several reviews [13, 34, 40], including the recent review by Connolly and Bolton [41] for a complete compilation of these results.



In general, it has been found that under the correct combination of electronic coupling, thermodynamic driving force, solvent and temperature, P-Q systems readily undergo photoinitiated electron transfer as shown in Fig. 2. Singlet excitation localizes on the porphyrin, which has the energetically lowest-lying

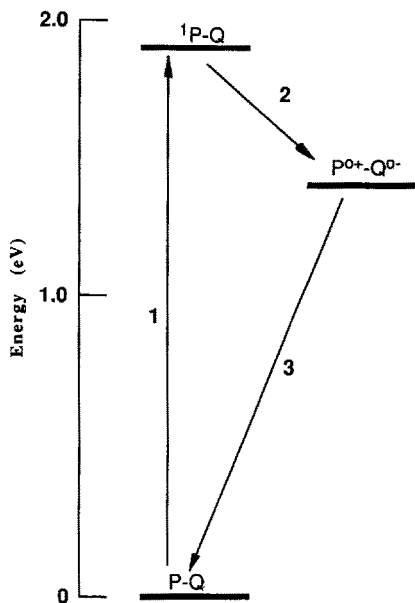


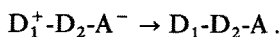
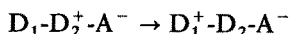
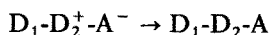
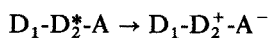
Fig. 2. Transient states of a typical porphyrin-quinone dyad molecule and related electron transfer pathways

first excited singlet state. The singlet state may, of course, decay by the usual photophysical processes of internal conversion, fluorescence, and intersystem crossing to the triplet. Competing with these processes is donation of an electron to the attached quinone to give a $P^{\bullet+}-Q^{\bullet-}$ charge separated state. The charge separated state has stored within it a certain fraction of the energy of the excited singlet state, just as the corresponding states in the photosynthetic reaction center store part of the energy of the excited special pair. The amount of chemical potential energy stored in $P^{\bullet+}-Q^{\bullet-}$ is a function of the redox properties of the two moieties involved. The quantum yield of charge separation depends upon the particular system, but can approach unity under favorable conditions. Eventually, this charge separated state recombines to give the P-Q ground state and releases the stored energy as heat.

These P-Q dyads thus do a good job of functionally mimicking the gross features of the photoinitiated charge separation step of the reaction center. The study of such systems and the interpretation of the results in terms of modern electron transfer theory have contributed substantially to our understanding of photo-initiated electron transfer and the various factors which affect it. However, the very factors which facilitate rapid photoinitiated electron transfer in the dyads also tend to facilitate charge recombination (step 3 in Fig. 2). The charge separated states typically have lifetimes in solution of a few hundred ps or less. Thus, the P-Q systems, and dyad systems in general, are unable to reproduce the long-lived charge separation which is characteristic of the photosynthetic reaction center, and which allows the organism to harvest the energy stored within the state. As we shall see, this limitation may be overcome by more complex molecular devices.

5 Triads

As discussed above, the photosynthetic reaction center solves the problem of rapid charge recombination by spatially separating the electron and hole across the lipid bilayer. In order to achieve photoinitiated electron transfer across this large distance, the reaction center uses a multistep sequence of electron transfers through an ensemble of donor and acceptor moieties. The same strategy may be successfully employed in photosynthesis models, and has been since 1983 [42–45]. The basic idea may be illustrated by reference to a triad D_1 - D_2 -A, where D_2 represents a pigment whose excited state will act as an electron donor, D_1 is a secondary donor, and A is an electron acceptor. Excitation of D_2 will lead to the following potential electron transfer events.



The excited state of D_2 will donate an electron to the nearby acceptor. The resulting charge separated state may recombine to the ground state. However, competing with charge recombination is a second electron transfer step in which the secondary donor D_1 donates an electron to the D_2 cation to yield a final charge separated state D_1^+ - D_2 -A $^-$. If the system has been designed correctly, this state may have a substantially increased lifetime due to the greater distance between the electron and hole. Ultimately, however, the final charge separated state will recombine to give the ground state unless it is intercepted by another donor or acceptor.

The general strategy of multistep electron transfers in triad-type molecules has proven to be a useful one for maximizing the quantum yield of charge separated states formed by photoinitiated electron transfer, the lifetimes of these states, and the amount of energy stored therein. As a result, the strategy has been exploited in a variety of molecular devices, many of which are reviewed below.

5.1 Types of Triad Systems

The following ten types of triad donor-acceptor molecules may be differentiated:

- | | |
|-----------|--------------|
| 1. D-D-A* | 6. A-A-D* |
| 2. D-D*-A | 7. A-A*-D |
| 3. D*-D-A | 8. A*-A-D |
| 4. D-A*-D | 9. A-D*-A |
| 5. D*-A-D | 10. A*-D-A . |

We will now discuss the most likely sequence of electron transfer events in each case, assuming that the redox potentials of the donors and acceptors have been selected in a logical manner for sequential electron transfer. The first five systems have two donors and one acceptor. Types 1 and 2 undergo photoinitiated electron transfer to yield $D-D^+-A^-$, which can either recombine or go on to yield D^+-D-A^- . Thus, these two types can in principle give rise to long lived, energetic charge separated states in high yield. Type 3, however, can only undergo electron transfer to the acceptor in a single step, either directly through space or with some involvement of the intervening donor moiety. This architecture is thus seen to offer no real advantage over the simple dyads mentioned above. On the other hand, in properly designed systems, *energy* transfer between the donor species to generate case 2 may occur. Thus, the secondary donor may act as an antenna for the primary donor. Some examples of this effect are given below.

Triads of type 4 will not offer any advantage over D-A systems in terms of lifetimes for charge separation, but they can in principle increase the efficiency of the system by providing a higher effective concentration of quencher for the acceptor excited state. This will allow more effective competition with other pathways for deactivation of the excited state. Type 5 triads again offer no apparent advantages in terms of increased lifetime for charge separation. However, the presence of two donors increases the pigment to acceptor ratio, allows one to drive each acceptor moiety closer to capacity at low light levels, and may offer advantages if A is capable of functioning as a two-electron acceptor.

Triad types 6–10 all have one donor and two acceptors. Again, only 6 and 7 can capitalize on the multistep electron transfer strategy for increasing the lifetime of the final charge separated state. Triad 8 can convert to 7 via energy transfer if the excited state energy levels are suitable. Triads 9 and 10 offer the same advantages and disadvantages as 4 and 5, respectively.

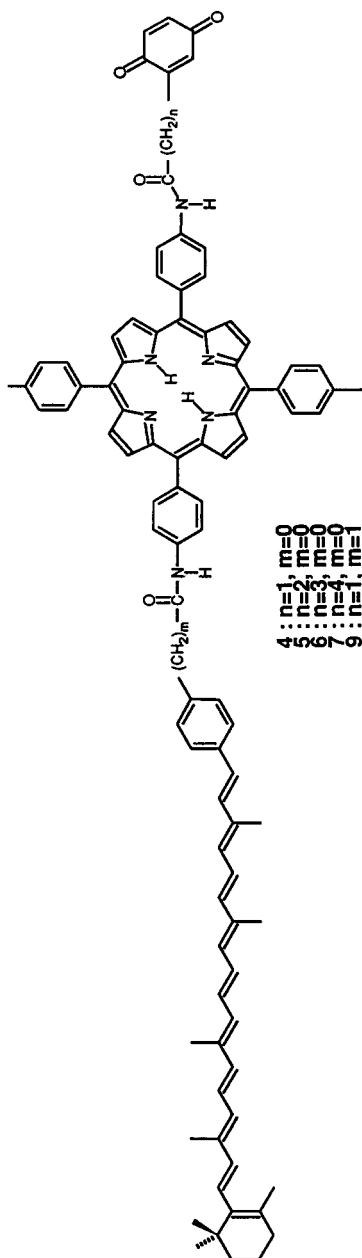
Although actual molecular systems corresponding to any of the above-mentioned 10 types of triad could be readily constructed, examples of only some of them have appeared so far. In the next sections, we will discuss molecular examples of types 1, 2, 3, 5, 6 and 9.

5.2 Examples of Triads

5.2.1 Systems with Two Donors

5.2.1.1 $D-D^*-A$ and D^*-D-A Triads

The first biomimetic triad of the D-D-A type, C-P-Q triad **4**, was reported in 1983 [42–44, 46]. It consists of a porphyrin chromophore covalently linked to both a benzoquinone-type electron acceptor and a carotenoid polyene. The carotenoid serves as the secondary donor in the system. It also performs two auxiliary functions. It acts as an antenna by absorbing light in spectral regions where the porphyrin does not absorb strongly and transferring singlet excitation



to the porphyrin. Carotenoid antenna function is observed in the natural photosynthetic apparatus, and therefore the singlet energy transfer in **4** is biomimetic. The carotenoid polyene also rapidly quenches the triplet state of the porphyrin by triplet energy transfer in relatives of **4**. Thus, the carotenoid mimics one of the processes by which carotenoid polyenes prevent the sensitization of singlet oxygen formation by the triplet states of chlorophylls in photosynthetic organisms. Singlet oxygen must be minimized because it is extremely reactive and will damage the organism if it is present. These two energy transfer aspects of carotenoids in photosynthesis have been examined in a variety of carotenoporphyrin model systems [47–51].

High resolution $^1\text{H-NMR}$ experiments have demonstrated that **4** adopts an extended conformation in solution, with the quinone and carotenoid moieties directed out, and away from the porphyrin rather than folded back across it [52, 53]. The UV-VIS spectrum indicates that in absorption, the porphyrin, carotenoid, and quinone moieties act essentially independently, rather than as a single large delocalized system. A variety of time resolved fluorescence, absorption, and other spectroscopic measurements [52– 60] have demonstrated that excitation of the porphyrin moiety of **4** is followed by the events depicted in Fig. 3. The first excited singlet state of the porphyrin can decay by a variety of pathways, but the major route is electron transfer to the quinone (step 2). As one would expect by analogy to the P-Q systems mentioned above, the resulting $\text{C-P}^+-\text{Q}^-$ state can decay rapidly to the ground state by charge recombination (step 3). In the triad, however, a second forward electron transfer (step 4) competes with charge recombination. In this step, the carotenoid donates an electron to the porphyrin radical cation to yield a final $\text{C}^+-\text{P-Q}^-$ charge separated state. In this state, the positive and negative charges are not on adjacent moieties, but are substantially separated in space. Thus, charge recombination might be expected to be slow. Indeed, in dichloromethane the lifetime of $\text{C}^+-\text{P-Q}^-$ is ~ 300 ns, and in butyronitrile solution it is ~ 2 μs . Recalling that the lifetimes of charge separated states in related P-Q dyads were only a few hundred ps or less, it can be seen that the biomimetic two-step electron transfer strategy used in **4** is indeed effective.

The energies of the charge separated states depicted in Fig. 3 may be estimated by measuring the energies of the radical ions of model compounds, or of **4** itself, using cyclic voltammetry or other electrochemical methods. These methods fail to some extent to account for the possible stabilization of the charge separated states by coulombic interactions of the positive and negative charges. Although one may attempt to correct for these effects, the validity of such corrections is unknown. Therefore, no corrections were made in this work. The energy of the porphyrin first excited singlet state in **4** is 1.9 eV, as estimated from spectroscopic parameters. Of this energy, ~ 1.4 eV remains in the intermediate $\text{C-P}^+-\text{Q}^-$ species, and ~ 1.1 eV in $\text{C}^+-\text{P-Q}^-$. Thus, a substantial fraction of the initial excited state energy is preserved as chemical potential in the final $\text{C}^+-\text{P-Q}^-$ species.

The quantum yield of the final charge separated state in **4** was only ~ 0.04 in dichloromethane, where most of the photochemical work has been done, although it was higher in some other solvents [44]. Therefore, a number of investigations were undertaken in order to determine which factors were limiting the quantum

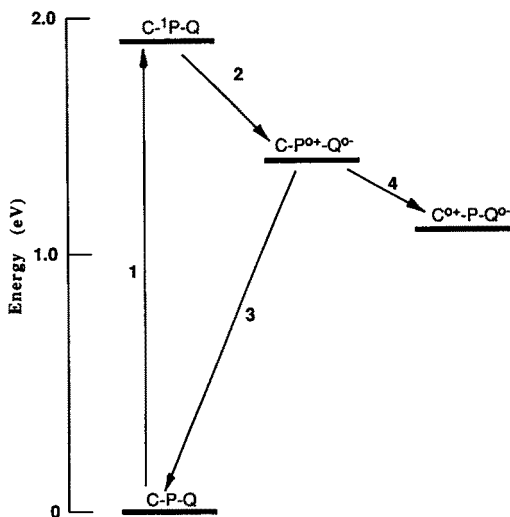


Fig. 3. Transient states of C-P-Q triad and relevant electron transfer pathways

yield, with a view toward the design and synthesis of new triads which might demonstrate higher yields.

The rate of the initial charge separation in 4 and similar molecules may be estimated from the fluorescence lifetime of the porphyrin moiety. It is assumed that the electron transfer rate constant is given by:

$$k_{et} = (1/\tau_f) - (1/\tau_0) \quad (3)$$

where τ_f is the fluorescence lifetime of the triad and τ_0 is the lifetime of a corresponding model system with the same photophysics as the triad, but lacking the electron transfer step. It has been found that the hydroquinone form of the triad or related materials make good models ($\tau_0 \sim 3.4$ ns). Using this method, the rate constant for step 2 in Fig. 3 was estimated to be $9.7 \times 10^9 \text{ s}^{-1}$ in dichloromethane [52]. This means that the quantum yield for the initial $\text{C-P}^{\bullet+}\text{-Q}^{\bullet-}$ state is 0.97. Therefore, the low quantum yield observed for 4 must be due to inefficient competition of step 4 with charge recombination (step 3).

As discussed above, electron transfer rate constants are dependent on donor-acceptor separation. Therefore, it was conceivable that altering the donor-acceptor separation in the C-P-Q triad might allow one to increase the overall yield of the forward electron transfer steps. The series of triads 5–9 was prepared in order to investigate this possibility [52]. Triad 8 is the 5, 10 isomer of 5. A corresponding series of P-Q molecules lacking the carotenoid moieties was also prepared. $^1\text{H-NMR}$ measurements allowed the determination of the time-average solution conformations of these molecules, based on porphyrin aromatic ring current induced changes in chemical shifts for the protons of the carotenoid and quinone moieties. In dichloromethane, all molecules were found to adopt primarily extended

conformations with the methylene chains in the all-anti conformation. Rate constants for step 2 were determined from fluorescence decay measurements. A plot of $\ln k_2$ vs. the edge-to-edge separation of the porphyrin and the quinone moieties for 4–8 and corresponding P-Q species is shown in Fig. 4. The data for seven molecules having 2, 3 or 4 methylene spacer groups between the porphyrin and the quinone yield a roughly linear plot. Although the data for the molecules with one methylene group do not fall on the line, there are a variety of reasons why this might be expected [52]. Thus, the triads and dyads with 2–4 methylene groups display the exponential distance dependence expected from Eq. 2, and the slope of the least-squares line in Fig. 4 yields a value of α of $0.6 \text{ \AA}^{-1}$. This value of α is somewhat lower than that found for some other P-Q and organic donor-acceptor systems, where the value appears to be about 1 [9, 13]. It was suggested [52] that this was a consequence of the fact that the time-average solution conformations found by NMR were the most extended ones possible. Any internal rotations about the linkage bonds during the lifetime of the porphyrin first excited singlet state and/or conformational inhomogeneity resulting from rotations about these bonds could only reduce the donor-acceptor separation. Thus, the measured value of α is a lower limit for the “true” value at the fixed donor-acceptor distances used in the Figure. In this connection, it should be noted that an α value of $0.55 \text{ \AA}^{-1}$ has recently been observed in a model system consisting of a porphyrin linked to a pyromellitimide acceptor via two covalent and reasonably flexible bridges [19].

Figure 4 demonstrates that in the C-P-Q triad series, the addition of methylene groups to the porphyrin-quinone linkage can only serve to slow down step 2 in

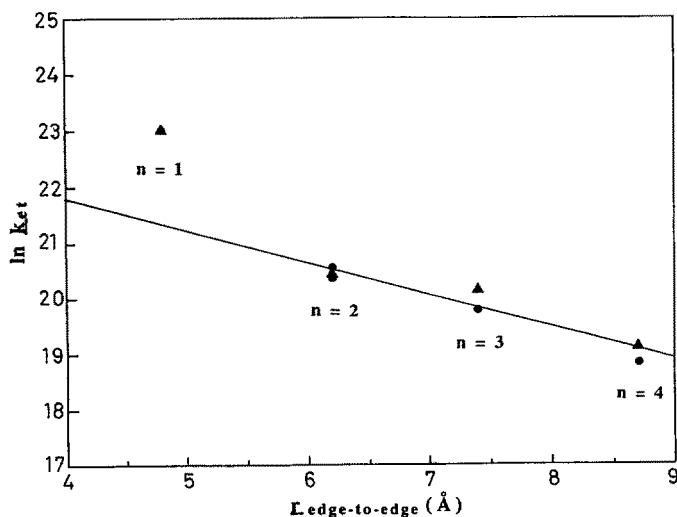


Fig. 4. Photoinitiated electron transfer rate constant (natural logarithm) vs. edge-to-edge porphyrin-quinone separation for C-P-Q triads 4–8 and related P-Q molecules. The separations shown are derived from $^1\text{H-NMR}$ measurements

Fig. 3, and therefore reduce the quantum yield of $C-P^+-Q^-$. However, this does not necessarily mean that the yield of the final C^+-P-Q^- state will be similarly reduced. Indeed, it was found that addition of a second methylene spacer as in **5** increased the quantum yield of the final state by a factor of 1.44 [56]. With **3** and **4** methylene groups (**6** and **7**) the yield decreased to 0.65 and 0.56 that of **4**, respectively. This complicated distance dependence for the yield of the final state is in part a consequence of the fact that increasing the porphyrin-quinone separation not only reduces the rate of step 2, but also that of charge recombination (step 3). The rate of the second forward electron transfer step 4 is essentially unaffected, since this step does not involve porphyrin-quinone electron transfer. Thus, increasing the separation will decrease the quantum yield of step 2, but increase the ratio k_4/k_3 , which determines the efficiency of the second electron transfer step. With **5**, the loss in quantum yield of step 2 is more than compensated for by the increase of efficiency of step 4, and the overall quantum yield increases. In **6** and **7**, any increase in the efficiency of step 4 evidently cannot compensate for the decrease in quantum yield for step 2, and the overall quantum yield decreases.

Although the rate constant for step 2 in the C-P-Q triads **4–7** is strongly distance dependent, that for charge recombination is not. The lifetimes for **4–7** all lie within the range 283–335 ns at ambient temperatures in dichloromethane [56]. It has been suggested that this may be due to the occurrence of a two-step charge recombination in these molecules. That is, the electron does not return directly to the carotenoid radical cation. Instead, the porphyrin donates an electron back to the carotenoid radical cation in a slow, thermally activated step to regenerate $C-P^+-Q^-$, and this state then rapidly recombines to the ground state. Some of the evidence for this suggestion comes from the fact that although moving the carotenoid from the 5, 15 arrangement with respect to the quinone to the 5, 10 arrangement as in **8** drastically decreases the quinone-carotenoid separation (by ~ 7 Å), the lifetime of the C^+-P-Q^- state remains at 285 ns (vs. 283 ns for **5**). On the other hand, increasing the carotenoid-porphyrin separation *would* be expected to alter the lifetime of the final state, as the rate determining step involves porphyrin-carotenoid electron transfer. Indeed, insertion of a methylene group in this linkage (triad **9**) increases the lifetime to 1 μ s.

Under some conditions, effects arising from interconversion of singlet and triplet forms of the charge separated state could also affect the lifetime. Such effects have been ignored in the above discussion.

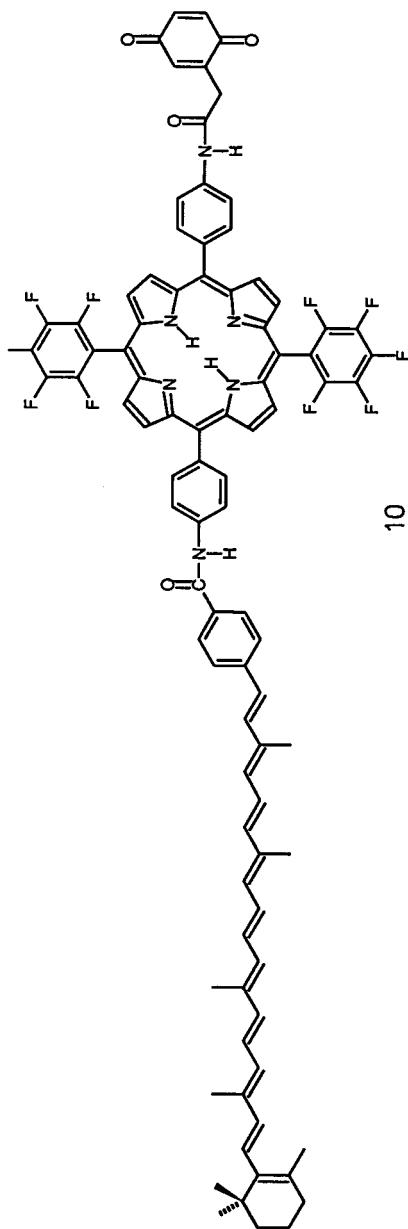
Another approach to increasing the yield of the C^+-P-Q^- state has recently been reported [61]. This strategy is based upon the dependence of electron transfer rates upon the free energy change for the reaction given in Eq. 1. Consider the effect of increasing the energy of the $C-P^+-Q^-$ intermediate while leaving the energies of the other states in Fig. 3 unchanged. Raising this energy is expected to decrease the rate of step 2, because this reaction occurs in the normal region of the Marcus curve. The rate of step 4, on the other hand, should be increased, as the driving force is increased and this reaction also lies in the normal region. The situation for the charge recombination reaction step 3, however, may be quite

different. Several studies of electron transfer in small organic molecules [9] and in P-Q and related systems [19–21] suggest that the dependence of the electron transfer rate constant on driving force certainly flattens out in the region of 1 eV, and very likely demonstrates inverted region behavior at higher driving force. Note that step 3 in Fig. 3 is therefore strongly into the inverted region. Increasing the energy of $C-P^+-Q^-$ would be expected to decrease the rate of charge recombination, and should therefore increase the efficiency of step 4 due both to the increased rate of this step and the projected decrease in the rate of step 3. This being the case, it should be possible to design a C-P-Q triad in which the loss in efficiency in step 2 is more than compensated for by a gain in step 4.

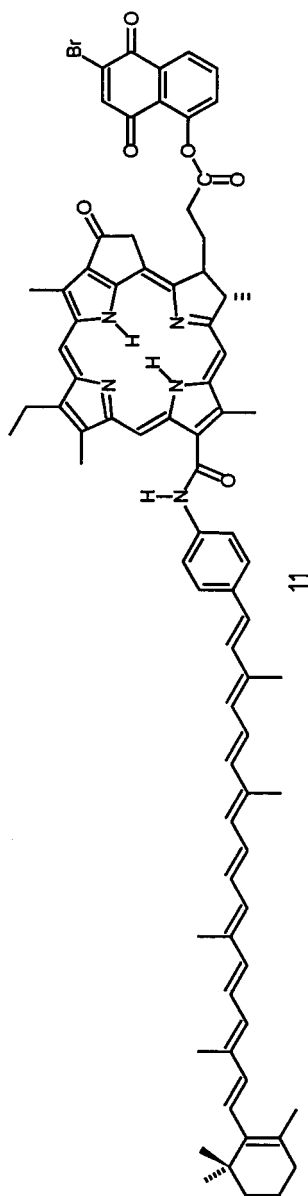
Triad **10** was designed in order to evaluate this strategy [61]. The triad is identical to **4**, except that the two *p*-tolyl substituents on the porphyrin ring have been replaced by pentafluorophenyl groups. These groups are strongly electron withdrawing, and would be expected to destabilize a positive charge on the porphyrin. Indeed, cyclic voltammetric measurements demonstrate that the energy of $C-P^+-Q^-$ has been increased by 0.2 eV, relative to that of the similar state in **4**. Fluorescence decay studies of **10** yield a lifetime of 0.67 ns for the first excited singlet state of the porphyrin. Equation 3 with the appropriate model compound yielded a photoinitiated electron transfer rate constant k_2 of $6.1 \times 10^8 \text{ s}^{-1}$. This is ~ 16 times slower than was observed for **4**, and corresponds to a quantum yield of 0.41 for step 2. Thus, the expected decrease in rate for step 2 is indeed observed.

Transient absorption studies demonstrated that the yield of the final C^+-P-Q^- state for **10** is 0.30 in dichloromethane. This increase by a factor of ~ 7 over that found for **4** must be due to a higher efficiency for step 4, as was hoped for. Indeed, the efficiency of this step has been increased from 0.04 in **4** to 0.73 in **10**. Thus, fine-tuning of the energetics of the various electron transfer steps in the C-P-Q triads is indeed a powerful tool for controlling quantum yield without necessarily affecting the amount of energy stored in the final charge separated state (this is essentially the same for both **4** and **10**).

As mentioned above, the natural photosynthetic reaction center uses chlorophyll derivatives rather than porphyrins in the initial electron transfer events. Synthetic triads have also been prepared from chlorophylls [62]. For example, triad **11** features both a naphthoquinone-type acceptor and a carotenoid donor linked to a pyropheophorbide (Phe) which was prepared from chlorophyll-*a*. The fluorescence of the pyropheophorbide moiety was strongly quenched in dichloromethane, and this suggested rapid electron transfer to the attached quinone to yield $C\text{-Phe}^+-Q^-$. Transient absorption studies at 207 K detected the carotenoid radical cation ($\lambda_{\text{max}} = 990 \text{ nm}$) and thus confirmed formation of a $C^+-\text{Phe}-Q^-$ charge separated state analogous to those formed in the porphyrin-based triads. This state had a lifetime of 120 ns, and was formed with a quantum yield of about 0.04. The lifetime was $\sim 50 \text{ ns}$ at ambient temperatures, and this precluded accurate determination of the quantum yield at this temperature with the apparatus employed.



10

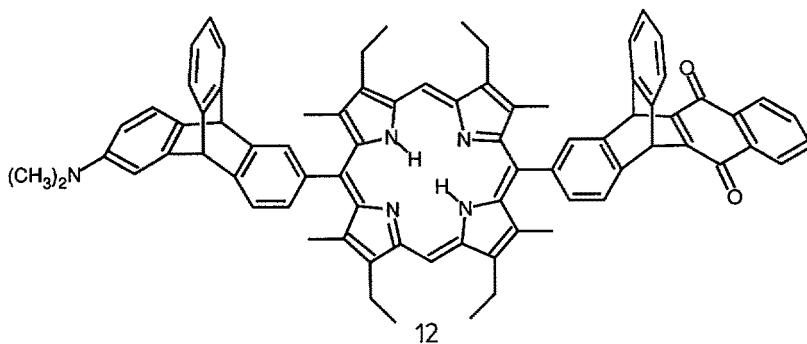


11

Energy transfer studies of **11** and related molecules demonstrated that the carotenoid moiety is active in antenna function (singlet-singlet energy transfer) and photoprotection (triplet-triplet energy transfer) in these molecules, just as it is in natural reaction centers [51, 62].

The similarity of the results for **4** and **11** confirms that although porphyrins and chlorophylls have somewhat different absorption spectra and other photo-physical parameters, porphyrin-based structures may still be used as valid models for certain aspects of natural photosynthetic energy conversion.

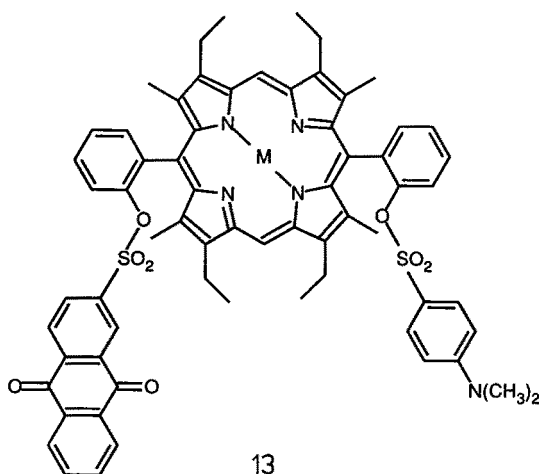
Since the initial reports of the C-P-Q triads, a number of other molecules of the D-D*-A or D*-D-A types have been described. Triad **12**, prepared by Wasielewski and coworkers, is a relative of the C-P-Q series in which the secondary donor is an aniline derivative (D), rather than a carotenoid [63]. The bicyclic bridges were introduced in order to add rigidity to the system. The fluorescence lifetime of the porphyrin moiety of **12** was found to be <30 ps. This result is consistent with rapid electron transfer to the quinone to yield $D-P^+-Q^-$. This result was confirmed by transient absorption measurements. The absorption results also revealed that this intermediate charge separated state decays with a rate constant of $1.4 \times 10^{10} \text{ s}^{-1}$ to a final charge separated state D^+-P-Q^- . Thus, the decay pathways are similar to those shown in Fig. 3 for the C-P-Q triads. This final state has a lifetime of 2.45 μs in butyronitrile (which is similar to that found for **4** in acetonitrile) [44], and is formed with a quantum yield of about 0.71. Thus, the efficiency of the transfer analogous to step 4 in Fig. 3 for this molecule is also about 0.71.



In **12**, the donor and acceptor moieties are chiral, and, as noted by the authors, the molecule therefore exists as a pair of diastereomers which are separable by chromatography. However, rotation about the linkages between the porphyrin macrocycle and the attached aryl rings must be very slow on the time scale of electron transfer. Thus, non-interconverting diastereomers should be present, with slightly different separations and orientations between the aniline donor and the quinone acceptor. This distribution would be expected to influence the decay kinetics of D^+-P-Q^- if charge recombination is via direct electron transfer. If a

two-step mechanism is followed, as was seen for some of the C-P-Q triads, the effect might be negligible.

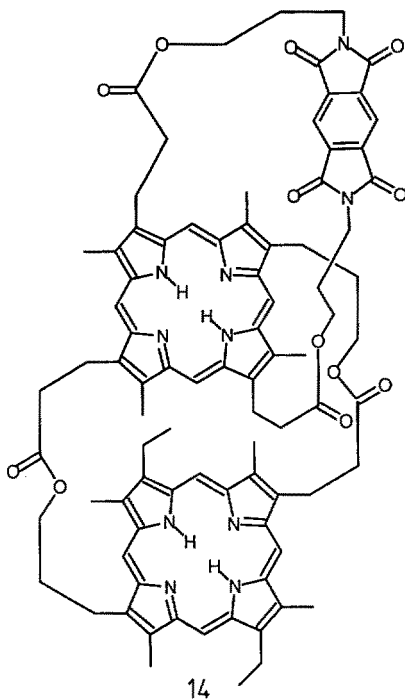
A relative of **12** has been prepared by Sanders, van der Plas, and coworkers [64]. Triad **13** features an *N,N*-dimethylaniline-type donor and an anthraquinone acceptor. These moieties are linked to the *ortho* positions of the porphyrin aryl groups, and this leads to a folded conformation for the molecule, as determined from NMR studies. Both the free base and zinc derivatives of **13** were prepared. The folded conformation might be expected to facilitate electron transfer among the components of the triad, and while this could enhance the quantum yield of the initial charge separated state, it might unfavorably affect the yield of the final $D^+ \text{-} P \text{-} Q^-$ state and its lifetime. Unfortunately, photochemical or spectroscopic studies were not reported.



Recently, a new type of C-P-Q triad was reported in which the carotenoid and quinone moieties were linked to the tetraarylporphyrin via "basket handle" linkages between opposite aryl groups [65]. This linkage positioned the carotenoid and quinone species above and below the plane of the porphyrin, rather than to the side, as confirmed by ^1H -NMR studies. Evidence for photoinitiated electron transfer in this molecule was provided by incorporating it into a phospholipid bilayer and detecting a light-induced photocurrent. Similar experiments had previously been reported with the other C-P-Q triads discussed above [55].

The abundance of cyclic tetrapyrroles in the bacterial reaction center naturally suggests the preparation of triads bearing two porphyrin moieties. A number of such systems have been described. Building upon their earlier work with D-A type systems [19, 66], Sanders, Beddard and coworkers have reported triad **14**, which consists of two doubly-linked porphyrins, one of which bears a pyromellitimide acceptor [66]. The pyromellitimide moiety is nearly as good an electron acceptor as benzoquinone ($E_0 = -0.55$ V vs. -0.51 V for benzoquinone). Triad **14**,

prepared as a mixture of diastereomers, was found by NMR spectroscopy to assume a stacked conformation. Fluorescence and transient absorption studies revealed that excitation of **14** yields P^*-P-A and $P-P^*-A$, which interconvert via rapid singlet-singlet energy transfer. $P-P^*-A$ rapidly donates an electron to A to generate $P-P^+-A^-$, which presumably goes on to give P^+-P-A^- , although the absorption data evidently do not allow one to distinguish between the two porphyrin radical cations. The lifetime of the final charge separated state is short (13–114 ps), due presumably to the strong electronic interactions among the moieties resulting from the stacked conformation and the similarity in redox potentials of the two porphyrin moieties.



In this connection, the authors also report an analog of **14** in which the two porphyrins and the acceptor assume a more extended conformation wherein the moieties are side-by-side, rather than stacked. The electronic coupling is not as good in this case, as demonstrated by the absorption spectrum. In this analog, both the photoinitiated electron transfer and the recombination of the P^+-P-A^- state are substantially retarded [66].

The authors state that it is possible to metallate the outer porphyrin moiety of **14** while leaving the inner porphyrin in the free base form. If this can be done with a metal such as zinc, the monometallated derivative should favor singlet energy transfer to the central porphyrin, which can serve as an electron donor to

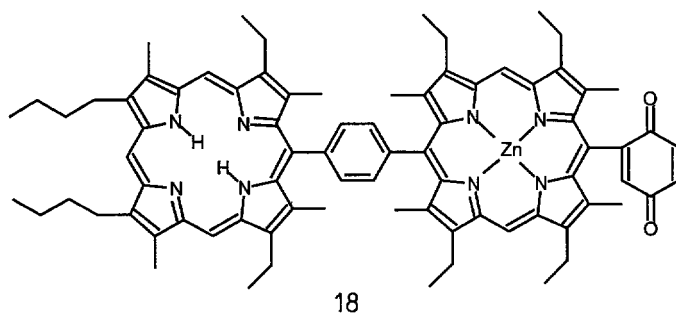
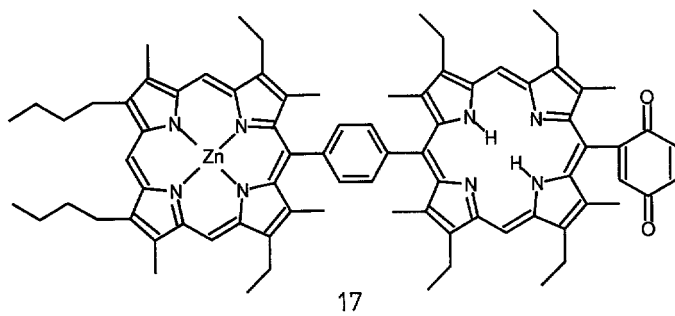
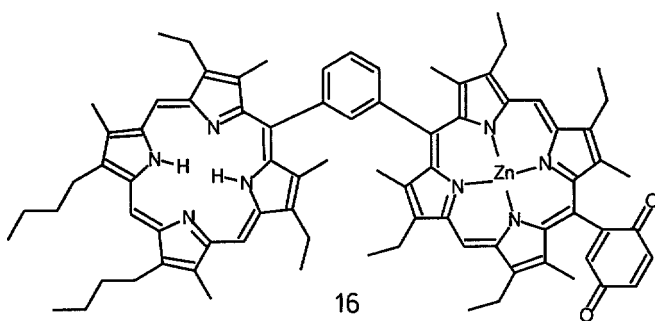
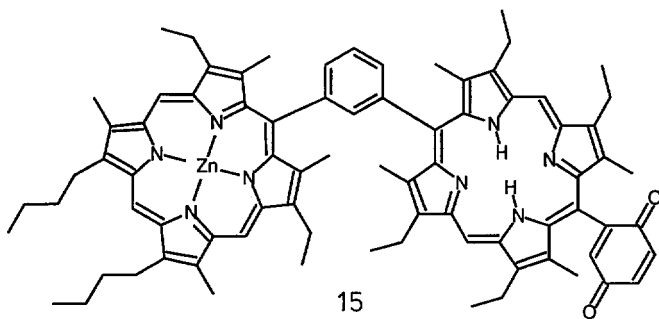
the pyromellitimide. In addition, the zinc in the outer porphyrin should stabilize a positive charge, and perhaps slow down charge recombination. Thus, this system promises to be a quite interesting one.

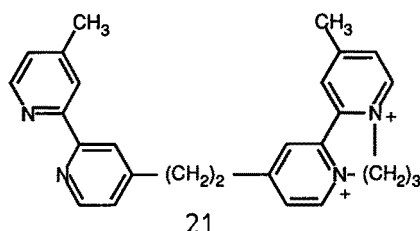
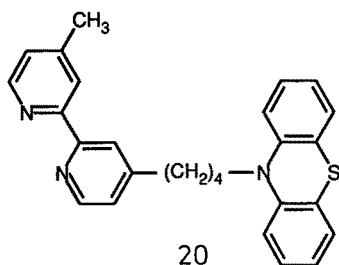
In 1982, Tabushi and coworkers developed some "gable" porphyrins in which two porphyrin moieties were linked to the same phenyl ring through their *meso* positions [67]. This provided a relatively rigid linkage between the two porphyrins, although torsional motions are still possible. Sessler and coworkers have extended this concept to the preparation of triads **15**–**18** [68, 69]. Within the "gable" (**15**, **16**) and "flat" (**17**, **18**) series of molecules, the isomeric structures have a zinc ion in the porphyrin either distal or proximal to the quinone acceptor. The absorption spectra of these molecules reveal significant electronic interaction between the porphyrins in the gable series, but less in the flat species. Steady-state fluorescence studies show that for all of these molecules, fluorescence is quenched relative to control molecules which do not bear the quinone moiety. This quenching is ascribed to electron transfer to the quinone. The details of this quenching could not be completely elucidated from the steady-state fluorescence data. In particular, the relative importance of energy transfer between the porphyrins and electron transfer could not be determined. However, some trends were evident. Triads **15** and **17**, in which the free base porphyrin is adjacent to the quinone acceptor, demonstrated more fluorescence quenching than analogs **16** and **18**, where the metallated porphyrin is proximal to the quinone. This is consistent with singlet energy transfer from the metallated to the free base porphyrins, as would be expected by analogy to many other porphyrin dimers. In **15** and **17**, electron transfer to the quinone would be facile, by analogy to previously reported P-Q molecules with a similar linkage. In **16** and **18**, however, the distance from the free base porphyrin to the quinone is much longer, and electron transfer to the acceptor should be slower and less efficient, leading to increased fluorescence. In spite of this effect, electron transfer is still relatively efficient in these molecules, and it was argued that superexchange interactions involving the central porphyrin are mediating the transfer process. It was also noted that quenching was always greater for the gable triads than for the corresponding flat species. This is consistent with the stronger porphyrin-porphyrin interactions seen for these materials in absorption.

The lifetimes of the final, presumably charge separated, states in **15** and **16** were both less than 100 ps, as determined from transient absorption studies [69]. These rather short lifetimes are likely due to the short, perhaps partially conjugated linkages between the three moieties which would be expected to facilitate charge recombination.

There is at present a lot of additional work going on in the area of porphyrin dimers linked to donors and/or acceptors, some of which will be discussed in later sections of this review.

The triad multistep electron transfer strategy is, of course, not limited to tetrapyrroles. For example, Meyer and coworkers have reported triad **19** $[\text{Ru}(\text{Me}(\text{bpy})\text{-}3\text{DQ}^{2+})(\text{Me}(\text{bpy})\text{-PTZ})_2]^{4+}$, which is based upon a ruthenium trisbipyridyl chromophore [70, 71]. The Mebpy-PTZ and Mebpy-3DQ²⁺ ligands are shown as structures **20** and **21**, respectively. This triad was again evidently

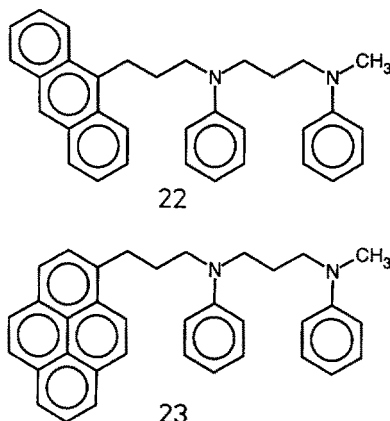




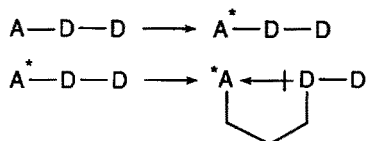
prepared as a mixture of closely related stereoisomers. The PTZ species serves as an electron donor, and the DQ^{2+} as an electron acceptor. (Thus, this molecule is actually of the D_2 -D-A type.) Fluorescence quenching and transient absorption data showed that at room temperature, excitation into the metal-to-ligand charge transfer (MLCT) state produced a long-lived charge separated state of the form $[(Me(bpy)-3DQ^+)(Ru^{II}(Me(bpy)-PTZ^+)(Me(bpy)-PTZ)]^{4+}$. This state had a lifetime of 165 ns in dichloromethane, and was formed with a quantum yield of 0.26. There are two conceivable routes for the formation of this final state. By analogy with the C-P-Q triads in Fig. 3, the MLCT state could donate an electron to the DQ^{2+} species to form an intermediate Ru^{III} charge separated state, which could convert to the final state via electron transfer from a PTZ ligand. Alternatively, the MLCT state could be quenched by donation from the PTZ group, and the resulting intermediate charge separated state could donate an electron to the DQ^{2+} moiety to form the same final state. That is, this molecule either functions as a D-D*-A system, as in the C-P-Q triads, or as an A-A*-D device.

5.2.1.2 D-D-A* Triads

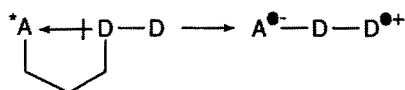
Although the excited singlet states of porphyrins are good electron acceptors as well as good donors, little triad work in this area has been reported so far. However, interesting molecules of the D-D-A* type with UV- or blue-light-absorbing chromophores have been reported, particularly by the Verhoeven [72] and Yang [73] groups. For example, in each of the triads **22** and **23**, the donors are *N,N*-dialkylaniline derivatives [73]. In **22** the acceptor is an anthracene, whereas in **23** it is a pyrene moiety. Steady state and time resolved fluorescence



and absorption studies of **22** show that in acetonitrile, the anthracene excited singlet state rapidly forms an intramolecular exciplex with the adjacent aniline:



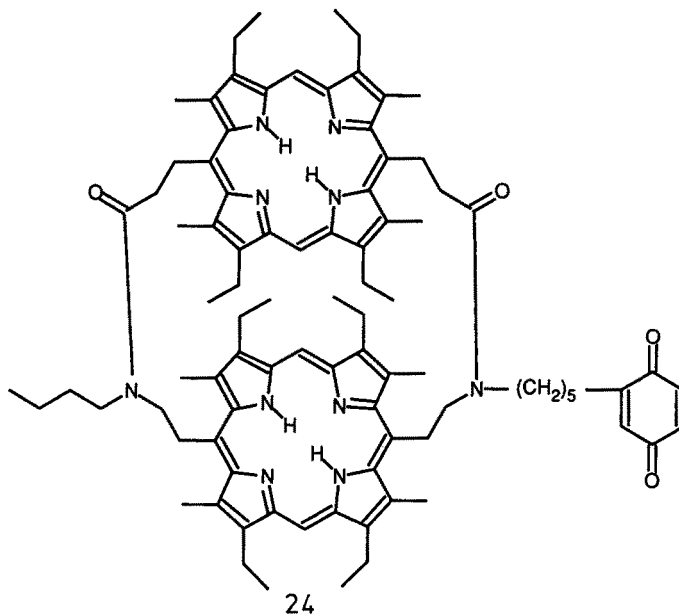
This exciplex has a large amount of charge transfer character, as shown by the solvent dependence of its fluorescence emission spectrum. The exciplex can then receive an electron from the secondary donor to form the final charge separated state:



The final state has a lifetime of about 2 ns, and decays to the anthracene triplet state. Similar behavior was noted for **23**, where the lifetime of the final charge separated state in dichloromethane was about 47 ns. The intermediate exciplex state in these molecules is formally analogous to an $\text{A}^--\text{D}^+-\text{D}$ species, which goes on by a second electron transfer to yield the final charge separated state.

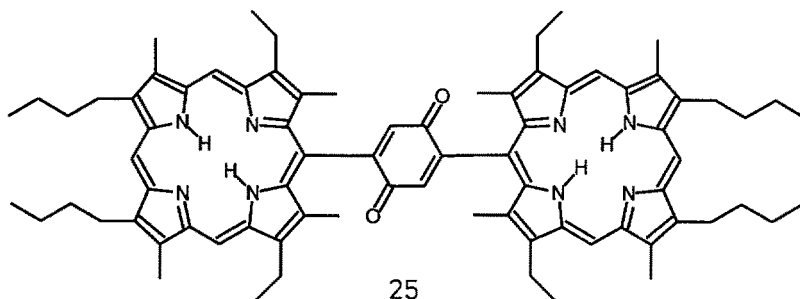
5.2.1.3 $\text{D}^+-\text{A}-\text{D}$ Triads

In these devices, the acceptor is joined to two donors which can in principle transfer electrons to it with comparable efficiencies. From the point of view of long-lived charge separation, molecules of this type offer no apparent advantages over simple D-A systems. However, as mentioned above, they may be useful in some other situations, especially as components of larger devices when A is a 2-electron acceptor. There are a few examples of porphyrin-quinone systems with this structure in the literature.



Triad **24** was reported by Sakata, Bolton, Mataga and coworkers [74]. The quinone is linked to the doubly-bridged diporphyrin moiety via a pentamethylene chain. The two etioporphyrins presumably assume some sort of stacked, face-to-face arrangement in solution, and this leads to blue-shifting of the Soret band and red-shifting of the visible Q-bands. $^1\text{H-NMR}$ spectra suggest that in spite of the long linkage, the quinone moiety is neither sandwiched between the porphyrins nor located above the porphyrin plane. Quenching of the fluorescence of **24** relative to that of a related diporphyrin model system suggests that electron transfer from the porphyrins to the quinone does occur. Time resolved fluorescence studies were also carried out. In tetrahydrofuran, the model porphyrin dimer has a lifetime of 10.1 ns. The fluorescence decay of **24** in this solvent consists of three components with lifetimes of 130 ps, 1.21 ns, and 8.10 ns in the ratio of 100:10:8, respectively. This suggests that several conformations of the molecule may be populated, and possibly that some of the quinone is present in the reduced form. It is also likely that to the extent that the two porphyrin moieties act as independent chromophores, energy transfer between them is taking place. The major, short-lived decay component suggests that electron transfer to the quinone is an efficient process. No information concerning the lifetime of the expected charge separated state was presented.

Triad **25** is another example of this general type [75]. As was the case with the previously discussed triads **15–18**, the absorption spectrum of **25** indicates some degree of excitonic interaction between the porphyrins. The fluorescence quantum yield of **25** is $\leq 5 \times 10^{-6}$, which indicates efficient quenching of the porphyrin singlet states, presumably by electron transfer. No information concerning the lifetime of any charge separated state was presented, but one would predict that it would be extremely short.

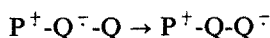
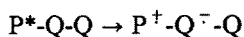


Molecules such as **25** present some interesting but as yet unrealized possibilities. For example, such a molecule with a reasonably long lived P^+-Q^--P charge separated state would in principle be capable of absorbing another photon and, given the proper energetics, of forming $P^+-Q^--P^+$. If one of the porphyrin moieties were metallated, the process could in principle be selectively carried out using two different wavelengths of light. One can envisage possible applications in the field of molecular electronics and molecular data processing.

5.2.2 Systems with Two Acceptors

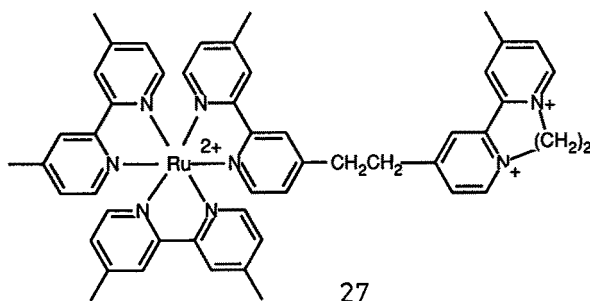
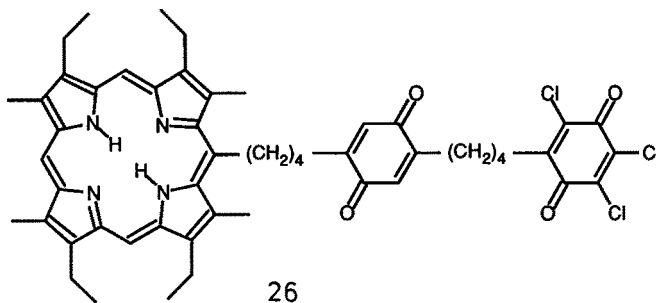
5.2.2.1 D^*-A-A Triads

The year 1983 marked the appearance not only of the triad photosynthesis mimics with two donor moieties (C-P-Q), but also those with two acceptors (P-Q-Q). The first such molecule, **26**, was reported by Sakata, Mataga and coworkers [45, 76]. Transient absorption studies on the picosecond time scale revealed that excitation of the porphyrin moiety resulted in rapid formation of the porphyrin radical cation. This result was interpreted in terms of the following series of events.



The second electron transfer step was designed into the molecule by making the second quinone a better electron acceptor than the first. Evidence for this step is provided by the lifetime of the charge separated state, which was about 300 ps in benzene. A similar molecule lacking the second quinone moiety had a lifetime of only about 130 ps.

Thus, **26** evidently mimics the BPh to Q_A to Q_B electron transfer sequence that occurs in the natural reaction center. One might wonder, however, why the lifetime of the final P^+-Q-Q^- state is so short, given the relatively long methylene chains joining the moieties and the much longer lifetimes found for the D-D-A triads. A likely possibility is that the flexible methylene chains allow the molecule to fold back on itself, so that the cation and anion are rather close together and charge



recombination can occur rapidly. $^1\text{H-NMR}$ studies have suggested that this may indeed be the case [77].

Some very interesting examples of $\text{D}^*\text{-A-A}$ systems have been reported by Mallouk and coworkers [78, 79]. In one of these systems, dyad **27** forms a covalently linked donor-acceptor component $\text{RuL}_3^{2+}\text{-2DQ}^{2+}$ which is exchanged onto the surface of zeolite L which has previously been ion-exchanged with benzylviologen (BV^{2+}). The 2DQ^{2+} moiety enters the pores of the zeolite, which also contain benzylviologen ions, but the large ruthenium complex cannot. Thus, the proposed structure of the system is as diagrammed in Fig. 5. Emission and transient diffuse reflectance studies show that excitation of the ruthenium moiety is followed within 5 ns by electron transfer to the 2DQ^{2+} moiety to generate an intermediate charge separated state, $\text{RuL}_3^{3+}\text{-2DQ}^{\cdot+}$. In analogy with the P-Q-Q system described above, a second electron transfer from the $2\text{DQ}^{\cdot+}$ moiety to the benzylviologen generates a final $\text{RuL}_3^{3+}\text{-2DQ}^{2+}\text{-BV}^{\cdot+}$ state. (In principle, the negative charge may be moved onto additional BV^{2+} moieties if they are present in the pore.) The final charge separated state has a lifetime of about 37 μs , and is formed with a quantum yield of $17 \pm 5\%$.

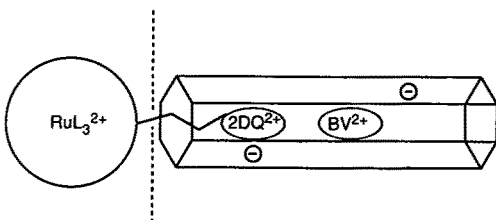
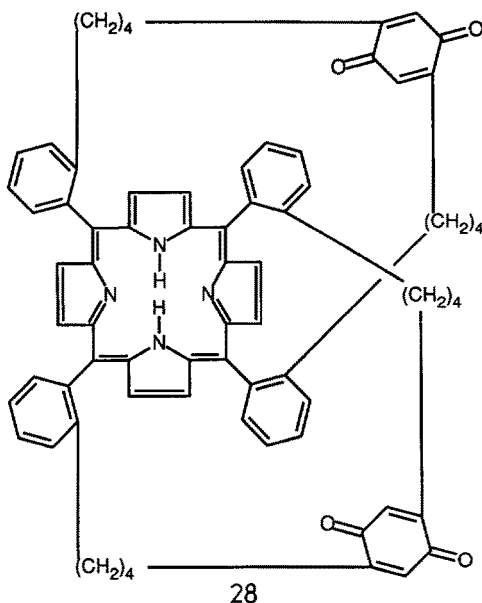


Fig. 5. Schematic diagram of the interaction of dyad **27** with the surface of zeolite L containing benzylviologen [78]

5.2.2.2 *A-D*-A Triads*

Systems of this type offer no inherent advantage over simple D*-A dyads in terms of the lifetime of the charge separated state. However, they can in principle lead to more efficient quenching of the donor excited state, for a particular combination of donor, acceptor, and linkage, because the rate of quenching is in effect multiplied by a factor of 2.

Staab and coworkers have prepared stacked Q-P-Q triad **28** [80–83]. An X-ray structure determination of the molecule shows that the quinones are situated directly above and below the plane of the porphyrin, with their planes parallel to the porphyrin plane and 3.4 Å from it. Steady state fluorescence measurements demonstrate strong quenching of the porphyrin first excited singlet state, which in turn suggests rapid electron transfer. Additional data were obtained from fluorescence lifetime measurements [83]. In dichloromethane, for instance, the lifetime of an analog of **28** in which the quinones were replaced with redox inactive dimethoxyphenyl substituents was 9.0 ns. In **28**, this lifetime was reduced to 260 ps.

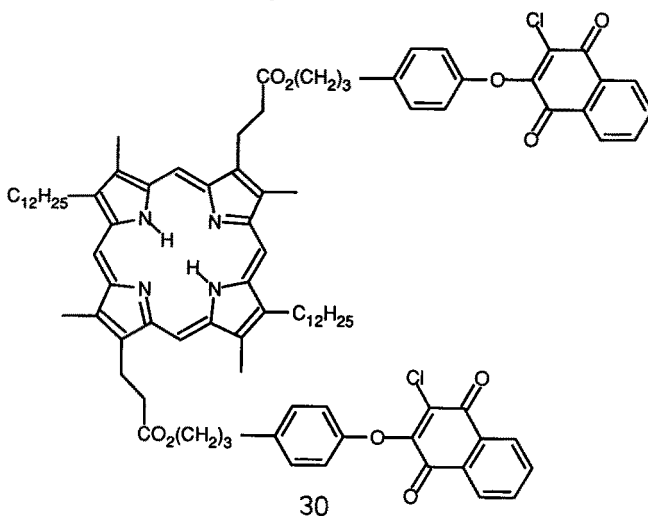
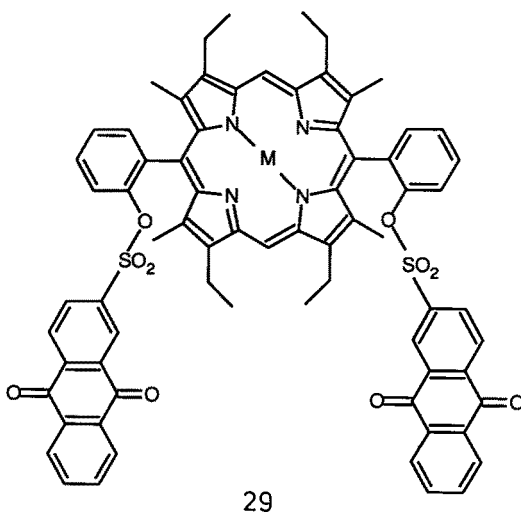


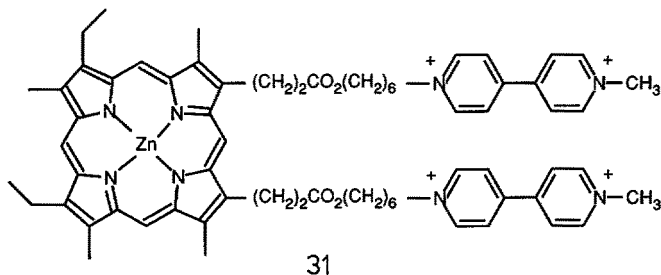
Comparison of the time resolved data in several solvents for **28** with that for a similar molecule in which one of the quinones was replaced by a dimethoxyphenyl group showed an increase in the lifetime of the fluorescence decay, as would be expected from the removal of a second acceptor, as discussed above. However, the data are complicated by the fact that the decays of the dimethoxyphenyl analog were decidedly biexponential. This result was interpreted in terms of an orbital symmetry effect on the electron transfer reaction. Interesting solvent and temperature dependencies were also observed with **28**.

Sanders, van der Plas, and coworkers prepared Q-P-Q system **29** along with the D-P-Q triads discussed above [64], and Maruyama and coworkers have

reported the synthesis of Q-P-Q **30** and related Q-P-Q molecules [84], but the photochemistry and photophysics of these triads was not discussed.

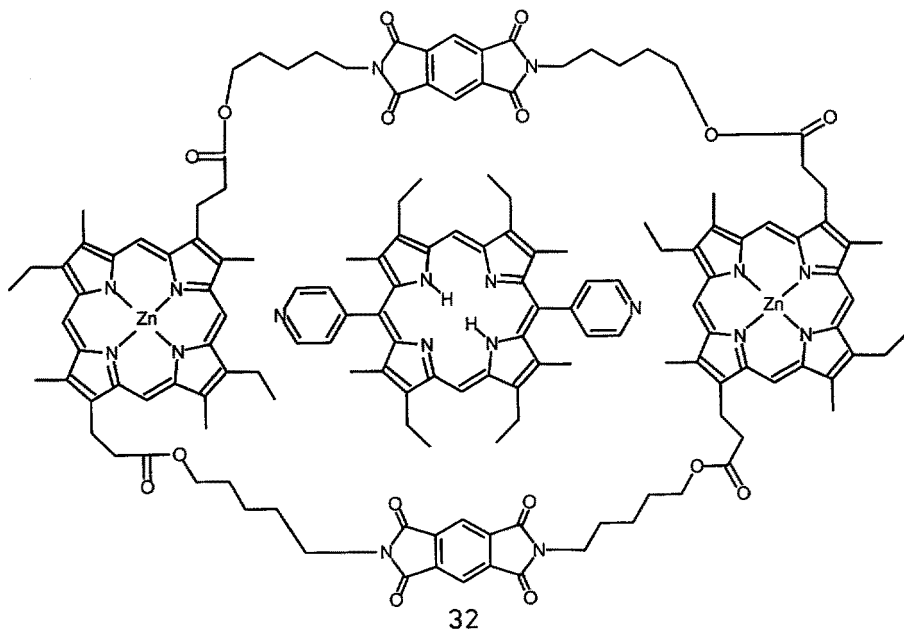
Electron acceptors other than quinones have been used in this type of system. For example, Mataga and coworkers have reported a series of zinc porphyrins linked to two methylviologen acceptors by chains of various lengths [85]. The results obtained for one of these molecules, **31**, will be discussed briefly. The fluorescence lifetime of the porphyrin moiety of the MV^{2+} -P- MV^{2+} in DMSO was found to be 720 ps, whereas that of the parent zinc porphyrin was about 3 ns. The fluorescence quenching is indicative of electron transfer to form $MV^{\cdot+}$ -P $^{\cdot-}$ - MV^{2+} . The identity of this product state was confirmed by transient absorption studies which showed the presence of the porphyrin and viologen radical cations. The lifetime of the charge separated state was surprisingly long — 160 ns. It was



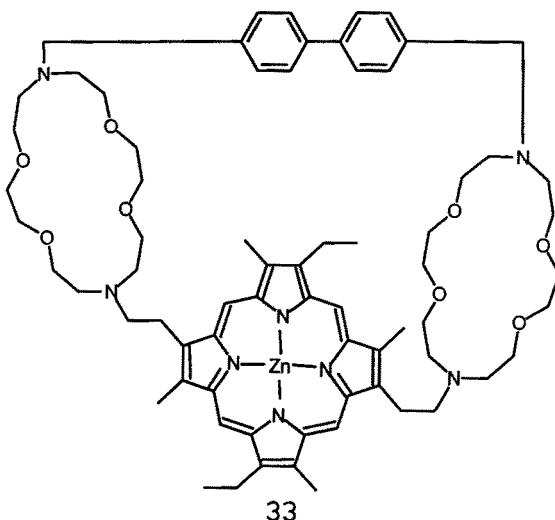


suggested that in DMSO solution, the molecule exists in a conformation where a viologen moiety is relatively close to the porphyrin, and is able to accept an electron from it. Once this occurs, the porphyrin and the reduced viologen moiety are both positively charged, and the resulting repulsions induce the molecule to assume a more extended conformation in which charge recombination is retarded.

Sanders and coworkers have prepared an interesting molecular assembly **32** in which the central porphyrin moiety is held in a sandwich conformation between the two pyromellitimide acceptors by coordination of its pyridyl groups with the zinc ions of the two peripheral porphyrin moieties [86]. Steady state fluorescence studies revealed that the fluorescence of the central porphyrin was quenched by at least 90% relative to the unbound material. This was interpreted in terms of electron transfer to the pyromellitimide moieties. Of course, energy transfer from the metallated porphyrins to the central free base porphyrin might also be expected in this molecule.



An interesting variation on this theme has been reported by Lehn and coworkers. In 1986, they reported the synthesis of macrocycle **33**, which consists of a zinc porphyrin bearing two linked cyclic binding subunits [87]. It was later found that addition of silver triflate to a solution of **33** in methanol resulted in the incorporation of a silver ion in each of the binding subunits [88]. Thus, the complex may be represented as $\text{Ag}^+ \cdot \text{P} \cdot \text{Ag}^+$. The porphyrin fluorescence of the silver complex was quenched, and transient absorption studies demonstrated that the porphyrin singlet state was quenched with a rate constant of $5.0 \times 10^9 \text{ s}^{-1}$ to yield a charge separated state $\text{Ag}^0 \cdot \text{P}^+ \cdot \text{Ag}^+$. Some quenching of the porphyrin triplet



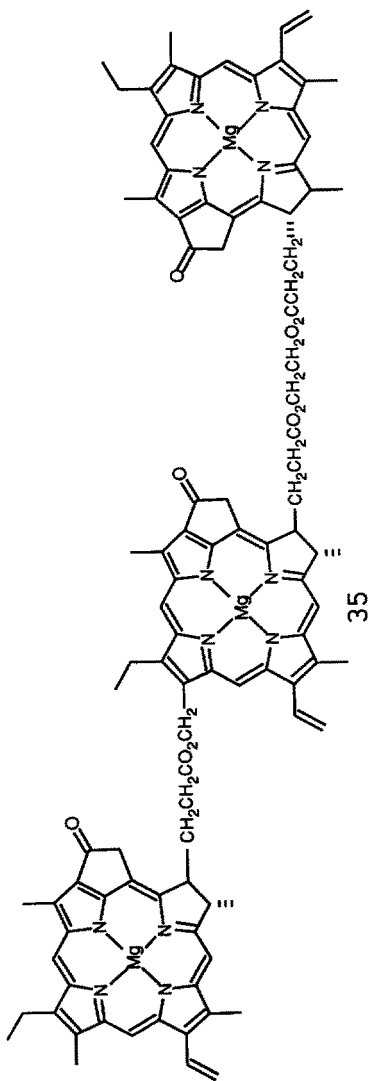
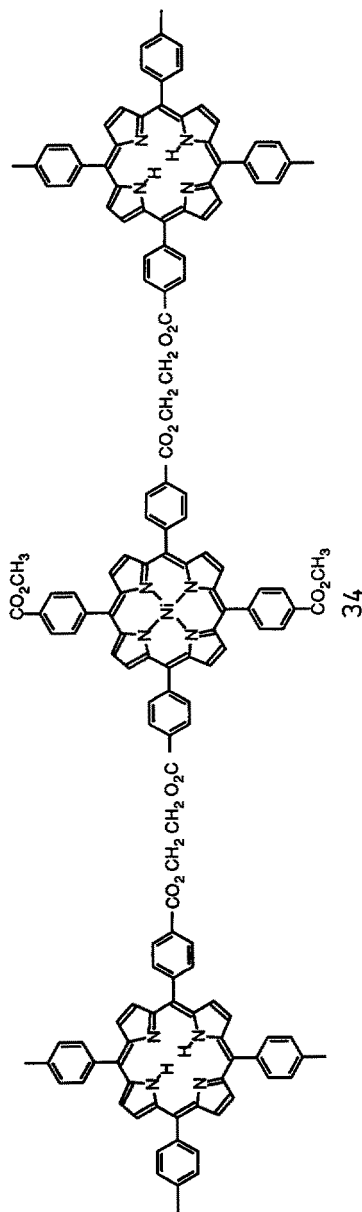
state also occurred ($k = 1.25 \times 10^7 \text{ s}^{-1}$). The porphyrin radical cation absorption decayed by complex kinetics with a half-life of about $5 \mu\text{s}$. The long lifetime and complex kinetics suggest that silver (0) atoms are likely displaced from the macrocycle after they are formed.

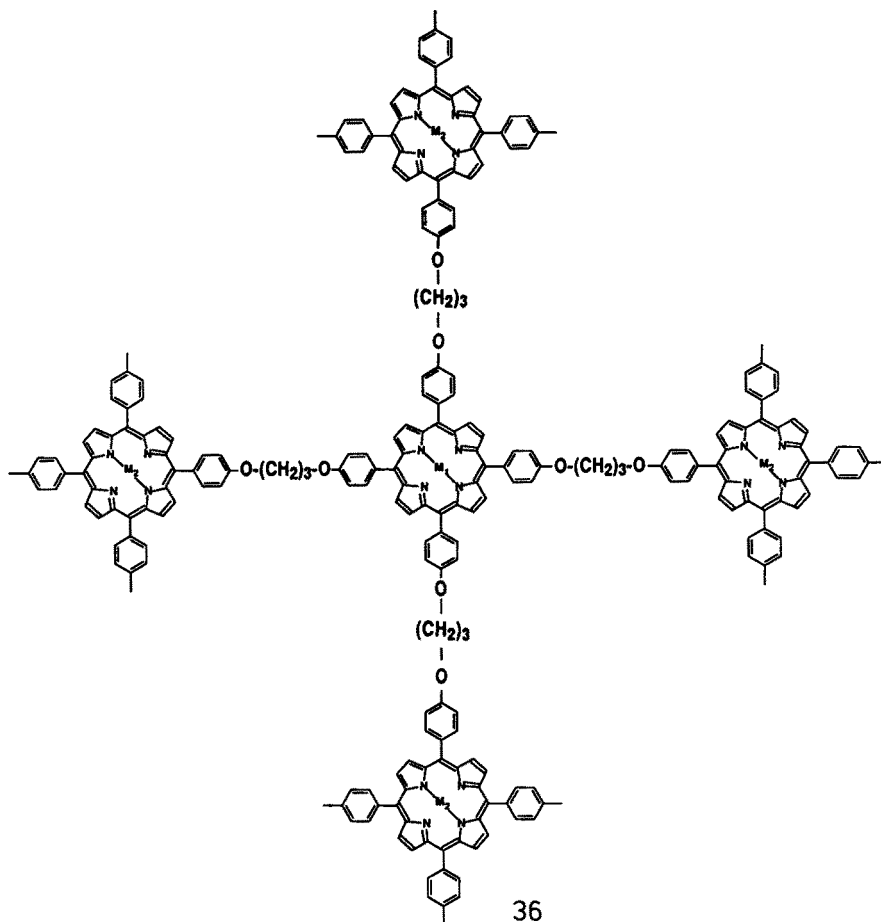
6 More Complex Molecular Devices

As the above discussion illustrates, the various types of triad systems provide a fertile ground for research. The body of knowledge accumulated through studies of unlinked donor acceptor systems, simple dyads, and triads may be coupled with the results of theoretical investigations of electron transfer to design triads for a variety of electron or energy transfer purposes. Some theoretical aspects of the design problem have been addressed [89, 90]. The interesting results for the triad molecules suggest that additional examples of cooperative effects and new strategies for photoinduced electron transfer at the molecular level might be found in even more complex molecular devices. This field is just beginning to be explored. Some promising results are reviewed below.

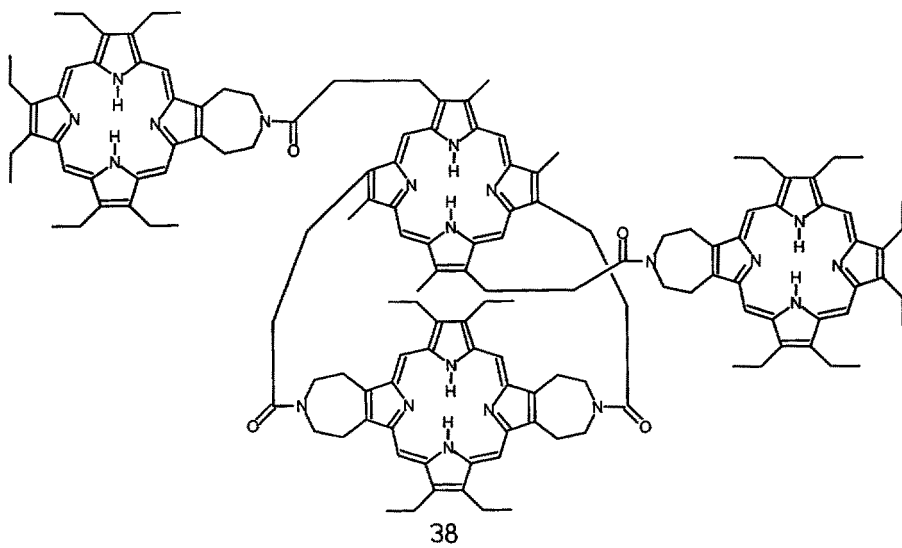
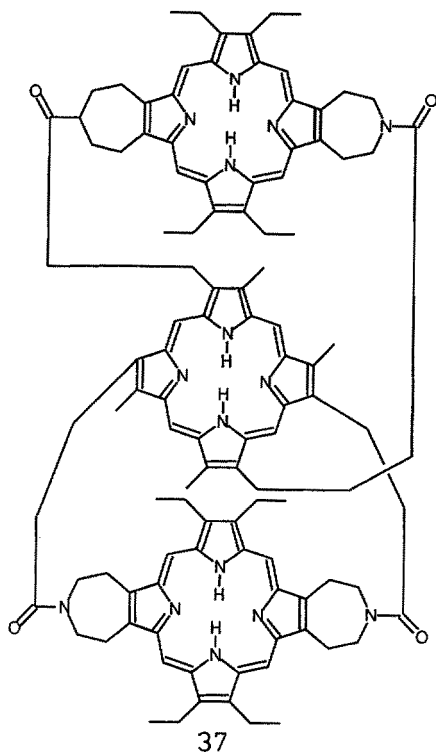
6.1 P_n Systems

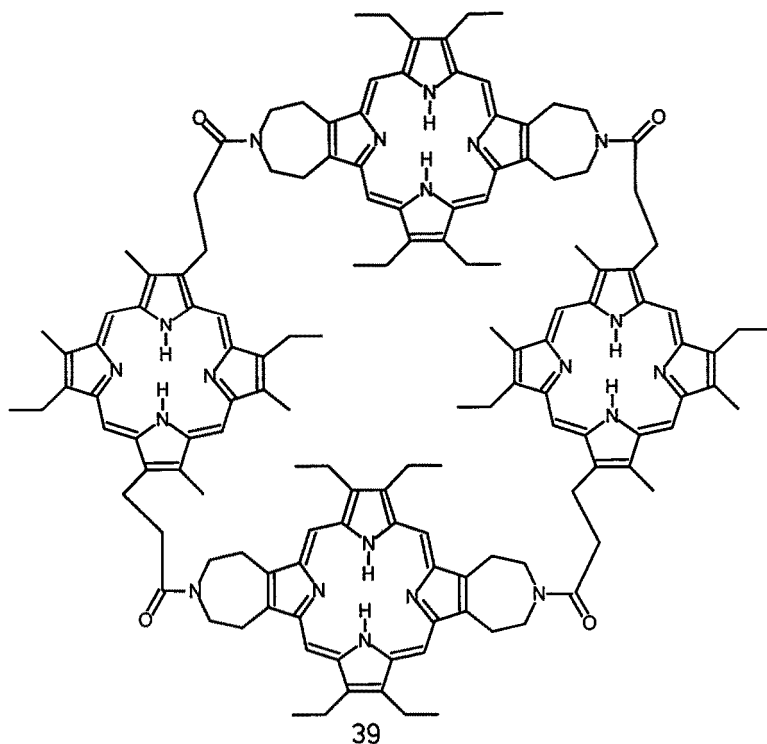
Oligomers containing three or more porphyrin or chlorophyll subunits have been known for some time. The references noted above [30–37] should be consulted for details. A few of the more interesting examples are represented by structures 34 [91], 35 [92], 36 [30, 93], 37 [94], 38 [35], 39 and a related hexamer [95]. To date,





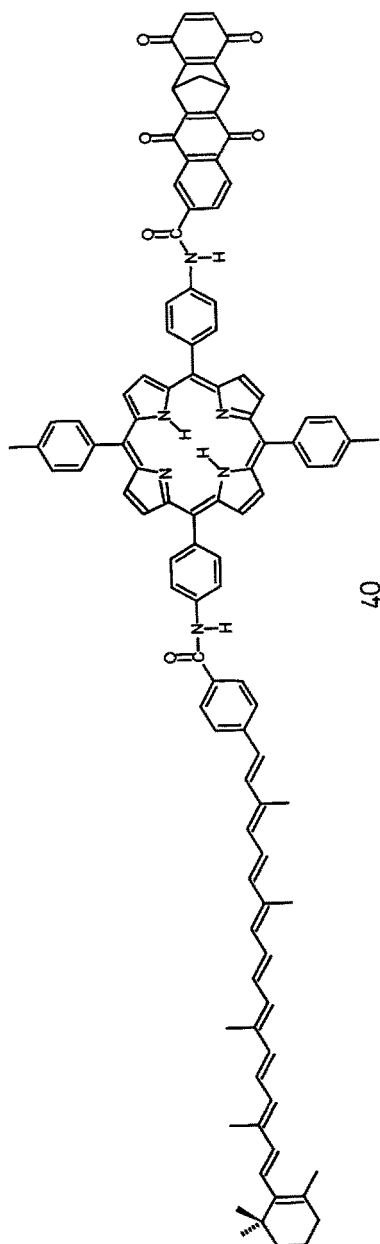
these structures have been studied mainly in the context of the degree of interporphyrin interaction as it affects the absorption spectrum and singlet energy transfer properties, rather than as models for photosynthetic electron transfer. Clearly, some of these materials could be promising models for the chlorophyll antenna arrays found in many organisms. In most cases, electron transfer would not be expected in such systems because the potential charge separated states lie at higher energy than the lowest lying porphyrin first excited singlet states. However, this situation could be altered by proper substitution of metal ions into some of the porphyrin moieties, and/or by substitution on the periphery of the porphyrins in order to stabilize positive or negative charges. More work in this area will certainly appear in the next few years. Interesting work on electron transfer (not necessarily photoinitiated) between metallated porphyrin dyads has been reported in the context of investigations of cytochromes and other biological redox systems, but that work is outside the scope of this review.





6.2 D₂-A₂ Systems

Tetrad **40** provides a good illustration of how the addition of new electron transfer pathways to a molecular device can enhance the quantum yield of long lived charge separation [96, 97]. The molecule is a hybrid of the C-P-Q and P-Q-Q triad systems discussed above. There are two important things to note about the structure of **40**. In the first place, the quinones are linked by a rigid bicyclic bridge, and the carotenoid, porphyrin and quinone moieties are joined by amide bonds, which impart some rigidity to the structure by virtue of their partial double bond character. The purpose of these features is to ensure that the molecule remains in an extended conformation, rather than folding up and possibly short-circuiting the expected electron transfer sequence. In addition, the benzoquinone, which is the best electron acceptor, is located farther from the porphyrin than the naphthoquinone. This arrangement sets up the system for sequential electron donation from the porphyrin to the naphthoquinone, and on to the benzoquinone moiety. The response of this C-P-Q_A-Q_B tetrad to excitation of the porphyrin is illustrated in Fig. 6. The energies of the various charge separated states have been estimated from cyclic voltammetric studies, as mentioned above for the triad systems. As might be expected from the previously discussed porphyrin-quinone



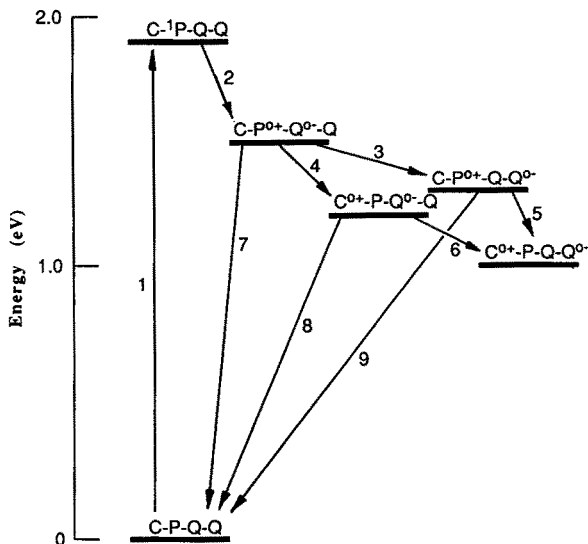
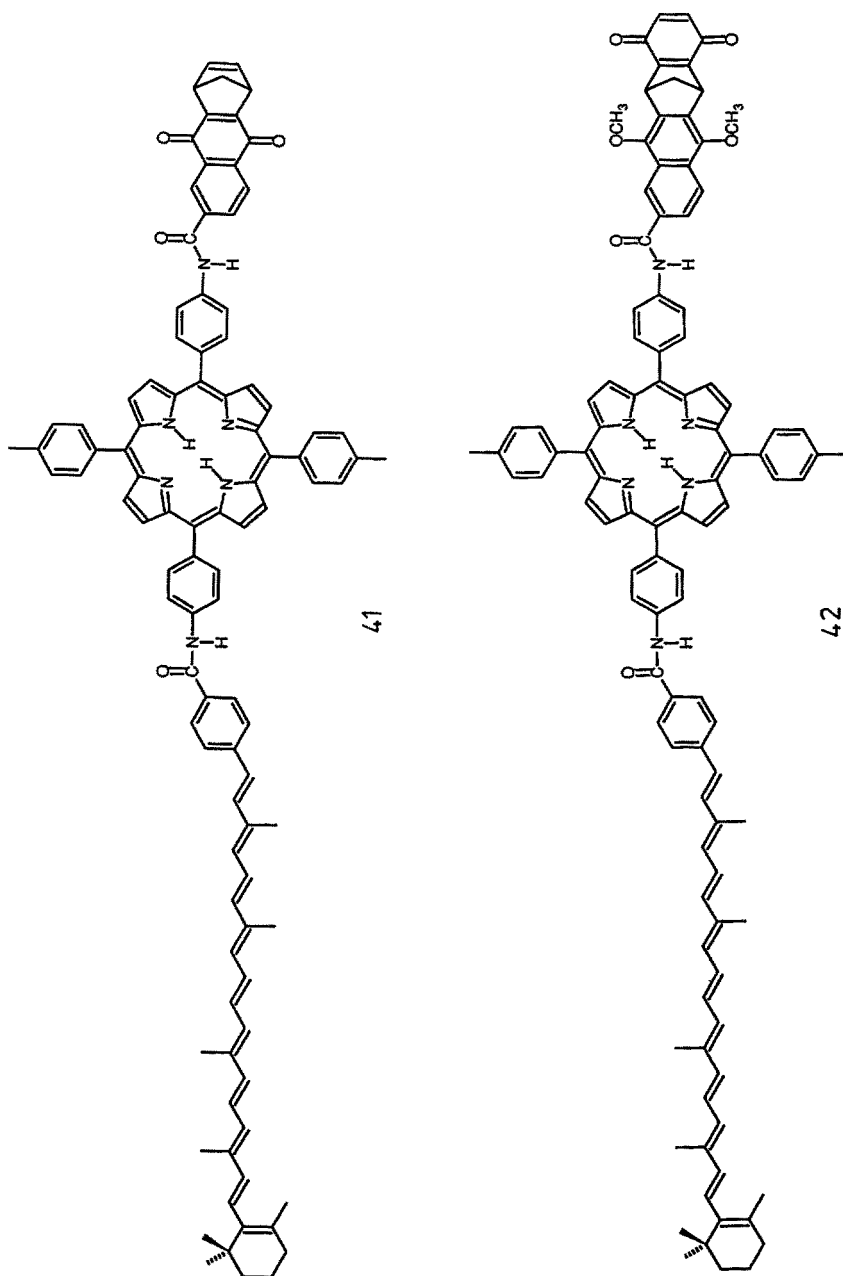


Fig. 6. Transient states of C-P-Q-Q tetrad **40** and relevant electron transfer pathways

systems, the porphyrin first excited singlet state donates an electron to the naphthoquinone to yield $\text{C-P}^+-\text{Q}_\text{A}^--\text{Q}_\text{B}$ (step 2 in the figure). Single photon counting fluorescence decay studies of **40** in dichloromethane solution yield a rate constant of $k_2 = 6.7 \times 10^{10} \text{ s}^{-1}$. Thus, the quantum yield of step 2 is essentially unity. Competing with charge recombination of $\text{C-P}^+-\text{Q}_\text{A}^--\text{Q}_\text{B}$ (step 7) are two additional electron transfer reactions (steps 3 and 4), each of which generates a new intermediate ($\text{C-P}^+-\text{Q}_\text{A}^--\text{Q}_\text{B}^-$ and $\text{C}^+-\text{P-Q}_\text{A}^--\text{Q}_\text{B}$). Steps 5 and 6 compete with recombination of these intermediates to produce the same final charge separated state $\text{C}^+-\text{P-Q}_\text{A}^--\text{Q}_\text{B}^-$. Transient absorption studies (Fig. 7) show that this state has a lifetime of 460 ns at 295 K and is formed with a quantum yield of 0.23. At 240 K the quantum yield has increased to about 0.5.

The details of the multistep electron transfers undergone by **40** may best be appreciated by reference to the results for two model compounds **41** and **42**. Triad **41** is similar to the tetrad, except that it lacks the final benzoquinone moiety. Excitation of the porphyrin leads to the production of $\text{C-P}^+-\text{Q}_\text{A}^-$ with a quantum yield of essentially 1, as was observed for **40**. In common with other C-P-Q triads, this state goes on to produce a final $\text{C}^+-\text{P-Q}_\text{A}^-$ species. However, the quantum yield of this state is only 0.04, and its lifetime is about 70 ns (Fig. 7). The low quantum yield is due to the fact that only a single, relatively inefficient electron transfer step (analogous to step 4 in Fig. 6) competes with charge recombination of $\text{C-P}^+-\text{Q}_\text{A}^-$. With the tetrad **40**, a similar pathway is still available, but in addition there is a second, relatively efficient pathway which also competes with charge recombination and is responsible for most of the quantum yield of the final state.

Molecule **42** retains the benzoquinone moiety, but the naphthoquinone has been converted to a dimethoxynaphthalene species which is not a good electron



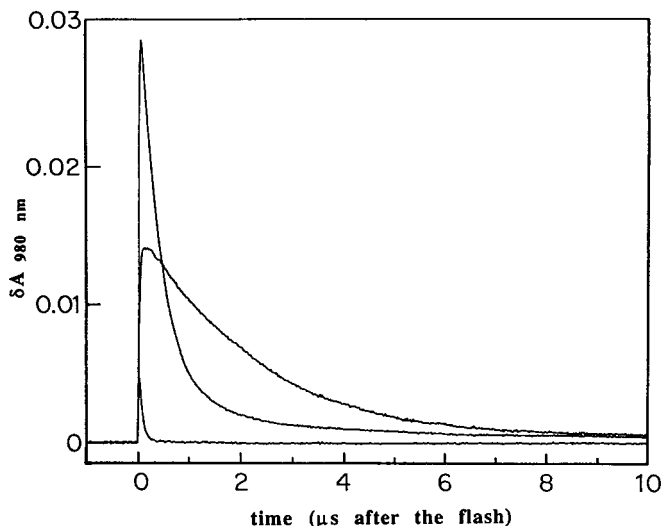
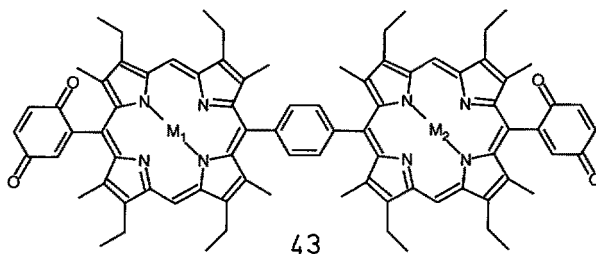


Fig. 7. Transient absorption (980 nm) of ca 1×10^{-4} M solutions of **40** (*upper trace*), **41** (*lower trace*) and **42** (*middle trace*) in dichloromethane at ambient temperature following pulsed laser excitation with 590 nm light. The curves have been normalized so that relative transient absorption reflects relative quantum yield

acceptor. Absorption of light by the porphyrin moiety produces a final charge separated state of the form $C^+-P-Q_A(OMe)_2-Q_B^-$ with a lifetime of 1.9 μs and a quantum yield of 0.11 (Fig. 7). The reduced quantum yield relative to **40** is due in part to the fact that in **42**, the photoinitiated electron transfer step must occur directly from $C^{-1}P-Q_A(OMe)_2-Q_B$ to yield $C-P^+-Q_A(OMe)_2-Q_B^-$ and is therefore a very long-range transfer. Fluorescence decay measurements show that this step is indeed slower ($k = 9.6 \times 10^8 s^{-1}$), and that its quantum yield is only 0.77. The overall quantum yield of $C^+-P-Q_A(OMe)_2-Q_B^-$ is further reduced by slow electron transfer from the carotenoid moiety which must compete with charge recombination to the ground state (analogous to step 9 in Fig. 6). With tetrad **40**, however, the reduced donor-acceptor separation for the initial electron transfer event leads to a much more rapid transfer and a quantitative yield of the initial $C-P^+-Q_A^-Q_B$ state in spite of the reduced exergonicity for this step due to the substitution of a naphthoquinone for the benzoquinone species. As mentioned above, two subsequent electron transfer routes are then available for formation of the final state. The fact that significant photoinitiated electron transfer occurs at all in **42** may indicate involvement of the linkage bonds in the electron transfer process [96].

It is clear from these results that the availability of additional electron transfer pathways in **40** has led to a substantial enhancement of the quantum yield of the final state relative to the two model systems which feature fewer electron transfer steps to attain related final states. This strategy should be useful in the design of other complex molecular devices.

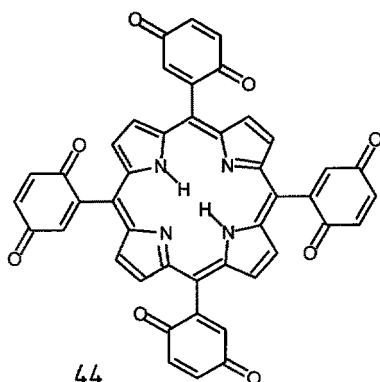


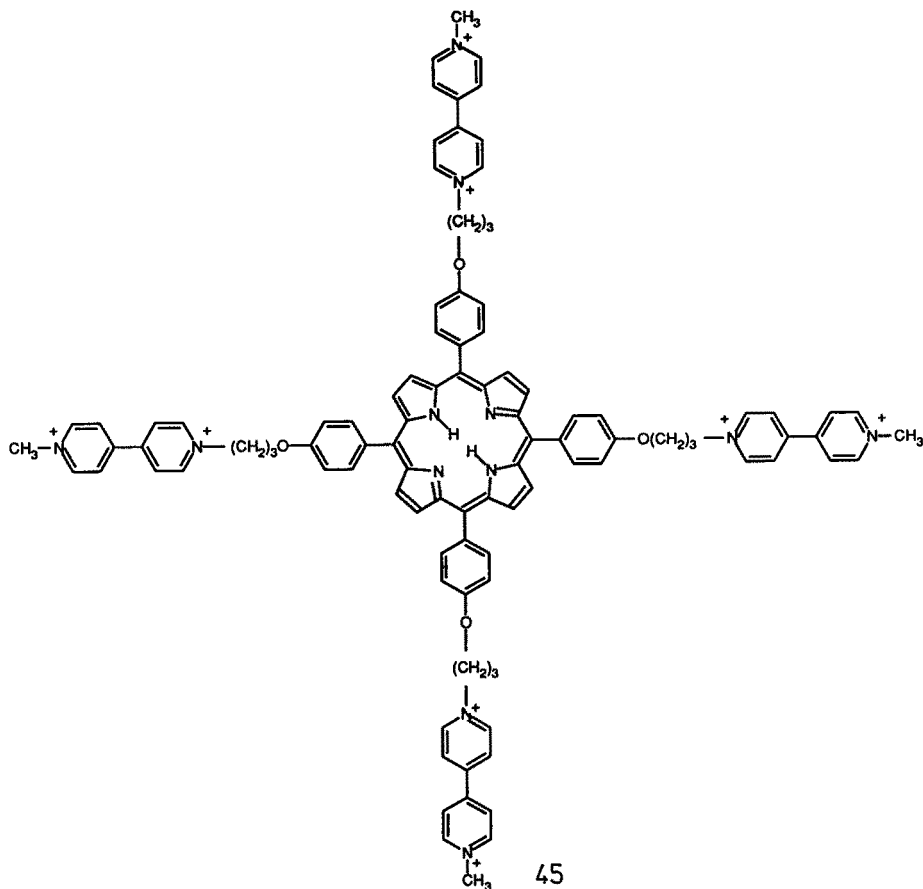
The Q-P-P-Q tetrad **43** has been synthesized by Sessler and coworkers [69, 98]. As expected, it demonstrates strong quenching of the porphyrin fluorescence, and this presumably occurs by electron transfer. It is probable that selective metallation of such a tetrad would produce a species which would behave as a triad in a manner analogous to **17** and **18**, but it is not obvious that such a molecule would have any significant advantages over these systems. As is the case with a number of the other complex systems, **43** may in principle demonstrate stereoisomerism when rotations about the linkage bonds are slow on the time scales of electron and energy transfer.

Sanders and coworkers have prepared a cyclic molecule featuring two zinc porphyrin donors linked to two pyromellitimide acceptors as a precursor to **32** [99, 100]. The photochemical and photophysical properties were not discussed.

6.3 D-A₄ Systems

Molecules of this type can in principle display extremely efficient quenching of an excited donor by the four linked acceptors. An example of such a molecule is PQ₄ species **44**, which was reported by Dalton and Milgrom [101]. The fluorescence quantum yield for the porphyrin was estimated to be less than 10⁻³, which is

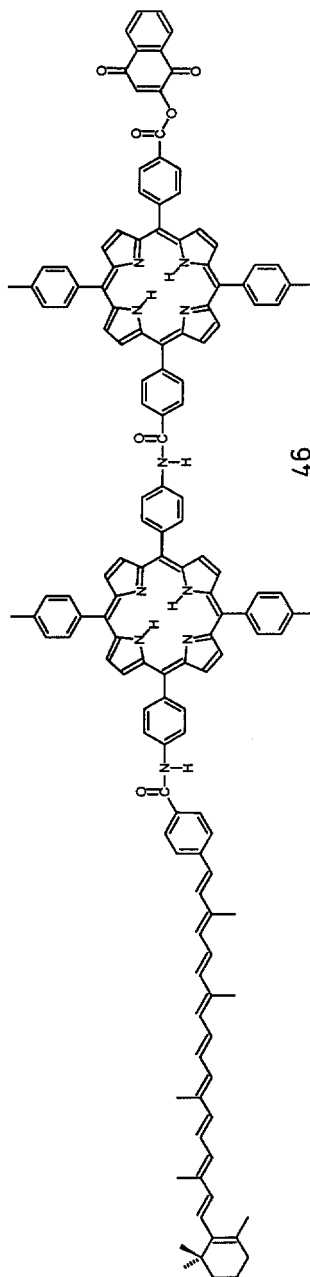




consistent with rapid and efficient electron transfer to the attached quinone moieties. Of course, even one quinone linked to the porphyrin in this manner is a very efficient quencher. Milgrom has also prepared a porphyrin bearing four methylviologen acceptor groups (45) [93].

6.4 D₃-A Systems

The C-P_A-P_B-Q tetrad 46 has recently been reported [102]. This molecule was prepared using the synthetic methodology developed for the C-P-Q triads. The two porphyrin moieties have essentially identical visible spectra, and there is little interaction between the chromophores in absorption. The emission spectra are also essentially identical for the two porphyrins, and their first excited singlet



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states are virtually isoenergetic. On the other hand, they differ in their redox properties by virtue of the linkage bonds. Upon excitation, the tetrad undergoes the complex series of events depicted in Fig. 8. The two first excited singlet states are produced in essentially equal amounts. Fluorescence decay studies indicate that singlet energy transfer between them (steps 5 and 6) occurs rapidly on the time scale of the electron transfer events which follow. The porphyrin singlet states may decay by the usual photophysical processes summarized in steps 2 and 4 in the figure. Competing with these processes is electron transfer from P_B to the attached naphthoquinone derivative (step 7) to yield $C-P_A-P_B^+-Q^-$. The fluorescence decay studies of **46** and appropriate model systems show that in anisole solution, the rate constant for this step is about $2.4 \times 10^8 \text{ s}^{-1}$. This initial intermediate may, of course, undergo charge recombination (step 9), but the energetics shown in Fig. 8 suggest that a second electron transfer step competes with recombination to yield $C-P_A^+-P_B-Q^-$. This species may then go on via step 10 to produce a final charge separated state $C^+-P_A-P_B-Q^-$. Indeed, transient absorption studies detect the carotenoid radical cation corresponding to this state. The final species is produced with a quantum yield of 0.25 and has a lifetime of 2.9 μs .

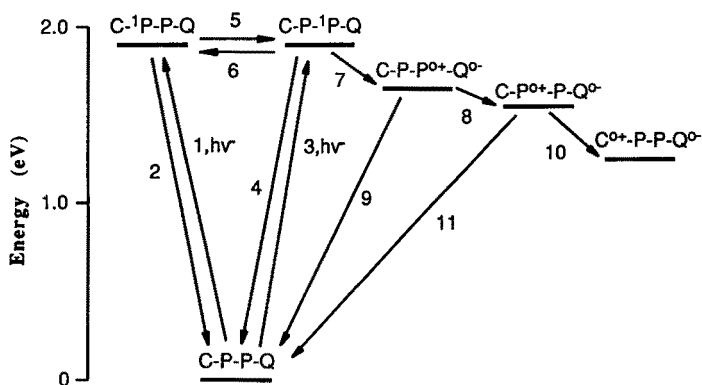


Fig. 8. Estimated energies of transient states of C-P-P-Q tetrad **46** and relevant energy and electron transfer pathways

As mentioned above, the energy levels in Fig. 8 have been estimated from cyclic voltammetric studies and may be slightly in error in that they do not explicitly correct for coulombic stabilization of intermediates such as $C-P_A-P_B^+-Q^-$. If such stabilization were to drop the energy of $C-P_A-P_B^+-Q^-$ below that of $C-P_A^+-P_B-Q^-$, then the formation of the final $C^+-P_A-P_B-Q^-$ state might be thought of as a single step from $C-P_A-P_B^+-Q^-$ in which the porphyrin P_A facilitates the transfer via superexchange [8, 26]. As was noted earlier, the accessory bacteriochlorophyll in the natural reaction center may play a similar role.

7 Conclusions

Perusal of the above examples demonstrates that building artificial reaction centers which materially duplicate the functions of the natural photosynthetic reaction center is by no means an impossibility. Indeed, the molecules discussed here are but the ancestors of better designed and sometimes more complex molecular devices which are being prepared at this time, and which will demonstrate higher quantum yields for charge separation, longer lifetimes for the states produced, and less wastage of potential energy. Improved biomimetic antenna systems and photoprotective agents will also be prepared in the laboratory. Rapid progress is expected in the next five years.

Although the multicomponent systems discussed above were mostly prepared in an effort to learn more about natural photosynthetic energy conversion, they may have other applications. One possibility is in the construction of electronic devices at the molecular level. For example, a molecular shift register memory based on porphyrin diquinone molecules has recently been proposed [103]. The physical length of molecules such as **46** (~ 75 Å) makes them particularly attractive as candidates for inclusion in fabricated devices. Molecular electronics is only one aspect of a more general problem which must be faced with these devices if they are ever to be of practical utility: how does one extract the stored energy from them in a practical way? Although some work has been done in this area, the problem is still far from being solved.

8 Acknowledgements

Much of the work performed at Arizona State University was supported by the National Science Foundation (CHE-8903216, CHE-8515475, INT-8514252, and INT-8701663) and by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (DE-FG02-87EDR13791). We gratefully acknowledge the contributions of the many colleagues, students, and postdoctoral associates who have contributed to this work, and whose names are listed in the references. DG thanks Professor F. C. De Schryver for his hospitality at the Katholieke Universiteit Leuven during the preparation of this manuscript. This is publication no. 33 from the Arizona State University Center for the Study of Early Events in Photosynthesis. The Center is funded by U.S. Department of Energy grant no. DE-FG02-88ER13969 as part of the USDA/DOE/NSF Plant Sciences Center program.

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Artificial Photosynthetic Model Systems Using Light-Induced Electron Transfer Reactions in Catalytic and Biocatalytic Assemblies

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Artificial photosynthetic devices provide a means for the use of solar light in generating fuel materials and valuable chemicals and for the removal of environmental pollutants. Control of photosensitized electron transfer reactions and development of catalysts for utilizations of the intermediate electron transfer products are essential aspects in designing artificial photosynthetic systems. Homogeneous and heterogeneous catalysts as well as biocatalysts (enzymes and cofactors) can be coupled to photochemically induced electron transfer reactions and effect photosynthetic transformations such as hydrogen evolution, CO₂-fixation, hydrogenation, and hydroformylation processes. The progress in tailoring artificial photosynthetic devices in the context of thermodynamic and kinetic limitations of such systems is described. Integrated systems, where catalytic performance and control of electron transfer reactions which occur in organized assemblies are specifically emphasized.

List of Symbols and Abbreviations

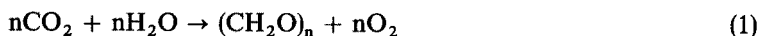
PS-I	Photosystem I
PS-II	Photosystem II
ET	Electron transfer
NADP ⁺	Nicotinamide adenine dinucleotide phosphate
NADPH	Dihyronicotinamide adenine dinucleotide phosphate
NAD ⁺	Nicotinamide adenine dinucleotide
NADH	Dihyronicotinamide adenine dinucleotide
S	Photosensitizer
D	Electron donor
Q	Quencher
ϕ	Quantum yield
k_s	Rate constant for charge separation of encounter complex of photoproducts
k_b	Rate constant for back reaction of photoproducts
τ	Life-time
k_{et}	Electron transfer rate constant
MLCT	Metal to ligand charge transfer
bpy	Bipyridine
η_s	Fraction of reduced photoproduct resisting recombination with oxidized photosensitizer
η_D	Fraction of reduced photoproduct resisting recombination with oxidized electron donor
η_P	Fraction of usable photoproducts for storage, that are stabilized against recombination
PVS ^o	<i>N,N'</i> -(3-Propylsulfonato)4,4'-bipyridinium
TEOA	Triethanolamine
mV	Millivolt
EDTA	Ethylenediamine tetraacetic acid
C_nV^{2+}	<i>N,N'</i> -Dialkyl-4,4'-bipyridinium, alkyl viologen
C_8V^{2+}	<i>N,N'</i> -Dioctyl-4,4'-bipyridinium, octyl viologen
C_4V^{2+}	<i>N,N'</i> -Dibutyl-4,4'-bipyridinium, butyl viologen
F	Faraday constant
N	Avogadro Number
r	Radius
MW	Molecular Weight
ATP	Adenosine triphosphate
CoA	Coenzyme A
MV^{2+}	<i>N,N'</i> -Dimethyl-4,4'-bipyridinium, methyl viologen
DQS	<i>N,N'</i> -Dipropylsulfonato-2,2'-bipyridinium
Eo	Eosin
BMV^{2+}	<i>N,N'</i> -Dibenzyl-4,4'-(3,3'-dimethyl)bipyridinium
$C_{14}MV^{2+}$	<i>N</i> -Dodecadecyl- <i>N'</i> -methyl-4,4'-bipyridinium
PCP	Polyvinylpyridinium
dpm	Diphenylphosphinobenzene- <i>m</i> -sulfonate

TN	Turnover Number
dRFI	Deazariboflavin
bpz	Bipyrazine
FDR	Ferredoxin reductase
LipDH	Lipoamide dehydrogenase
Zn-TMPyP ⁴⁺	Zn(II)- <i>meso</i> -(<i>N</i> -tetramethylpyridinium)porphyrin
AlcDH	Alcohol dehydrogenase
GluDH	Glutamate dehydrogenase
LacDH	Lactate dehydrogenase
AlaDH	Alanine dehydrogenase
β -HButDH	β -Hydroxybutyrate dehydrogenase
MB ⁺	Methylene blue
MPMS ⁺	<i>N</i> -Methyl phenazonium methyl sulfonate
λ	Wavelength
MalE	Malic enzyme
IcitDH	Isocitrate dehydrogenase
Fum	Fumarase
Asp	Aspartase
HyD	Hydrogenase
ForDH	Formate dehydrogenase
NitraR	Nitrate reductase
NitriR	Nitrite reductase

1 Introduction

The industrialized society of our world utilizes energy at a rate of 10^{17} cal year⁻¹, a value that multiplies itself every 15–20 years [1, 2]. It is estimated that ca. 80% of our energy resources are fossil fuels (oil, gas, and coal). These energy supplies are continuously being depleted, and it is assumed that the fossil fuel supplies will end within the next century. Alternative energy sources are vital for the future development of mankind [3]. The sun provides the highest reservoir of available energy. In principle, solar light could supply all our energy needs [4]. The solar energy flux corresponds to 10^{20} cal year⁻¹, and thus coverage of ca. 1% of the world's surface by solar light conversion and storage devices (operating at 10% efficiency) could provide all energy needs for mankind [1].

The photosynthetic process in nature represents a sophisticated biochemical system for the conversion and storage of solar light energy in the form of fuel products [5–9]. In photosynthesis, carbon dioxide and water are converted to carbohydrates, (Eq. (1)), using solar light as energy source. The global quantities of CO₂, carbonates, and bicarbonates is estimated to be 10^{16} tons [10]. This



quantity is subjected to dynamic processes and is influenced by the activities of mankind [11] (Fig. 1). Photosynthesis is the source of fossil fuels generated within the past one hundred million years. The yearly quantity of produced biomass is estimated [12] to be ca. 2×10^{11} tons year⁻¹. The products of the photosynthetic apparatus provide the chemicals and energy source for the catabolic (heterotrophic) cycle of living organisms. In the heterotrophic cycle, synthesis of complex carbon

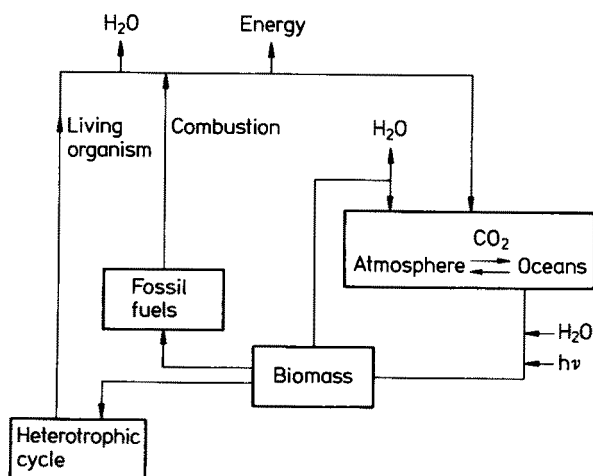


Fig. 1. Carbon dioxide cycle in universe

materials, and degradation of organic compounds to CO_2 and water and concomitant supply of energy (Krebs cycle) occurs. In addition, combustion of fossil fuels and biomass is a central route for depleting the photosynthetic products.

Constant increase of the world's population and industrialization of modern countries, together with depletion of global vegetation, results in an unbalanced relation between photosynthesis and the CO_2 -generating processes [13]. A continuous increase in atmospheric CO_2 concentration is realized [14] (Fig. 2). Substantial ecological concern is directed to the increase of CO_2 content in the atmosphere, as the "greenhouse effect" could trigger a rise in surface temperatures and abrupt climatic changes [15]. Thus, development of man-made artificial photosynthetic devices, could provide two complementary responses to these universal problems:

- i) Artificial photosynthetic devices, mimicking natural photosynthesis to the extent that abundant materials (i.e., CO_2 , H_2O) are converted to fuel products, could be a universal source for fuel compounds and energy supply.
- ii) Artificial photosynthetic systems could intervene in the continuous increase of atmospheric CO_2 concentration, and provide resolution for this worrying ecological problem.

The photosynthetic process involves photochemical reactions followed by sequential dark chemical transformations (Fig. 3). The photochemical processes occur in two photoactive sites, photosystem I and photosystem II (PS-I and PS-II, respectively), where chlorophyll a and chlorophyll b act as light-active compounds [6, 8]. Photoinduced excitation of photosystem I results in an electron transfer (ET) process to ferredoxin, acting as primary electron acceptor. This ET process converts light energy to chemical potential stored in the reduced ferredoxin and oxidized chlorophyll. Photoexcitation of PS-II results in a similar ET process where plastoquinone acts as electron acceptor. The reduced photoproduct generated in PS-II transfers the electron across a chain of acceptors to the oxidized chlorophyll of PS-I and, consequently, the light harnessing component of PS-I is recycled. Reduced ferredoxin formed in PS-I induces a series of ET processes,

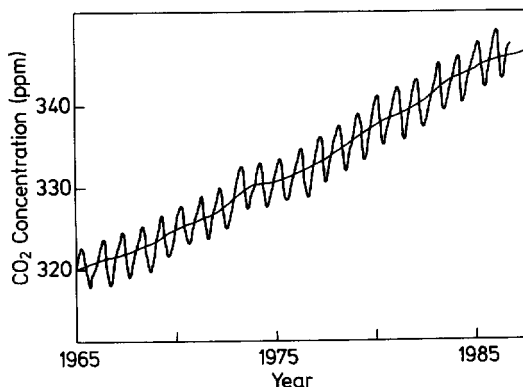


Fig. 2. Annual atmospheric CO_2 -concentration measured at Mauna Loa Observatory, Hawaii. Fluctuations originate from seasonal photosynthetic performance (taken from Ref. [14])

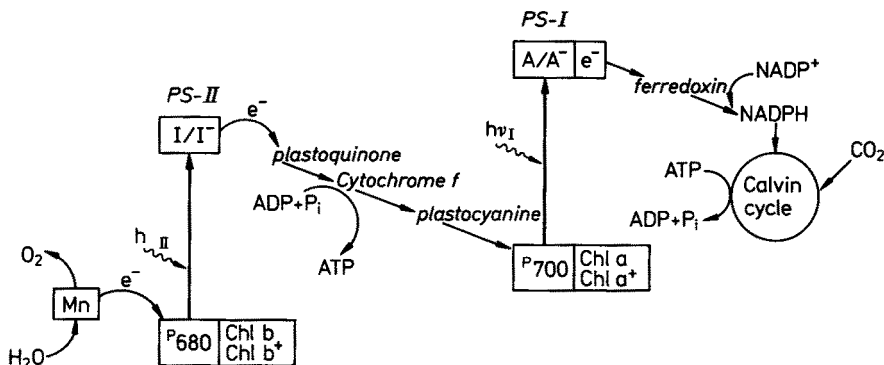


Fig. 3. Sequence of photochemical processes in the photosynthesis cycle (Z-scheme)

ultimately reducing the cofactor NADP^+ to NADPH . This reduced cofactor acts as electron source for the Calvin cycle, where CO_2 is reduced to carbohydrates in a complex sequence of biocatalyzed transformations [10]. The oxidized chlorophyll of PS-II mediates the biocatalyzed oxidation of water to oxygen. From a physico-chemical point of view, the synchronous sequence of transformations involved in photosynthesis include a photochemical part, where light energy is converted to chemical potential through ET reactions, and a set of dark chemical reactions where the ET photoproducts are utilized in driving endoergic CO_2 -fixation.

The objectives of this account are to review the problems involved in tailoring man-made photosynthetic systems and to highlight the scientific accomplishments in artificial photosynthesis. The chemical methodology of linking catalysts, biocatalysts and photosystems into integrated photosynthetic assemblies will be discussed.

2 Photoinduced Electron Transfer Reactions

2.1 Kinetics of Photoinduced Electron-Transfer

Deactivation of an excited species can proceed through radiation or radiationless decays, energy transfer quenching, or electron transfer routes. The operation of artificial photosynthetic devices relies mainly on electron-transfer (ET) processes induced by an excited species [16, 17]. Two general mechanisms can be involved in the ET process of an excited species: Reductive ET quenching of an excited species, S^* , by an electron donor D, results in the redox products S^- and D^+ (Fig. 4a). Alternatively, oxidative quenching of the excited species by an electron acceptor, A, can occur (Fig. 4b), resulting in the electron transfer products S^+ and A^- .

Electron transfer reactions involving excited species have been characterized theoretically [18–21] and experimentally [22–25]. The event of ET from an excited

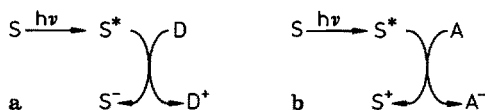
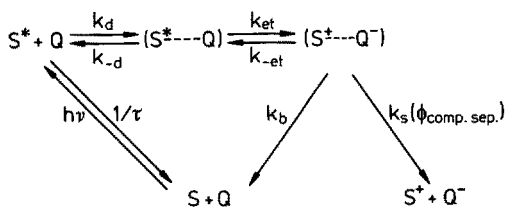


Fig. 4a, b. Electron transfer, ET, quenching mechanisms of an excited species, S^* . **a)** Reductive ET quenching by an electron donor, D ; **b)** oxidative ET quenching by an electron acceptor, A

compound, and generation of the charge-separated products, involves several sub-processes that are outlined in Scheme 1. The excited species forms a geminate complex with the quencher component, Q , and electron transfer leads to the encounter cage complex of ET products. Rapid recombination of these intermediates to the ground-state reactants competes with the charge separation of the redox components. The overall anticipated rate constant for the bimolecular ET process can be expressed [26] by the partial rate constants of the sequential steps, and is given by Eq. (2). Although effective electron transfer quenching is desired to accumulate the encounter complex of photoproducts, the charge separation yield of the encounter complex of photoproducts, $\phi_{\text{comp. sep.}}$, is an important factor controlling the effectiveness of formation of the redox products. The value for the charge separation yield of the primary encounter complex is given by Eq. (3), and thus maximum efficiencies will be obtained when $k_s \gg k_b$. The overall charge separation yield, ϕ_s , is thus determined by the effectiveness of the ET quenching process as well as the yield for the separation of the encounter complex of photoproducts, and is given by Eq. (4), where τ_0 is the lifetime of the excited species.



Scheme 1. Sequence of reactions involved in ET quenching of an excited species, S , and charge separation of photoproducts, S^+ and Q^-

$$k_{\text{obs}} = \frac{k_b}{1 + \frac{k_b}{k_s} + \frac{k-d}{k_{\text{et}}} \left[1 + \frac{k_{\text{-et}}}{k_s} + \frac{k_b}{k_{s-}} \right]} \quad (2)$$

$$\phi_{\text{comp. sep.}} = k_s / k_b + k_s \quad (3)$$

$$\phi_s = \frac{k_s}{k_b + k_s} \left[\frac{k_{\text{et}} \tau_0 [A]}{1 + k_{\text{et}} \tau_0 [A]} \right] \quad (4)$$

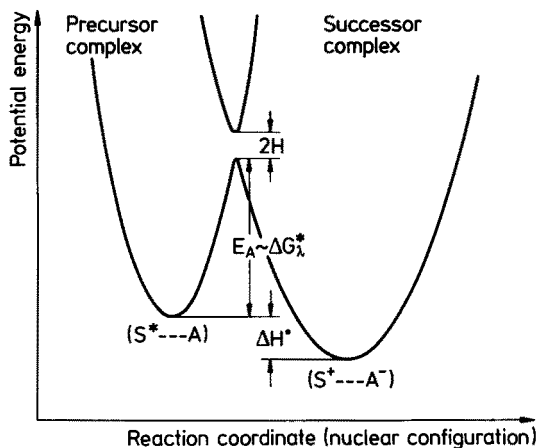


Fig. 5. Energy scheme for photoinduced electron transfer through an activated photosensitizer-electron acceptor complex

The electron transfer rate constants, k_{et} and k_{-et} , have a direct impact on the yield of charge-separated products. The energy profile for the ET process is displayed in Fig. 5. The electron transfer rate constant k_{et} is given by Eq. (5), where ΔG_{λ}^* represents the activation parameter, or the reorganization energy involved in the activation of the encounter complex through bond length alteration and/or reorganization of solvation shells. Marcus theory [18, 19] relates the reorganization energy to the overall free energy, ΔG° , in the ET process, as given by Eq. (6). Thus, according to Marcus theory, k_{et} is diffusion controlled for ET reactions exhibiting small and negative ΔG° values, while k_{et} will be small when $\Delta G^{\circ} \geq 0$, or when ΔG° exhibits high negative values.

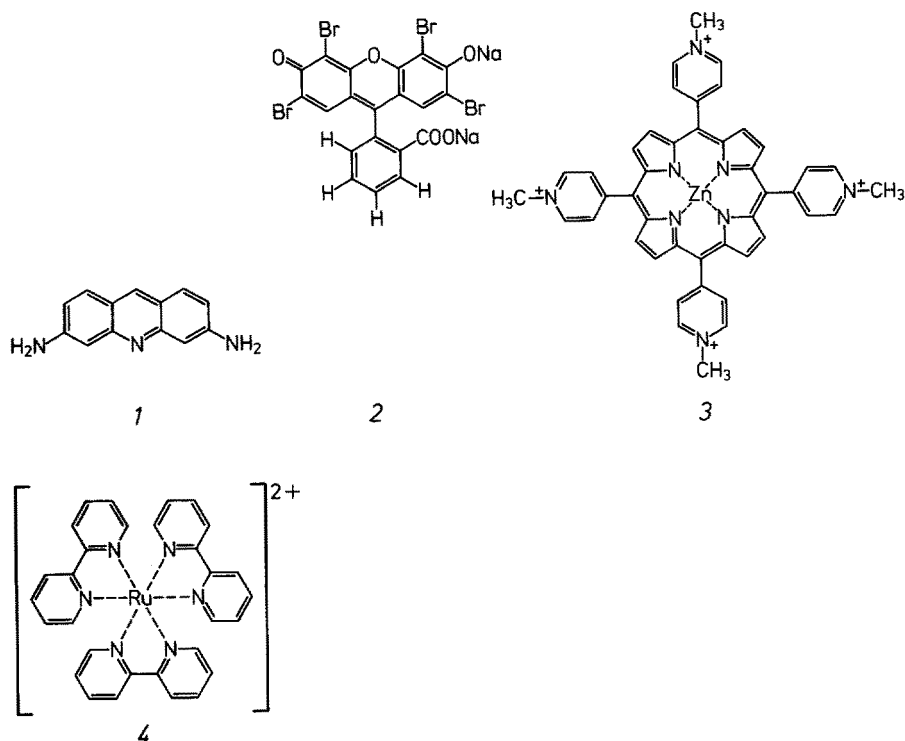
$$k_{et} = \text{constant} \exp(-\Delta G_{\lambda}^*/RT) \quad (5)$$

$$\Delta G_{\lambda}^* = \Delta G^*(0) \left[1 + \frac{\Delta G^{\circ}}{4\Delta G_{\lambda}^*(0)} \right]. \quad (6)$$

2.2 Light-Harvesting Compounds

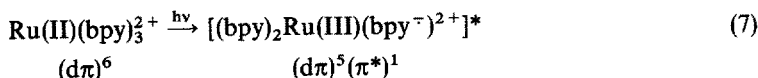
Absorption of light is the energy input step that triggers the ET process. The absorbed light is stored as chemical energy in the excited state. Light harvesting compounds for artificial photosynthetic systems require broad and effective absorption properties in the visible spectral range of solar radiation, high chemical stability, and proper photophysical behavior (lifetime and redox properties) to allow subsequent ET reactions. Organic dyes and transition metal complexes have been extensively studied as light harnessing compounds that initiate ET processes upon light absorbence. Organic dyes [27, 28] such as proflavine (1) or eosin (2) are capable of inducing ET reactions, although exhibiting moderate chemical

stabilities. Synthetic porphyrins [29, 30] or phthalocyanins [31] such as Zn(II)-*meso*-(*N*-tetramethylpyridinium)porphyrin (**3**) were extensively used as artificial dyes mimicking the functions of chlorophyll in natural photosynthesis. Even more promising have been polypyridyl transition-metal complexes [32–36]. In these compounds, light absorbance originates from metal-to-ligand charge transfer transitions (MLCT). Upon excitation, an electron is promoted from the metal-based $d\pi$ orbital to a low-lying π^* level on the polypyridyl ligand. These



MLCT-excited states exhibit good chemical stabilities, sufficiently long lifetimes to exploit in ET reactions and often show redox features that can be utilized in useful photosynthetic transformations. Furthermore, the absorption range of these complexes can be tuned and extended from the near infrared through the visible spectral range by altering the central metal or by chemically modifying the surrounding ligand [32].

Among the polypyridyl complexes, Ru(II)-*tris*-bipyridine (**4**), $\text{Ru}(\text{bpy})_3^{2+}$, and chemically modified Ru(II)-polypyridyl complexes have been most extensively studied [32]. The MLCT transition of $\text{Ru}(\text{bpy})_3^{2+}$, Eq. (7), proceeds with unit quantum efficiency and the excited state is relatively long-lived (0.62 μs). The



species is an effective oxidant ($E^\circ[*\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+] = 0.84 \text{ V}$) as well as an efficient reducing entity ($E^\circ[*\text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}] = -0.86 \text{ V}$) (Fig. 6). Thus, the excited state could participate in oxidative or reductive ET quenching processes, and the resulting reduced photoproduct, $\text{Ru}(\text{bpy})_3^+$, or the respective oxidized photoproduct, $\text{Ru}(\text{bpy})_3^{3+}$, exhibit redox properties that can be utilized in subsequent photosynthetic transformations. A variety of related polypyridyl complexes such as $\text{Os}(\text{bpy})_3^{2+}$, $\text{Cr}(\text{bpy})_3^{3+}$, $\text{Fe}(\text{bpy})_3^{2+}$, and $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ reveal proper photophysical properties that allow their application in photoinduced ET reactions [32–36].

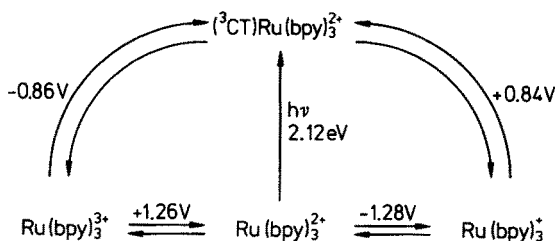


Fig. 6. Energy levels and redox potentials of $\text{Ru}(\text{bpy})_3^{2+}$ in its excited state and ground states

3 Artificial Photosynthetic Systems

An artificial photosynthetic system is an assembly that converts light energy into chemical energy being stored in the reaction products [37–39]. Light energy conversion occurs through a photoinduced ET reaction, while the storage process utilizes the ET photoproducts in subsequent oxidation and reduction processes generating endoergic products ($\Delta G^\circ > 0$). The basic configuration of artificial photosynthetic device is exemplified in Fig. 7: Photoexcitation of the light harnessing component, S, results in ET and formation of the redox products A^- and D^+ . Subsequent reduction of the substrate P_1 and concomitant oxidation of P_2 by A^- and D^+ respectively, recycles the system components, and light energy is converted into chemical energy, provided that the process (Eq. (8)) is endoergic ($\Delta G > 0$).

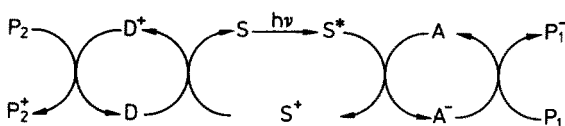
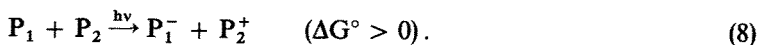


Fig. 7. General scheme of an artificial photosynthetic device: S — photosensitizer, A — electron acceptor, D — electron donor, P_1 and P_2 — reactants (substrates) for the reduction and oxidation processes, respectively

Table 1. Endoergic photosynthetic transformations and their thermodynamic characteristics

Transformation	ΔG° (kcal mole ⁻¹)	ΔG° (per e ⁻ (eV))	n (e ⁻)
$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)}$	57	1.23	2
$\text{H}_2\text{O(l)} + \text{CO}_2\text{(g)} \rightarrow \text{HCO}_2\text{H(l)} + 1/2 \text{O}_2$	68	1.46	2
$\text{H}_2\text{O(l)} + \text{CO}_2\text{(g)} \rightarrow \text{CH}_2\text{O(g)} + \text{O}_2\text{(g)}$	125	1.35	4
$2 \text{H}_2\text{O(l)} + \text{N}_2\text{(g)} \rightarrow \text{N}_2\text{H}_4\text{(l)} + \text{O}_2\text{(g)}$	181	1.95	4
$\text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{CH}_3\text{OH(l)} + 3/2 \text{O}_2\text{(g)}$	168	1.21	6
$\text{N}_2\text{(g)} + 3 \text{H}_2\text{O(l)} \rightarrow 2 \text{NH}_3\text{(g)} + 3/2 \text{O}_2\text{(g)}$	162	1.17	6
$\text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{CH}_4\text{(g)} + 2 \text{O}_2\text{(g)}$	196	1.06	8

Table 1 summarizes several redox transformations that can be accomplished in artificial photosynthetic assemblies including the photolysis of water, carbon dioxide reduction, and nitrogen fixation processes. The endoergicities of these transformations, and the number of electrons involved in the reduction processes, are also indicated in the table. It is evident that the energy per electron to drive the various transformations are met by visible light quanta.

Although the thermodynamic feasibility to design artificial photosynthetic processes is obvious, practical assembly of such systems confronts substantial difficulties. Thermodynamic limitations accompanying artificial photosynthetic systems have been considered theoretically [40–42], and the recent progress in the subject has been reviewed [43, 44] in several articles and monographs [45, 46].

3.1 Back Electron Transfer Reactions: Problems and Resolutions

Intrinsic limitations of an artificial photosynthetic system include the thermodynamically favoured back electron transfer reactions of the intermediate photoproducts [47, 48]. For an oxidative ET quenching process the destructive back electron reactions are given by Eq. (9) and (10). The fraction of usable photo-



products for storage, that are stabilized against recombination, is η_P , Eq. (11), where η_S and η_D are the fractions of reduced photoproduct resisting recombination with the oxidized photosensitizer and the oxidized electron donor, respectively.

$$\eta_P = \eta_S \cdot \eta_D \quad (11)$$

In a homogeneous phase, the recombination of the primary photoproducts are often almost diffusion controlled ($k_b \approx 10^9\text{--}10^{10} \text{ M}^{-1} \text{ sec}^{-1}$), and consequently the usable fraction of photoproducts for secondary storage processes is limited.

Extensive efforts have been directed in recent years towards the development of organized photochemical assemblies that are capable of stabilizing the photoproducts against back electron transfer reactions. The approaches include the design of microheterogeneous organized microenvironments where vectorial ET reactions proceed [47, 48]. Such systems exhibit, on the microscopic level, recognition elements that allow effective ET quenching, but subsequently retard the back ET processes through local interactions of the photoproducts with the microenvironment. Microheterogeneous systems controlling back ET processes and operating by electrostatic or hydrophobic-hydrophilic interactions are exemplified in Fig. 8a and b.

Figure 8a shows the application of a negatively charged interface in a system composed of a positively charged photosensitizer and a neutral electron acceptor. Through organization of the photosystem in the interfacial medium, association of the photosensitizer, S^+ , to the charged interface occurs. Upon photoinduced ET, the resulting photoproducts are oppositely charged, and electrostatic attraction of the oxidized photoproduct and selective repulsion of the reduced species by the charged interface take place. As a result, the recombination of the photo-generated photoproducts is retarded, and vectorial ET occurs. Figure 8b exemplifies the control of the back ET process in a microheterogeneous hydrophilic-hydrophobic, water-oil, system. The photosystem is organized in the hydrophilic aqueous compartment of the system. Upon photoinduced ET, the reduced photoproduct exhibits hydrophobic properties and consequently is extracted from the aqueous phase to the oil phase. As a result of the different hydrophilic-hydrophobic interactions of the photoproducts with their microenvironment, the reactive species are separated by means of the two phases and stabilized against back ET.

Microheterogeneous environments that control photosensitized ET processes by means of electrostatic interactions include micelles [49–52], polyelectrolytes [53, 54], colloids [55–57], and clays [58, 59]. Hydrophilic-hydrophobic organized microenvironments include micelles [49, 50], water-in-oil and oil-in-water micro-

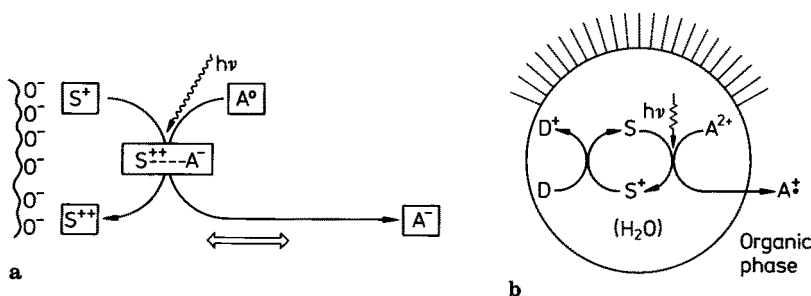
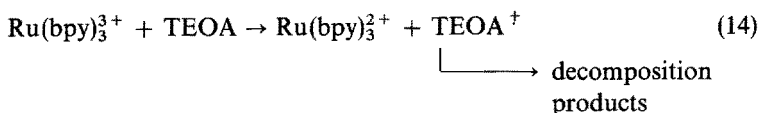
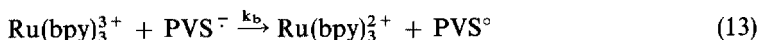
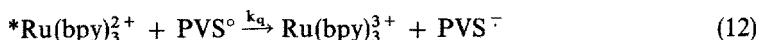


Fig. 8a, b. Control of photoinduced ET reactions in organized microenvironments: **a)** application of charged interfaces to effect charge separation and retard recombination processes by means of electrostatic interactions; **b)** application of water-oil two phase systems in charge separation and stabilization of photoproducts against back reactions by means of hydrophobic-hydrophilic interactions

emulsions [60–63], and vesicles [64, 65]. Organized microenvironments controlling back electron transfer reactions can also be designed at the molecular level. For example, β -cyclodextrin has been applied [66] as a molecular receptor that stabilizes the photoproducts against recombinations by the selective association of one of the reaction products into the receptor cavity.

The general topic of photosensitized electron transfer reactions in microheterogeneous media has been extensively reviewed [67, 68] and is described in detail in other chapters of this series. Here only representative compositions of organized systems will be described to introduce the topic and to highlight the participation of microheterogeneous systems in tailored photosynthetic assemblies. The photosensitized reduction of N,N' -(3-propylsulfonato)-4,4'-bipyridinium (**5**) PVS° , using $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and triethanolamine, TEOA, as sacrificial electron donor has been examined in a homogeneous aqueous phase and in a microheterogeneous system composed of a SiO_2 colloid. The quantum efficiency for the formation of the ET product PVS^- in the microheterogeneous system is $\phi = 0.04$, a value that is 8-fold higher than that observed in the homogeneous phase. Time-resolved spectroscopic studies have revealed the functions of the SiO_2 colloid in controlling the photoinduced ET process by means of electrostatic interactions. The primary step in the reduction of PVS° involves the oxidative ET quenching process of excited $\text{Ru}(\text{bpy})_3^{2+}$ by Eq. (12). The resulting photoproducts recombine with a diffusion-controlled rate constant, $k_b = 7.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, (Eq. (13)). Irreversible oxidation of TEOA by the oxidized photoproduct $\text{Ru}(\text{bpy})_3^{3+}$ (Eq. (14)) provides a competitive pathway to the back ET reaction. The low quantum yield of PVS^- in the homogeneous phase represents the fraction of intermediate photoproducts that survives the recombination reaction through the competitive



irreversible pathway. In the microheterogeneous SiO_2 colloid a similar sequence of reactions leads to the photoinduced reduction of PVS. The intermediate photoproducts (Eq. (13)) are, however, oppositely charged and electrically interact with the highly negatively charged SiO_2 colloid interface (surface potential, -170 mV) [69]. The positively charged photoproduct is attracted by the colloid surface while the reduced counter-component PVS^- is repelled by the interface. As a result, the recombination rate of the intermediate photoproducts, $k_b = 5.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, is substantially retarded as compared to that in the homogeneous phase. Consequently, the intermediate photoproducts are stabilized against back ET and a substantially higher fraction of the oxidized photoproduct is reacting through

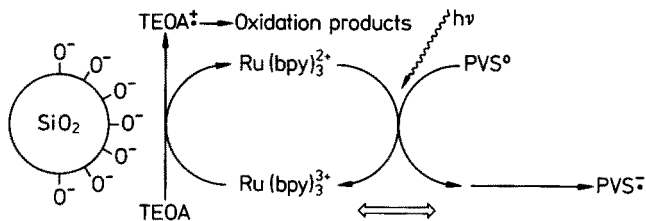
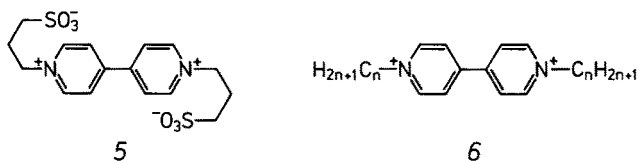


Fig. 9. Control of the photosensitized reduction process of *N,N'*-(3-propylsulfonato)-4,4'-bipyridinium, PVS, in a microheterogeneous system composed of a SiO₂ colloid



the irreversible pathway accumulating PVS⁻, and a high quantum efficiency for PVS⁻ formation is observed under steady-state illumination. The electrostatic functions of the SiO₂ colloid in controlling the vectorial photosensitized reduction of the SiO₂ colloid in controlling the vectorial photosensitized reduction of PVS⁰ is schematically outlined in Fig. 9.

Control of the photosensitized ET reaction by means of hydrophobic-hydrophilic interactions is exemplified in an organized water-in-oil microemulsion system. The water-in-oil microemulsion provides a transparent high-surface-area, microheterogeneous system composed of water droplets (80–100 Å diameter) suspended in a continuous organic phase. The photosensitized reduction of a homologous series of dialkylated bipyridinium salts (6) has been examined in a water-in-oil microemulsion using Ru(bpy)₃²⁺ as photosensitizer and triammonium ethylenediamine tetraacetic acid, (NH₄)₃EDTA, as electron donor [60]. The series of electron-acceptors exhibits hydrophilic character but reduction of the bipyridinium series is anticipated to yield an hydrophobic product at a certain alkyl chain length due to removal of one of the positive charges. Table 2 summarizes the quantum efficiencies of C_nV⁺ formation in the water-in-oil organized photosystem. It is evident that C₈V⁺ (n = 8) shows a substantial increase in the quantum efficiency, as compared to the shorter alkylated relays. Time-resolved spectroscopic studies have elucidated the functions of the organized microemulsion system in controlling the photoinduced reduction of C_nV²⁺. The results of time-resolved studies are also provided in Table 2. The primary ET quenching process, Eq. (15), is of similar effectiveness for the entire C_nV²⁺ series. Yet, separation of the intermediate photoproducts in the resulting encounter cage complex is strongly affected by the structure of the reduced product. It can be seen from Table 2 that the quantum efficiency for the separation of C₈V⁺ is ca. 6.6-fold more effective than that of C₄V⁺. Thus, charge separation of the hydrophobic species C₈V⁺ is assisted as compared to that of the hydrophilic photoproduct, C₄V⁺, in the microemulsion medium.

Table 2. Charge separation and steady-state quantum yields and recombination rates in the photosensitized reduction of C_nV^{2+}

n	1	4	6	8	14	18
φ_s^a	0	0.006	0.036	0.040	0.050	0.054
$10^9 k_b (M^{-1} s^{-1})^b$	^d	26	8	0.7	0.33	1.2
$10^3 \varphi_{s,s}^c$	$< 10^{-5}$	0.8	2.5	7.5	8.1	7.2

^a Charge separation quantum efficiency of the encounter cage complex of photoproducts, Eq. (15).

^b Recombination rate constants of intermediate photoproducts, Eq. (16).

^c Quantum efficiencies of C_nV^+ formation under steady state illumination.

^d No charge separation of C_1V^+ is observed in the water-in-oil microemulsion.

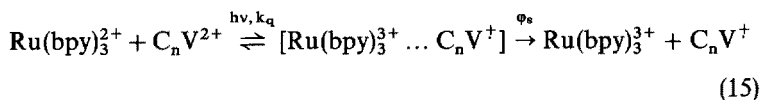


Table 2 also reveals that the bimolecular recombination rate, Eq. (16), of the hydrophobic photoproduct, C_8V^+ is retarded by a factor of 37 as compared to the hydrophilic intermediate, C_4V^+ . Thus, the microheterogeneous water-in-oil

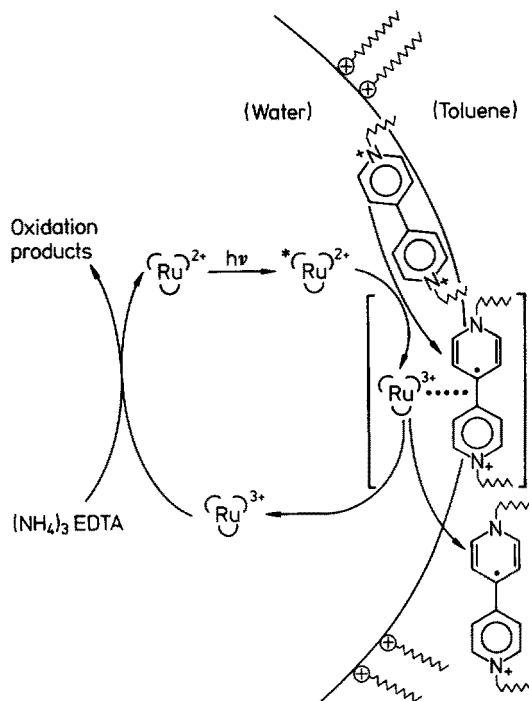
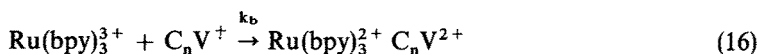


Fig. 10. Control of the photosensitized reduction of N,N' -dialkyl-4,4'-bipyridinium electron acceptors, C_nV^{2+} , in a water-in-oil microemulsion system

microemulsion provides two complementary functions in controlling the photo-sensitized ET process, as shown in Fig. 10. i) It assists charge separation of the primary encounter complex of photoproducts through extraction of the hydrophobic counterpart of the complex into the oil phase, and ii) selective localization of the reduced and oxidized photoproducts by means of the aqueous and oil phases retards the recombination rate of the intermediate species. Stabilization of the photoproducts against the back ET reactions in the organized assembly allows the effective competitive oxidation of the sacrificial electron donor, and consequently, high quantum yields are obtained for C_nV^+ , ($n \geq 8$) under steady-state illumination.



Other closely related microheterogeneous environments such as micelles [70] or tailored electron relays capable of micellization upon reduction [71], operate by related hydrophilic-hydrophobic interactions in controlling photosensitized ET processes. Similarly, separation of photoproducts at the molecular level, by means of hydrophobic interactions, has been accomplished by utilizing cyclodextrin receptors [66, 72]. This host component selectively associates one of the photoproducts into the hydrophobic receptor cavity and consequently back ET is retarded.

3.2 Catalysis in Artificial Photosynthetic Systems

Utilization of photoinduced ET products in subsequent fuel generation routes is the ultimate goal of artificial photosynthesis. The intermediate ET photoproducts must meet, as a fundamental condition, proper thermodynamic redox potentials for driving the specific fuel-generation reaction. Yet, it appears that the raw materials that could act as source compounds for the fuel products, are chemically inert and require the participation of catalysts for their activation. Raw materials for the fuel products should be abundant compounds. It is also advantageous to generate fuel products that lead in the fuel consumption process (energy release) to the original raw materials of the photosynthetic device. Thereby, a closed mass-balanced cycle could be generated, and accumulation of waste materials is eliminated. Furthermore, a useful compound should release maximum energy in the fuel consumption process, thus generating a stable product of low energy content. These considerations imply that the source materials for the photosynthetic device exhibit chemical stability and, consequently, poor chemical reactivities. Catalysts are therefore essential ingredients in artificial photosynthetic devices.

Water and carbon dioxide provide the most attractive and abundant source materials for the fuel products of an artificial photosynthetic device, as seen in Fig. 11. These two compounds are the outcome of the heterotrophic cycle providing the energy sources of the living organism, and the result of consumption of fossil fuels by mankind. Not surprisingly, both of the materials exhibit high chemical

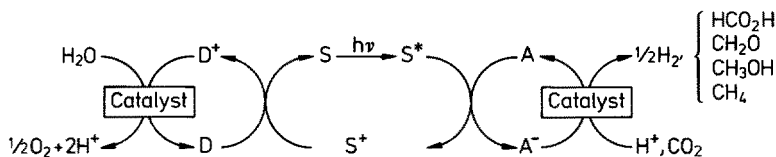
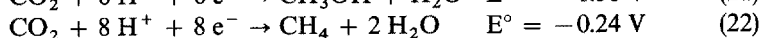
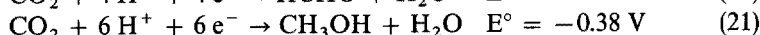
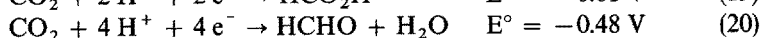
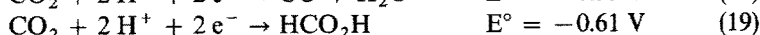
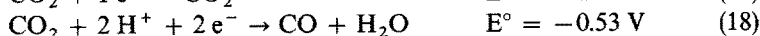


Fig. 11. Photolysis of water and CO₂-fixation in an artificial photosynthetic system

stability and inertness. For example, CO₂ is a linear triatomic molecule where the C=O bond length corresponds to 1.161 Å, $\Delta G_f^\circ = -94.26 \text{ cal mol}^{-1}$ [73]. The stabilities of water and carbon dioxide is evidenced by their high electrochemical overpotential for direct electron transfer reactions. Similar considerations are adequate for the reduction of other abundant materials such as nitrogen, nitrate and phosphate.

A further complication involved in the conversion of these abundant materials to fuel products relates to the multi-electron oxidation-reduction processes accompanying the generation of the fuel products. While a photosensitized ET process is a single ET transformation, the reduction of CO₂ or water involves multi-electron transfer reactions. This difficulty is best exemplified in the different reduction routes of CO₂ outlined in Eqs. (17–22). It is obvious that the thermodynamic reduction potential for generating C₁-fuel products becomes positive as the number of electrons involved in the reduction process increases [74]. Thus, multi-electron reduction processes are thermodynamically favoured over the single ET transformation. The same argumentations apply for the oxidation of water, Eqs. (23) and (24), where the multi-electron oxidation of water to molecular oxygen is thermodynamically favoured over the one-electron oxidation process. Thus, single ET products generated in photochemical transformations



should be transferred into electron-sink entities, or multi-electron charge relays, capable of inducing multi-electron oxidation or reduction processes. Catalysts could provide effective charge storage entities for such multi-electron redox transformations. The discussion reveals a third limitation of artificial photosynthetic devices. Reduction of CO₂, for example, could lead to five different

C₁-reduction products and certainly to higher oligomerized reduced products. Also, reduction of CO₂ in an aqueous medium is anticipated to be accompanied by the competitive reduction of water (H₂ evolution), see Eq. (25). Thus, the intermediary redox species generated in an ET process could yield a mixture of products. Catalysts could play a central role in inducing selectivity and in controlling a desired specific route that utilizes the ET products. Thus, one can define three complementary functions of catalysts in artificial photosynthetic devices:

- i) The catalyst should activate the substrate towards the redox transformation.
- ii) The catalyst should act as a multi-electron redox relay.
- iii) The catalyst should induce selectivity and specificity towards the designed redox transformation.

Mother nature has resolved the various limitations involved in multi-electron processes. Unique assemblies composed of cofactors and enzymes provide the microscopic catalytic environments capable of activating the substrates, acting as multi-electron relay systems and inducing selectivity and specificity. Artificially tailored heterogeneous and homogeneous catalysts as well as biocatalysts (enzymes and cofactors) are, thus, essential ingredients of artificial photosynthetic devices.

3.2.1 Heterogeneous Catalysts in Artificial Photosynthetic Systems

Heterogeneous catalysts provide solid interfaces in conjunction with liquid or gaseous phases of the reactants and products [75, 76]. A variety of heterogeneous metal catalysts, i.e., Fe, Ni, Pt, Pd, or metal oxides such as NiO, MnO₂, MgO, RuO₂ are catalytically active in various chemical transformations such as hydrogenations, oxidations, isomerizations, dehydrogenations, or cracking. The activities of the heterogeneous catalysts are determined by the bulk chemical composition of the catalyst material and are substantially influenced by the surface properties of the catalyst. The basic step of heterogeneous catalyzed chemical transformations includes the chemical adsorption of the reactants to the catalytic surface. Adsorption can proceed through a dissociative mechanism, i.e. dissociation of molecular hydrogen on a metal surface, or by an associative mechanism, i.e. adsorption of olefins. Adsorption of reactants to the catalytic surface controls the distances, orientations and activation of the reactants towards the specific chemical transformation. Comprehensive studies have revealed that structural features of the catalyst surface (steric order and distances of the atoms composing the surface, crystal defects, i.e. steps or kinks) are dominant in controlling the catalyst properties [77–79]. Another important factor influencing the heterogeneous catalyst activity is the extent of dispersion and porosity of the catalyst. Highly dispersed catalytic materials provide an extensive surface between the reactant phase and the catalytic interface. Indeed, highly dispersed heterogeneous catalysts on SiO₂, Al₂O₃, zeolites, and polymer matrices, exhibit high catalytic activities. Often, sinergetic effects are observable, where the support affects the catalytic properties of the immobilized catalyst [80].

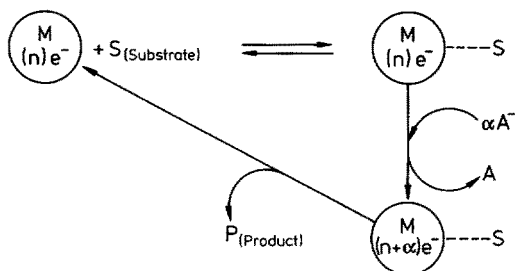


Fig. 12. Schematic functions of a metal colloid as catalyst and microelectrode in the multi-electron reduction of a substrate

Heterogeneous catalysts could participate in photosensitized electron transfer reactions (artificial photosynthetic devices), through two complementary functions: i) The heterogeneous catalyst could adsorb the reactant and activate it towards the specific reduction or oxidation processes. ii) The heterogeneous metal catalyst could act as an electrode accepting the electrons from the photogenerated reduced product. Thereby, the metal catalyst could act as a sink for electrons generated by photoinduced single ET processes (Fig. 12). Thus, the solid interface provides a medium for multi-electron communication with the activated substrate.

For a bulk macroscopic electrode, where reduction (or oxidation) of a solution species occurs, the limiting current i_l is given by Eq. (26), where Z is the number of electrons participating in the redox process, F is the Faraday constant, D_0 and C_0 are the diffusion coefficient and concentration of the solution species respectively, and δ is the width of the diffusion layer [81]. In an artificial photosynthetic

$$i_l = ZFD_0C_0/\delta \quad (26)$$

device, ET communication between the charge carrier (reduced electron acceptor or oxidized donor) and the heterogeneous catalyst is the essence of the catalytic process (Fig. 12). Thus, the rate of mass transfer of the charge carrier to the catalyst surface will control the rate of the catalytic transformation. Hence, to obtain maximum rates, decrease of δ , the diffusion layer, or increase of the electrode surface area is essential. Therefore, highly dispersed heterogeneous catalysts will contribute to effective activation of the substrates and to improved ET communication with the photogenerated charge carriers [82]. The bimolecular rate constant for the ET communication of the photogenerated relay, A^- , and colloid particles, is given by Eq. (27), where N is the Avogadro number, D is the diffusion coefficient of the relay, and r is the radius of the colloid particle. A further advantage of

$$k = 4\pi NDr^2 \quad (27)$$

including small colloid particles ($r = 30\text{--}100 \text{ \AA}$) as catalysts in artificial photosynthetic devices involves the lack or decrease of light-scattering phenomena. This allows improved utilization of the incident light in the energy conversion pathways. Ingenious methods for the preparation of heterogeneous catalysts in colloidal

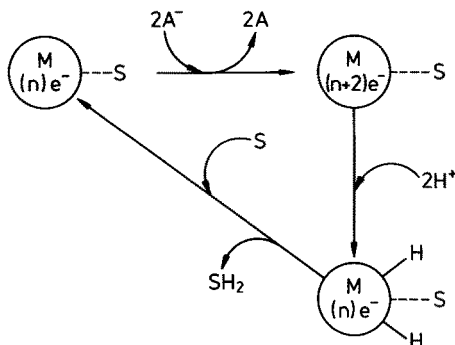


Fig. 13. Schematic functions of a metal colloid in the “in situ” generation of H-atoms and hydrogenation of a substrate

forms have been developed [83]. For preparing metal colloids, chemical means (i.e. reduction by hydrogen [84], citrate [85], hydrazine [86]), photochemical methods [87], radiolytic means [88], or vacuum evaporation techniques [89] were widely applied. The technique and experimental conditions for preparing the colloids have been found to affect the size and shape of the particles, and consequently, colloid materials of different catalytic activities are obtained [90]. Usually, colloids are stabilized against aggregation by polymers. The nature of the polymer support often affects the properties of the resulting colloidal catalyst [91].

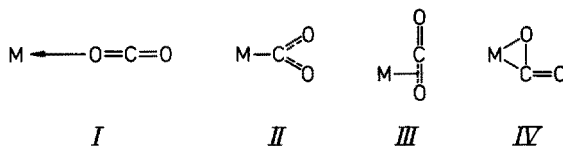
An alternative route for the participation of heterogeneous catalysts in artificial photosynthetic devices involves the induction of an “in situ” catalyzed hydrogenation mechanism (Fig. 13). Hydrogenation of various compounds such as olefins, acetylenes, or CO_2 , proceeds on various heterogeneous catalysts through the concomitant associative activation of the substrates and dissociative activation of molecular hydrogen [92, 93]. The intermediate formed upon dissociation of hydrogen on a metal surface can be alternatively generated by charging the electrode with electrons supplied by the photogenerated reduced relay, followed by protonation of the charged surface, see Fig. 13. Activation of a substrate on the catalytic surface towards hydrogenation could lead to the multi-electron hydrogenated product, provided that the hydrogenation process is faster than the competitive H-atom dimerization process (H_2 -evolution).

3.2.2 Homogeneous Catalysts in Artificial Photosynthetic Systems

The possibilities to tune the activities of homogeneous catalysts through structural modification of the ligands, and the relative ease to follow their catalytic mechanism by spectroscopic and structural characterization of catalytic intermediates, highlight the advantages of using homogeneous catalysts in artificial photosynthetic devices. The broad potential applicability of homogeneous catalysts in artificial photosynthetic devices relies on some of their fundamental characteristics:

i) The metal center of transition-metal complexes can exist in several oxidation states. Consequently, the metal center could act as a multi-electron charge relay for redox transformations.

ii) The metal is capable of binding ligands in several modes of coordination. Consequently, different activation modes of the ligand are feasible, and product specificity can be designed in the catalytic transformations through tailoring the activation modes of the ligand. For example, the electronic configuration of CO_2 corresponds to $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (1\pi_g)^4$. The weakly bonded $1\pi_g$ electrons could be donated to vacant metal orbitals, and CO_2 complexes of the general structure **I** could originate from carbon dioxide acting as Lewis base. On the other hand, electron donation from the metal to the $2\pi_u$ vacant orbitals could result in complexes of structure **II**, where CO_2 acts as a Lewis acid. Other coordination modes [94–96] could involve interaction of $1\pi_u$ electrons with vacant metal orbitals to form π -complexes of structure **III**, or coordination of carbon dioxide to the metal center followed by back donation to CO_2 could yield cyclic structures such as **IV**:



iii) Selection of different ligands affects the properties (i.e., stabilities) of the complexes. Ligand modification of the homogeneous catalysts allows the control

Table 3. Representative CO_2 and N_2 complexes and their IR spectral characteristics

Complex	$\nu(\text{CO}_2)$ or $\nu(\text{N}_2)$ cm^{-1}
$[\text{Mo}(\text{CO}_2)_2(\text{PMe}_2\text{Ph})_4]$	1760, 1510, 1335
$[\text{Fe}(\text{CO}_2)(\text{PMe}_3)_4]$	1620, 1108, 612
$[\text{Co}(\text{CO}_2)(\text{PPh}_3)_3]$	1890
$[\text{Rh}(\text{OH})(\text{CO}_2)(\text{CO})(\text{PPh}_3)_2]$	1602, 1351, 821
$[\text{RhCl}(\text{CO}_2)(\text{PBu}_3)_2]$	1668, 1630, 1165, 1120
$[\text{RhCl}(\text{CO}_2)(\text{PEt}_2\text{Ph})_2]$	1658, 1620, 1238, 827
$[\text{RhCl}(\text{CO}_2)(\text{PMe}_2\text{Ph})_2]$	1657, 1625, 1217, 996, 823
$[\text{Ir}(\text{OH})(\text{CO}_2)(\text{CO})(\text{PPh}_3)_2]$	1636, 1310, 815
$[\text{IrCl}(\text{CO}_2)(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$	1550, 1230
$[\text{Ir}(\text{CO}_2)(\text{AsMe}_2\text{C}_6\text{H}_4)_2\text{Cl}]$	1550, 1220
$[\text{Ni}(\text{CO}_2)(\text{PEt}_3)_2]$	1660, 1635, 1203, 1009
$[\text{Pt}(\text{CO}_2)(\text{PPh}_3)_2]$	1640, 1370, 1320
$[\text{Cu}[\text{CH}(\text{NC})\text{CO}_2\text{Et}](\text{CO}_2)(\text{PPh}_3)_2]$	1600, 1400, 1365, 1320, 820
$[\text{Rh}_2(\text{CO}_2)(\text{CO})_2(\text{PPh}_3)_3]$	1498, 1368, 813
$[\text{Rh}_2\text{Cl}_2(\text{CO}_2)(\text{PPh}_3)_3]$	1630
$[\text{Ni}_2(\text{CO}_2)(\text{PC}_6\text{H}_{11})_3]_4$	1735
$[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{I}_2$	2129
$[\text{Os}(\text{NH}_3)_5\text{N}_2]\text{I}_2$	2033
$[\text{RhCl}(\text{N}_2)(\text{PPh}_3)_2]$	2152
$[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$	2105
$[\text{IrCl}(\text{N}_2)(\text{C}_8\text{H}_{12}\text{O}_4)(\text{PPh}_3)_2]$	2190
$[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$	2085

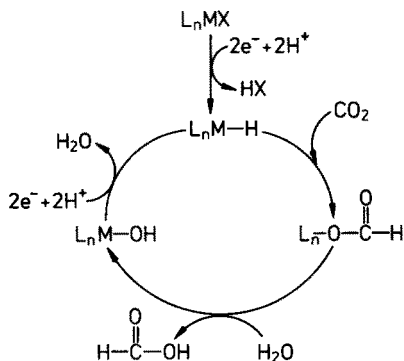
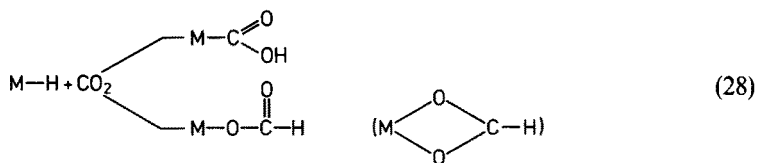


Fig. 14. A schematic cycle for CO_2 -reduction by an hydrido transition metal homogeneous catalyst

of their catalytic properties and the design of products specificity in chemical transformations. Numerous examples of transition-metal complexes with ligands such as CO_2 or N_2 , being the substrates for the production of fuel materials, are known [97, 98]. Table 3 summarizes a few examples of such structures. IR data of the coordinated ligands are included to indicate the activation modes of the bound ligands in the catalyst structure.

An indirect pathway for participation of homogeneous catalysts in artificial photosynthetic systems, involves the light-induced generation of an active homogeneous catalyst intermediate, acting as charge storage species and capable of reacting with the substrate. Such a reaction could lead to a multi-electron reduction product. Transition-metal complexes are capable of generating metal-hydride intermediates that act as a two-electron charge relay. Insertion of CO_2 , for example, could lead to metal-formate or metal-carboxylate coordinated products, Eq. (28), resulting in the two-electron fixation of CO_2 . Figure 14 outlines a cycle for the reduction of CO_2 through a metal-hydride intermediate catalyst [99, 100]. Other



complexes that could act as active intermediates for insertion of CO_2 include metal-alkyl or metal-aryl intermediates. Numerous examples of the insertion products of CO_2 into M-H and M-R bonds have been characterized and the subject has been extensively reviewed [99]. Table 4 summarizes the CO_2 insertion products of various transition-metal catalysts to indicate the broad array of metals capable of acting in this general catalytic cycle.

Table 4. Insertion products of CO₂ into metal-hydrides

Group	Complex	Insertion Product
Ib	[HCuPPh ₃] ₆	(Ph ₃ P) ₂ CuOCOH
VIb	HM(CO) ₅ M = Cr, Mo, W	HCOOM(CO) ₅
VIIb	ReH(dppe) ₂	Re(O ₂ CH)(dppe) ₂
VIIIb	FeH ₄ L ₃	Fe(O ₂ CH) ₂ L ₂
	CoH ₃ L ₃	Co(COOH)L _x
	RuH ₂ L ₄	Ru(O ₂ CH)HL ₃
	RhHL ₃	Rh ₂ H ₂ (CO ₂)L ₆
	PtH ₂ L ₂	PtH(O ₂ CH)L ₃

3.2.3 Biocatalysts in Artificial Photosynthetic Systems

Enzymes provide the catalytic entities in biological transformations. The unique characteristics of biocatalysts, namely, activation of substrates and acceleration of reaction rates at ambient temperatures, specificity towards substrates, and stereospecificity and chiroselectivity towards product formation, generate most sophisticated and effective catalysts [101]. Accordingly, extensive efforts of chemists and biochemists are directed towards harnessing chemical transformations by means of technological approaches utilizing enzymes [102, 103].

Numerous enzymatic processes require the participation of cofactors in biocatalytic processes [104, 105]. These relatively low-molecular-weight cocatalysts (MW < 1500) can be subdivided into two classes: (1) Cofactors that are integrated with the enzyme and are recycled within the biocatalytic transformation, i.e. flavin [106], pyridoxal phosphate [107], lipoic acid [108], and metal porphyrins [109], and (2) cofactors that require a separate biocatalytic regeneration process that provides a pre-generated cofactor acting as co-substrate of the enzymatic reaction [110, 111]. Important cofactors in this subclass are adenosine triphosphate (ATP), nicotinamide adenine dinucleotide (NAD⁺), nicotinamide adenine dinucleotide phosphate (NADP⁺), and coenzyme A (CoA). It is estimated that ca. 70% of enzymatic transformations in nature require the separate, active, regeneration of the cofactor. Among the enzymes requiring the separate regeneration of the cofactor, oxido-reductases participating in oxidation or reduction reactions (ET processes) play a major role. For example, reduction of CO₂ to formate [112] in *Clostridium kluyveri* bacteria proceeds through the intermediate formation of the acetyl CoA cofactor as outlined in Fig. 15a. A second example is the two-electron reduction of pyruvic acid to lactic acid using the NADH cofactor being generated through the biocatalyzed oxidation of ethanol, Fig. 15b. Table 5 summarizes several examples of complementary redox reactions mediated by different cofactors. By understanding the complementary functions of enzyme-cofactor assemblies, the possible participation of these biocatalytic assemblies in artificial photosynthetic devices can be envisaged:

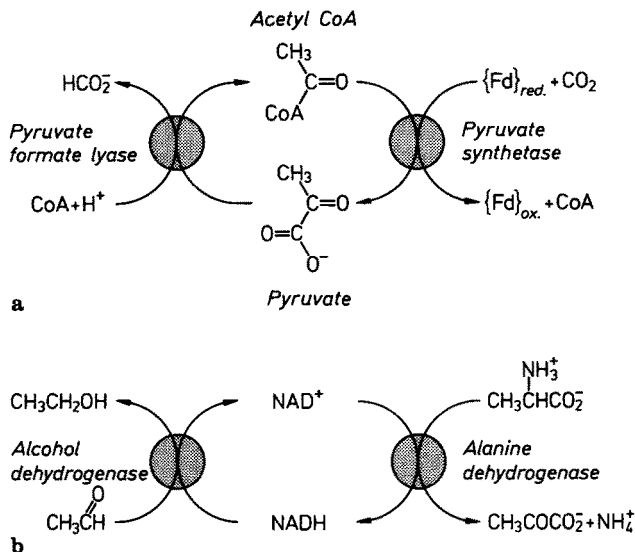
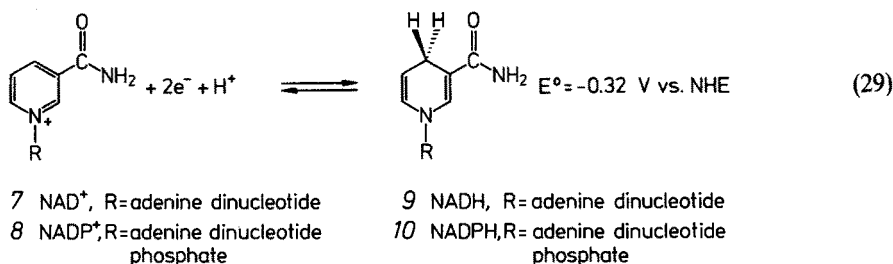
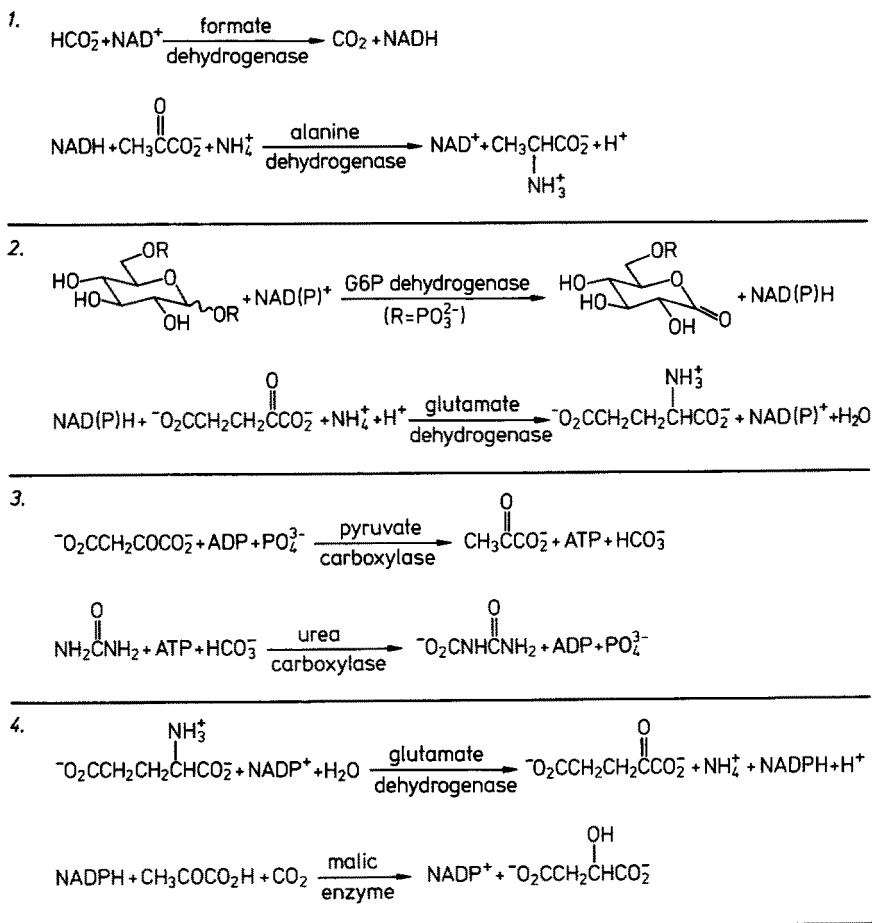


Fig. 15a, b. Biocatalyzed transformations coupled to the regeneration of cofactors: **a)** reduction of CO_2 to formate through regeneration of acetyl-CoA; **b)** reduction of pyruvic acid to lactic acid by regeneration of NADH cofactor

i) Enzymes provide active sites for activation of the substrates and act as charge storage sites for multi-electron redox reactions, i.e. CO_2 -fixation. Direct ET communication of the enzyme active site with its environment (another enzyme or electron source) is not feasible due to the insulating protein layer of the enzyme. The low-molecular-weight cofactors act as shuttlers mediating the ET processes and communicating the active sites of two enzymes.



ii) Cofactors act as multi-electron charge carriers for the enzyme active sites, and thus thermodynamically favoured multi-electron redox transformations are feasible. For example, nicotinamide adenine dinucleotide, NAD^+ (7), or nicotinamide adenine dinucleotide phosphate, NADP^+ (8), undergo a two-electron

Table 5. Examples of complementary cofactor-mediated biocatalytic redox transformations

reduction to form the dihydronicotinamide cofactors, NAD(P)H (**9**) and (**10**), Eq. (29). These reduced cofactors could provide reducing equivalents (hydride) to the enzymes.

iii) Different enzymes utilize a similar cofactor as ET mediator or charge carrier, i.e. NAD(P)⁺ or NAD(P)H. Thus, artificial photosynthetic systems that regenerate either an oxidized cofactor (NAD(P)⁺) or a reduced cofactor (i.e. NAD(P)H) could be coupled to various enzymes depending on the regenerated cofactor and a variety of light driven photosynthetic biotransformations could be envisaged [113].

iv) A further development of biocatalyzed artificial photosynthetic systems could involve substitution of natural cofactors by artificial electron carriers [113]. Specifically, reduced species generated by the photosensitized ET process could eventually act as electron shuttlers that communicate between the photosystem

and the enzyme active site. In this context, recent elegant studies have communicated the active sites of redox enzymes with bulk electrode materials through chemical modification of the biocatalysts by redox probes or by immobilization of the enzymes in redox polymers [114–116]. Similar approaches could be utilized to communicate the biocatalysts with artificial photosystems in organized assemblies [117].

4 Hydrogen Evolution and Hydrogenation Processes in Artificial Photosynthetic Systems

Photolysis of water to hydrogen and oxygen (see Table 1 and Fig. 11) provides one of the challenging processes that could generate fuel products by means of light-induced ET reactions. For studying the elementary steps involved in the hydrogen and oxygen evolution reactions (kinetics, intermediate species, etc.), the two half reactions can be separated and back ET reactions can be eliminated by applying sacrificial components that are complementary to the reduction process (H_2 -evolution) or oxidation reaction (O_2 -evolution). The concept of sacrificial systems is outlined in Fig. 16. The sacrificial H_2 -evolution system includes a sacrificial electron donor that upon oxidation undergoes subsequent irreversible decomposition, while the sacrificial O_2 -evolution system includes an electron acceptor being irreversibly decomposed upon reduction. The subject of H_2 -evolution and photolysis of water, has been extensively reviewed in various articles [118–121] and books [45, 46]. In the present article, only a few H_2 -evolution systems will be noted with the specific attempt to highlight integrated photosynthetic devices capable of controlling electron transfer in organized catalytic assemblies as well as to show that intermediates involved in H_2 -evolution can be further utilized in photosynthetic routes, i.e. hydrogenation processes.

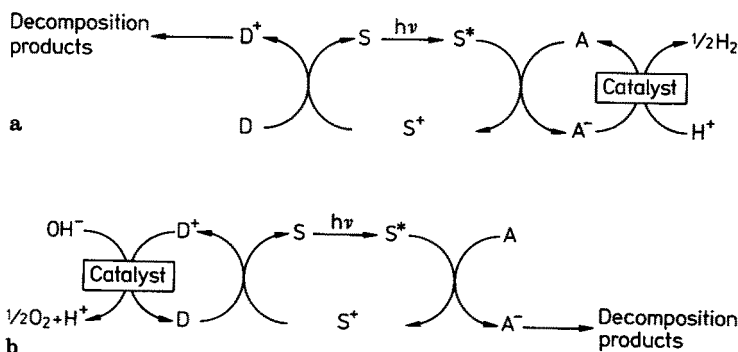
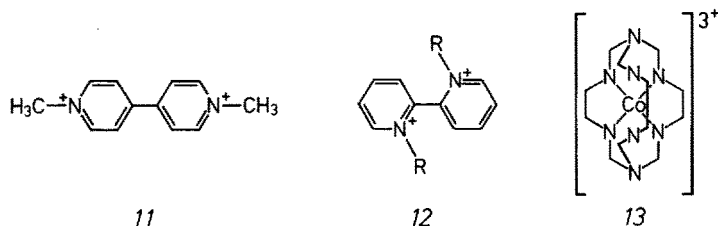


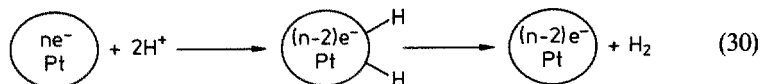
Fig. 16a, b. Examination of reduction and oxidation processes of artificial photosynthetic devices by means of sacrificial components: **a)** application of sacrificial electron donor in a photosensitized reduction process; **b)** application of a sacrificial electron acceptor in a photosensitized oxidation process

4.1 Photochemical H₂-evolution and Hydrogenation Processes Using Heterogeneous Catalysts

Noble-metal colloids composed of Pt, Rh, Au, Pd, Ru, Ag, and others, provide effective heterogeneous catalysts for H₂-evolution [122–126]. The basic configuration of the H₂-evolution system, Fig. 17a, includes a photosensitizer, S, an electron relay, A, and a sacrificial electron donor. Photosensitizers that have been widely applied include polypyridine metal complexes, i.e. Ru(bpy)₃²⁺ (**4**), metal porphyrins, i.e. Zn-*meso*-(tetra-*N*-methylpyridinium)porphyrin (**3**), or organic dyes, i.e. proflavine (**1**). Sacrificial electron donors include triethanolamine, TEOA, cysteine, ethylenediamine tetraacetic acid, EDTA, ascorbic acid, and others. As electron acceptors, *N,N'*-dialkylbipyridinium salts [127–130] such as *N,N'*-dimethyl-4,4'-bipyridinium (**11**), methyl viologen, or *N,N'*-diakyl-2,2'-bipyridinium, i.e. (**12**), have been employed extensively, although other compounds such as Co(III)-sepulchurate (**13**) [131], Rh(III)-*tris*-bipyridine, Ru(bpy)₃³⁺ [132], or even metal ions such as Eu³⁺ or V⁵⁺ [133] have been used. The photochemical cycle where methyl viologen, MV²⁺, acts as electron carrier that mediates H₂-evolution



is schematically presented in Fig. 17b. Mechanistic studies indicate that the Pt colloid acts as microelectrode being charged by the electron carrier [134, 135]. The charged particle reduces protons, generating surface-bound hydrogen atoms that subsequently dimerize and evolve H₂, (Eq. (30)):



Organized supramolecular photocatalytic assemblies for H₂-evolution, where the catalyst is immobilized in the organized microenvironment that controls the photosensitized ET process (see Sect. 3.1.) have been tailored. Photosensitized reduction of *N,N'*-dipropylsulfonato-2,2'-bipyridinium, DQS (**14**), using Ru(bpy)₃²⁺ as photosensitizer and triethanolamine, TEOA, as electron donor has been examined in a microheterogeneous media that included a negatively charged SiO₂ colloid and a citrate-stabilized Pt colloid [136]. In the absence of the SiO₂ colloid no H₂-evolution occurs, due to rapid back ET processes of the photogenerated intermediate redox products in the primary encounter cage complex. Organization

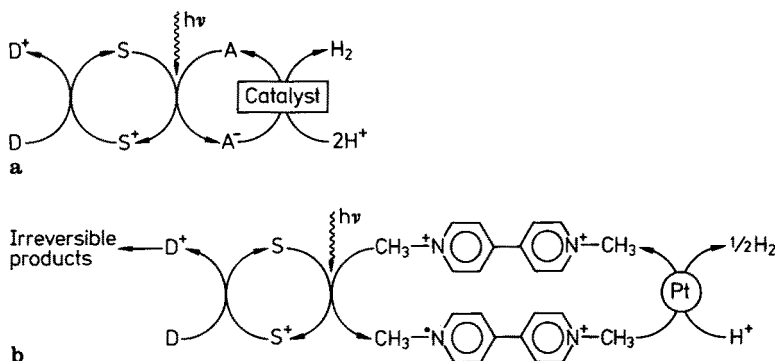
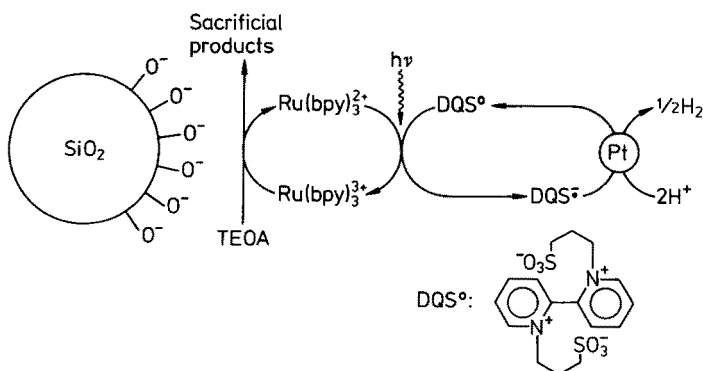


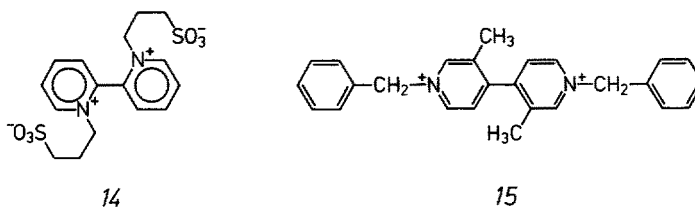
Fig. 17 a, b. Photosensitized H_2 -evolution systems: **a)** basic configuration including a photosensitizer, S, an electron acceptor, A, and electron donor, D, and H_2 -evolution catalyst. **b)** H_2 -evolution system including MV^{2+} as electron acceptor and a noble metal colloid as heterogeneous catalyst

of the photosystem in the presence of the SiO_2 colloid, Fig. 18, results in control of the photosensitized ET process and subsequent H_2 -evolution. ET quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$ results in an encounter cage complex associated with the SiO_2 interface. Electrostatic repulsion of DQS^- by the negatively charged colloid assists charge separation, and the resulting photoproducts are stabilized against back ET reactions through the selective repulsion of DQS^- from the SiO_2 interface. As a result, the reduced electron carrier mediates the effective H_2 -evolution at the Pt-catalyst site.

A closely related organized microheterogeneous system has been composed of a SiO_2 colloid on which a Pd catalyst is immobilized, and the photosystem includes eosin, Eo^{2-} (**2**), as photosensitizer, N,N' -dibenzyl-4,4'-(3,3'-dimethyl)bipyridinium, BMV^{2+} (**15**), as electron relay and TEOA as electron donor [137]. In a



homogeneous phase, no redox photoproducts are generated, and therefore subsequent H_2 -evolution is eliminated. The lack of charge separation in the

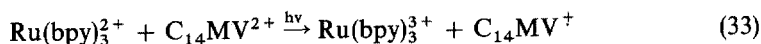


homogeneous phase is attributed to the formation of a ground-state photosensitizer-relay complex, Eq. (31), resulting in effective forward ET quenching but instantaneous recombination of the photoproducts in the complex structure, (Eq. (32)). The Pd-SiO₂ colloid acts in three complementary functions in controlling the photoinduced ET reaction and effecting hydrogen evolution, see



Fig. 19. The primary function includes the separation of the ground-state photosensitizer-electron relay complex by the selective association of the positively charged component of the complex, BMV^{2+} , to the colloid interface, and concomitant repulsion of Eo^{2-} from the charged particles. Once the complex has been separated, reductive ET transfer quenching of the photosensitizer by TEOA proceeds, and the resulting photoproducts are stabilized against recombination by means of electrostatic interactions. The reduced photoproduct Eo^{3-} is repelled by the colloid interface, while $TEOA^{\cdot+}$ is attracted by the colloid particles. The subsequent reduction of BMV^{2+} (by Eo^{3-} and $TEOA^{\cdot+}$) results in $BMV^{\cdot+}$ that is attracted by the negatively charged colloid and mediates H_2 -evolution at the Pd catalyst sites immobilized on SiO₂.

A related system that uses electrostatic and hydrophobic interactions as a means to retard back ET reaction and consequently enhance H_2 -evolution has been exemplified by Grätzel and his colleagues. Photoreduction of *N*-tetradecyl-*N'*-methyl-4,4'-bipyridinium, $C_{14}MV^{2+}$, (16), using $Ru(bpy)_3^{2+}$ as photosensitizer in the presence of a sacrificial electron donor, has been controlled [17, 138] in a micellar medium composed of positively charged micelles. The reduced photoproduct



$C_{14}MV^{\cdot+}$ formed upon ET, Eq. (33), exhibits hydrophobic properties and undergoes encapsulation into the micellar aggregate, while the oxidized photoproduct is repelled by the micellar interface. Back ET is thus retarded through the selective association of $C_{14}MV^{\cdot+}$ to the micelles. The ability to control the

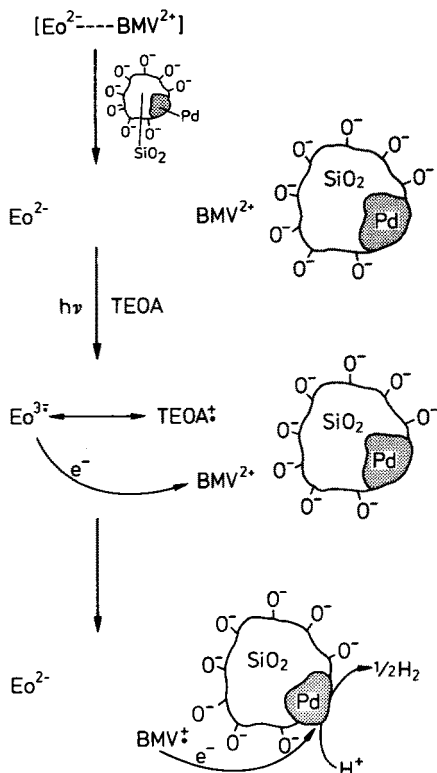


Fig. 19. Schematic functions of a Pd-SiO₂ colloid in controlling charge separation and H₂-evolution from a photosystem including eosin, Eo²⁻, as photosensitizer, *N,N'*-dibenzyl-4,4'-(3,3'-dimethyl)bipyridinium, BMV²⁺, as electron acceptor and triethanolamine, TEOA, as electron donor

photoinduced reduction of C₁₄MV²⁺ in a micellar medium, provides the principles to construct an integrated H₂-evolution system [139]. The photosystem has been introduced into a microenvironment containing a Pt-colloid stabilized by the polysoap polyvinylpyridinium with C₁₆ pendent groups, PCP-C₁₆ (Fig. 20). In the absence of the polysoap, the primary photoproducts recombine with a

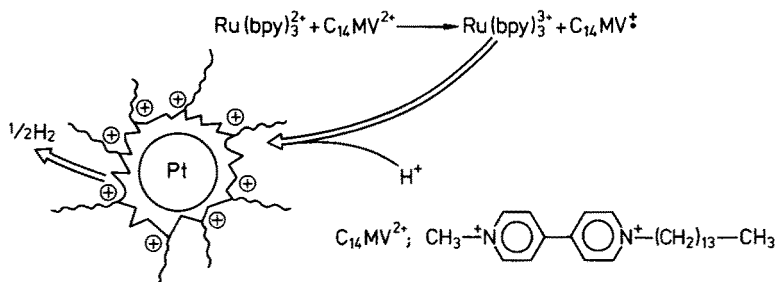
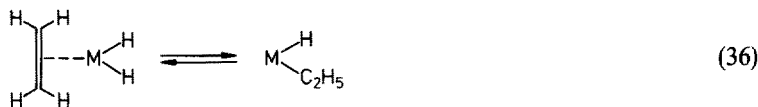
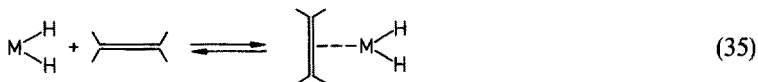


Fig. 20. Photosensitized H₂-evolution from an organized assembly composed of a Pt-colloid stabilized by a positively charged polymer matrix. Charge separation is effected by means of complementary electrostatic and hydrophobic interactions

diffusion-controlled rate constant, $k_b = 4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. In the presence of the polysoap and exclusion of the Pt catalyst, the recombination rate of the primary photoproducts is retarded, $k_b = 8 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, due to the selective association of C_{14}MV^+ to the polysoap core and concomitant electrostatic repulsion of the oxidized photoproduct $\text{Ru}(\text{bpy})_3^{3+}$. Stabilization of the primary ET photoproducts against a recombination results in effective subsequent H_2 -evolution in the presence of the polysoap-stabilized Pt-colloid.

Noble metals such as Pt, Pd or Rh act also as catalysts in hydrogenation processes of olefin or acetylenes. Hydrogenation of ethylene by molecular hydrogen on a metal surface involves a stepwise mechanism outlined in Eq. (34–37). In fact, dissociation of molecular hydrogen and formation of surface-adsorbed hydrogen, Eq. (34), corresponds to the intermediate catalytic species formed in the photo-



sensitized H_2 -evolution process through charging the metal by electrons and reduction of protons by the charged microelectrode, (Eq. (30)). Thus, activation of olefins or acetylenes on metal surfaces that concomitantly provide metal-hydrogen catalytic species could establish photosynthetic hydrogenation assemblies, provided that the hydrogenation pathway competes kinetically with the H_2 -evolution process. Photohydrogenation of ethylene to ethane, C_2H_6 , has been accomplished in a photosystem composed of $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer, N,N' -dimethyl-4,4'-bipyridinium, MV^{2+} , as electron relay, Na_2EDTA as sacrificial electron donor and in the presence of a polymer-stabilized Pt colloid [140, 141]. The quantum yield for ethane formation is $\phi = 9.9 \times 10^{-2}$, a value identical to the quantum efficiency of H_2 -evolution in the absence of ethylene. Thus, all of the surface-photogenerated hydrogen atoms are trapped by catalyst-activated ethylene.

The combination of surface-associated reactants with surface-bound H-atoms, occasionally leads to poor photoinduced hydrogenation of the reactant and parallelly to inhibition of H_2 -evolution. For such systems, tailored bifunctional heterogeneous catalysts have been developed [141], where cooperative catalytic effects are observed in the photohydrogenation reactions. Substitution of ethylene by acetylene, C_2H_2 , in the photosystem composed of $\text{Ru}(\text{bpy})_3^{2+}/\text{MV}^{2+}/\text{Na}_2\text{EDTA}$ and the Pt colloid results in inefficient hydrogenation of acetylene to ethylene, $\phi = 3.2 \times 10^{-3}$, but no H_2 -evolution occurs. The low quantum efficiency in the

hydrogenation route has been attributed to poor activation of acetylene by the Pt catalyst, while the inhibition effect towards competitive H_2 -evolution is attributed to the elimination of the dimerization process of surface-bound H-atoms by metal-associated acetylene species. With a Pd colloid, as catalyst in the photo-system, the photohydrogenation of C_2H_2 is even less effective, although the catalyst exhibits improved effectiveness for activation of acetylene towards hydrogenation. The inefficient activity of the latter photocatalytic assembly is attributed to the poor activity of the Pd-microelectrode in generating surface-bound H-atoms. On the other hand, an impressive catalytic activity towards photohydrogenation of acetylene is revealed by a bifunctional heterogeneous catalyst composed of Pt coated by islands of Pd, $\phi = 4.4 \times 10^{-2}$. It has been suggested that the bifunctional catalyst participates in the photohydrogenation of acetylene by two complementary cooperative functions, see Fig. 21. The Pt component acts as an effective microelectrode for acceptance of electrons from the photoreduced relay, and as metal surface for the generation of H-atoms. The Pd sites effectively activate acetylene towards hydrogenation, and act as a "hydrogen-sponge" for uptake of Pt-generated H-atoms, leading to the hydrogenation of Pd-activated acetylene. The bifunctional bimetallic heterogeneous catalyst simulates the cofactor-enzyme activities in natural systems. The Pt-component mimics the cofactor functions in charge accumulation and generation of reducing equivalents, H-atoms. The Pd sites resemble the function of the enzyme active site in activating the substrate towards the specific transformation (hydrogenation of acetylene). Only by immobilization of the Pd onto the Pt catalyst communication between the two catalysts is achieved, resembling the highly ordered cofactor-enzyme configurations required in biocatalytic transformations. Photohydrogenation of other organic compounds, i.e. 3-hexyne, 1,1-diphenylethylene, 3-pentanone, and butyraldehyde has been accomplished by this photosystem and different heterogeneous metal catalysts [142].

Ordered, organized multiphase assemblies for the hydrogenation of unsaturated organic compounds have been constructed [143]. Photohydrogenation of phenylacetylene (17) to styrene (18) has been accomplished in a water-oil two-phase system, see Fig. 22. The photosystem composed of $Ru(bpy)_3^{2+}$, N,N' -dioctyl-4,4'-bipyridinium, C_8V^{2+} , as electron relay and Na_2EDTA is localized in the aqueous phase, while the bifunctional Pt-Pd colloid and phenylacetylene are present in the oil phase. The photosystem generates as hydrophobic photoproduct, C_8V^+ , that is extracted into the oil phase, and acts as electron carrier for charging the heterogeneous catalyst. The metal microelectrode generates surface-active hydrogen atoms, being utilized in the hydrogenation of Pd-activated phenylacetylene.

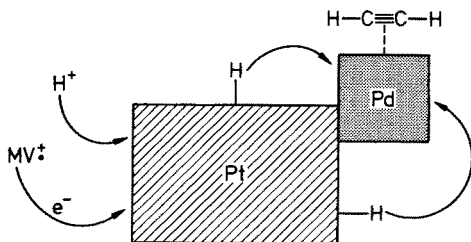


Fig. 21. Complementary functions of a bifunctional Pt-Pd colloid in the photoinduced hydrogenation of acetylene

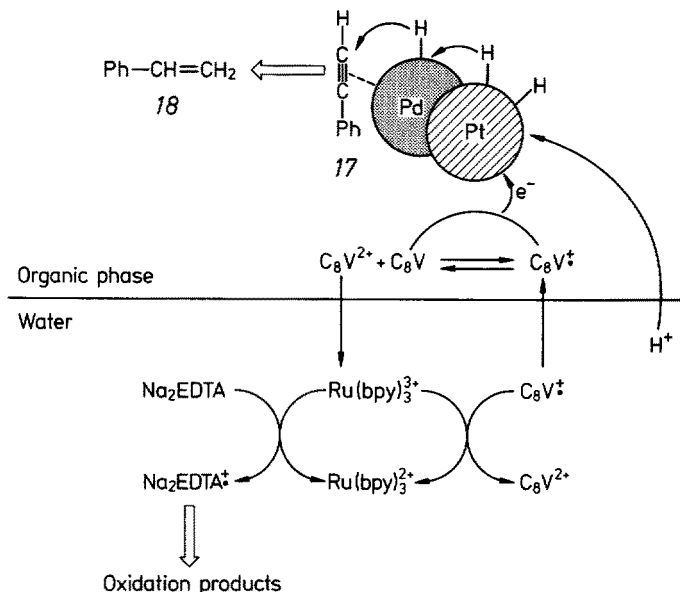


Fig. 22. Photoinduced hydrogenation of phenylacetylene in an organized water-oil two phase system. The photosystem is localized in the aqueous phase and the heterogeneous catalyst is present in the oil phase. Electron transfer communication between the two phases is mediated by C_8V^+

4.2 Cyclic Photolysis of Water by Heterogeneous Catalysts

Cyclic artificial photosynthetic systems (Fig. 11) include an oxidation process complementary to the reduction reaction. For light-driven reductive syntheses of valuable chemicals or for the removal of environmental pollutants the concept of utilizing a sacrificial electron donor can be adapted. Yet, for the application of artificial photosynthetic systems as fuel generation devices, several basic criteria must be met by the complementary oxidation process:

- The oxidized compound must be an abundant raw material to allow an economic fuel production process.
- The oxidized compound should include the chemical elements for the reduction process as well.
- The oxidation product should be a low-molecular-weight material, preferably a non-toxic gaseous compound.

All of these limiting criteria are met by suggesting water as the material to be oxidized in a cyclic photosynthetic device (Fig. 11). Extensive efforts have been directed towards the development of water oxidation catalysts, but only limited knowledge is available. It is certain that the design of water oxidation catalytic materials is a major challenge in future research in this area. The progress in developing oxygen evolution catalysts has been reviewed [45, 46, 144]. In the

present report, the progress in designing heterogeneous O_2 -evolution catalysts in organized assemblies or in cyclic photolysis of water will be mentioned. The aim is to reveal the problems involved in coupling O_2 -evolution catalysts to reductive photosynthetic transformations, and to highlight potential routes to circumvent these difficulties.

Photogenerated $\text{Ru}(\text{bpy})_3^{3+}$ (see Sect. 2.2) exhibits the proper oxidation potential, $E^\circ = 1.26 \text{ V}$, for water oxidation. It is assumed that O_2 -evolution catalysts should include metal sites that undergo oxidation to higher states and are capable of accumulating oxidation equivalent (holes). In this respect ruthenium dioxide, RuO_2 , has been widely investigated as heterogeneous oxygen evolution catalysts [145].

The catalytic activity of RuO_2 is schematically presented in Fig. 23, where holes are ejected from the photogenerated photosensitizer, S^+ , to the catalyst, and surface-adsorbed water is being oxidized. Integrated systems that include $\text{Ru}(\text{II})$ -tris-bipyridine as sensitizer, N,N' -dimethyl-4,4'-bipyridinium, methyl viologen, MV^{2+} , as electron mediator, and two heterogeneous catalysts; a Pt colloid sol and macrodispersed RuO_2 were reported to effect the cyclic photolysis of water with a low quantum efficiency of $\phi = 1.5 \times 10^{-3}$. In this system the primary photoinduced electron transfer reaction yields the intermediate photoproducts for water photolysis, see Fig. 24. The reduced photoproduct MV^+ acts as electron carrier for H_2 -evolution, while the oxidized photosensitizer $\text{Ru}(\text{bpy})_3^{3+}$ acts as hole carrier for the oxidation of water by RuO_2 . It has been emphasized that the successful operation of this system depends on the selection of an hydrophobic maleic anhydride-styrene copolymer as protective agent of the Pt sol [144]. With such organization of the system, the reduced photoproduct MV^+ , being hydrophobic, is associated with the polymer matrix and back ET of the intermediate photoproducts is retarded. Further improvement of the system has been reported by the application of an organized bifunctional catalyst composed of TiO_2 acting

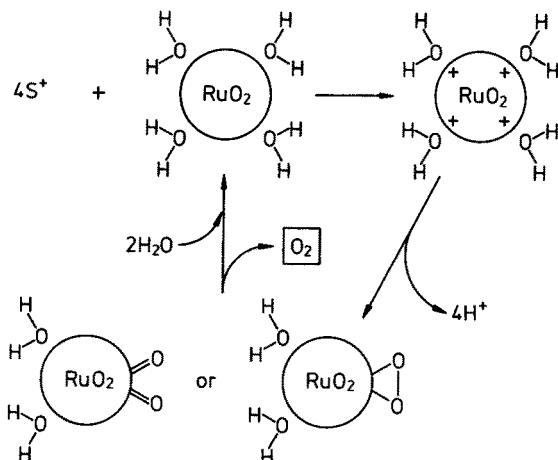


Fig. 23. Schematic function of the heterogeneous catalyst RuO_2 in the oxidation of water to O_2

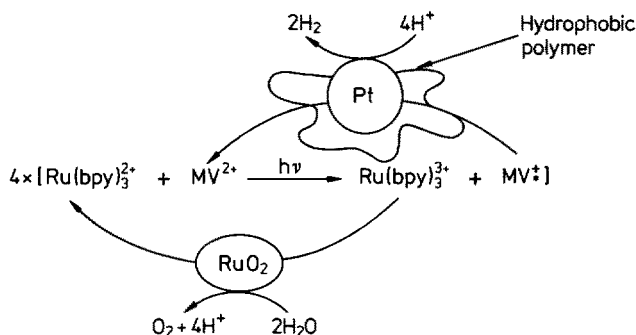


Fig. 24. Cyclic photolysis of water in an assembly composed of Pt and RuO_2 as H_2 - and O_2 -evolution catalysts, respectively

as support for ultrafine dispersed RuO_2 and Pt [146, 147]. The latter catalytic assembly combines a semiconductor material as support for the heterogeneous metal catalysts. The semiconducting property of the supporting matrix was used for the photosensitized cyclic cleavage of water using $\text{Ru}(\text{II})$ -tris-bipyridine complexes as light-harvesting materials, without any mediating electron carrier. Illumination of the $\text{TiO}_2/\text{Pt}/\text{RuO}_2$ catalyst in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ results in cyclic photolysis of water, see Fig. 25. The cleavage of water proceeds through charge ejection from the excited photosensitizer to the semiconductor conduction band acting as electron carrier to the Pt site, where H_2 -evolution occurs. The resulting oxidized photoproduct mediates oxygen evolution at the RuO_2 catalyst. Improved yields for water photolysis are obtained [147] by the application of a $\text{Ru}(\text{II})$ -tris-bipyridine photosensitizer that includes a didodecyl-substituted bipyridine ligand, $\text{C}_{12}\text{-Ru}(\text{bpy})_3^{2+}$. The enhanced activity of the latter photosensitizer is attributed to its hydrophobic character resulting in improved charge ejection by adsorption to the catalyst assembly.

The use of RuO_2 as oxygen evolution catalyst has been a subject of controversy and criticism [82, 148] in view of poor reproducibility of the catalyst activity. It is certain that mixed-metal valencies and substoichiometric RuO_x ($x < 2$) structures are essential for the catalyst activity [149, 150]. Also, the observation that RuO_2

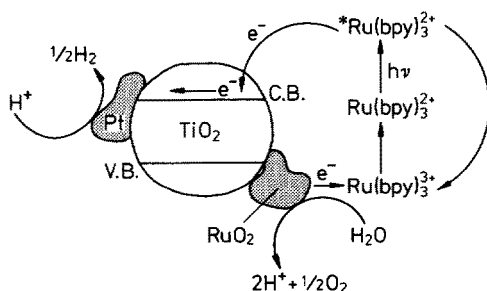


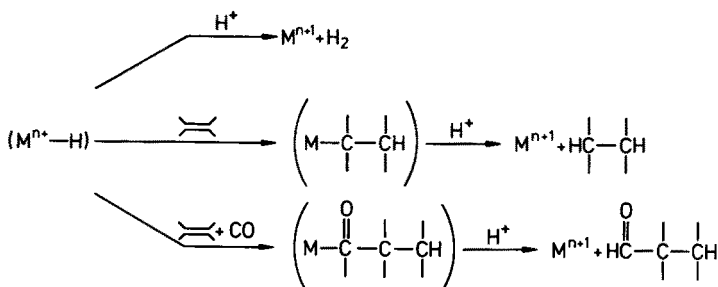
Fig. 25. Cyclic photolysis of water using $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and an immobilized catalytic assembly composed of $\text{TiO}_2/\text{Pt}/\text{RuO}_2$. The semiconductor TiO_2 component acts as electron carrier to the Pt catalyst

acts simultaneously as a hydrogen evolution catalyst introduces a severe limitation for its use as oxidation catalyst in cyclic photolysis of water [151]. Intermediate hydrogen atoms associated with the RuO_2 interface recombine with catalyst-associated oxygen species involved in the O_2 -evolution process. Consequently, the cyclic photolysis of water is short-circuited at the catalyst surface. Other metal oxides, i.e. IrO_2 [152] and polynuclear transition-metal hydroxo-complexes [153, 154] ($\text{M} = \text{Mn, Fe, Co, Ni}$), have been similarly reported as oxygen evolution catalysts. Of specific interest is the successful use of a polynuclear Mn(III) -hydroxo complex as O_2 -evolution catalyst, since it is the closest artificial analog to the biocatalytic manganese cluster operating in natural photosynthesis [155].

The brief review emphasizes the useful catalytic activities of metal oxides, i.e., RuO_2 , towards O_2 -evolution but points to their limitations as a result of surface recombination with intermediate H-atoms. Possible routes to circumvent these difficulties could involve elimination of surface H-atom through the application of homogeneous H_2 -evolution catalysts (see Sect. 4.3), and compartmentalization of the oxidation catalyst from the H_2 -evolution catalyst, i.e., liposomes. Alternatively, reduction of other substrates rather than water i.e. CO_2 , could lead to intermediate carbonous species being insensitive to oxidation by intermediate O-species.

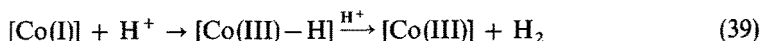
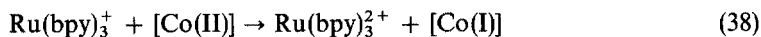
4.3 Photosensitized H_2 -evolution, Hydrogenation and Hydroformylation Processes through Homogeneous Catalysis

Photosensitized generation of hydrido-metal complexes in aqueous media provides a general route for H_2 -evolution, hydrogenation of unsaturated substrates (i.e. olefins, acetylenes), or hydroformylation of double bonds, see Scheme 2. Co(II) complexes, i.e. $\text{Co(II)-tris-bipyridine}$, Co(bpy)_3^{2+} , or the macrocyclic complex $\text{Co(II)-Me}_4[14]\text{tetraene } \text{N}_4$, act as homogeneous H_2 -evolution catalysts in photo-systems composed of Ru(bpy)_3^{2+} (or other polypyridine Ru(II) complexes) as photosensitizers and triethanolamine, TEOA, or ascorbic acid, HA^- , as sacrificial electron donors [156, 157]. Reductive ET quenching of the excited photosensitizer



Scheme. 2. Possible utilization of a photogenerated hydrido-metal complex in H_2 -evolution, hydrogenation and hydroformylation processes

results in $\text{Ru}(\text{bpy})_3^+$, acting as the ET mediator for the $\text{Co}(\text{II})$ -catalyst, as shown in Eq. (38). The resulting $\text{Co}(\text{I})$ species mediates H_2 -evolution presumably through the intermediate generation of a $\text{Co}(\text{III})$ -hydride species that effects H_2 -evolution by subsequent protonation, as in Eq. (39).

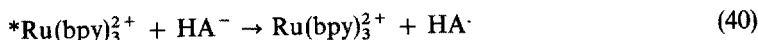


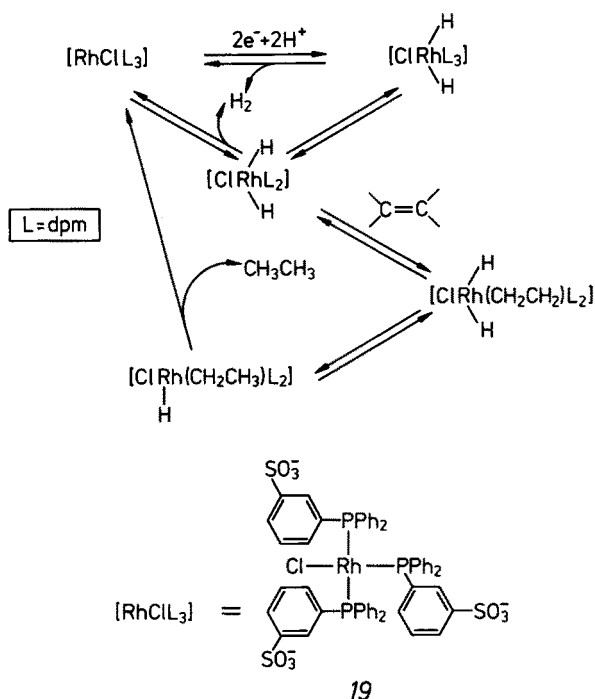
The water-soluble Wilkinson-type catalyst chlorotris(diphenylphosphinobenzene-*m*-sulfonate)rhodium(I), $\text{RhCl}(\text{dpm})_3^{3-}$ (**19**), acts as catalyst for H_2 -evolution [158], hydrogenation and hydroformylation [159]. In a photosystem composed of $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer, ascorbic acid, HA^- , as electron donor and $\text{RhCl}(\text{dpm})_3^{3-}$, hydrogen evolution proceeds with a quantum efficiency corresponding to $\phi = 0.033$. In the presence of ethylene or acetylene, hydrogen evolution is blocked and hydrogenation of the unsaturated organic substrates predominates. Table 6 summarizes the quantum yields for H_2 -evolution and

Table 6. Quantum efficiencies (ϕ) and turnover numbers (TN) of $\text{RhCl}(\text{dpm})_3^{3-}$ in photosystems for hydrogenation and H_2 -evolution

Substrate	Product	ϕ	TN- $[\text{RhCl}(\text{dpm})_3^{3-}]$
Ethylene	Hydrogen	0.033	59
	Ethane	0.018	40
	Hydrogen	0.011	17
Acetylene	Ethylene	0.0058	12
	Ethane	0.0013	1.5
	Hydrogen	0.002	11

formation of the hydrogenated products, as well as the turnover numbers of the catalyst in the photosystem. The photosensitized ET mechanism leading to the reduction of the rhodium catalyst involves reductive quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$, see Eq. 40. The resulting $\text{Ru}(\text{bpy})_3^+$ and oxidized ascorbate, $\text{HA}^\cdot$, act as electron carriers for the reduction of the rhodium catalyst. Although the catalytic intermediates involved in H_2 -evolution and hydrogenation processes are not known, a catalytic scheme transformation can be outlined on the basis of the Wilkinson catalyst performance, see Scheme 3. The photosystems applying $\text{RhCl}(\text{dpm})_3^{3-}$ as hydrogenation and H_2 -evolution catalyst suffer from degradation of the photosensitizer, presumably to form $\text{Ru}(\text{bpy})_2(\text{dpm})^+$. Other closely related homogeneous catalysts including $\text{RuCl}(\text{CO})(\text{dpm})_3^{3-}$, $\text{PtCl}_2(\text{dpm})_2^{2-}$, and $\text{PdCl}(\text{dpm})_3^{3-}$, act as H_2 -evolution and hydrogenation catalysts in the photosystem $\text{Ru}(\text{bpy})_3^{2+}$ /ascorbate [160].

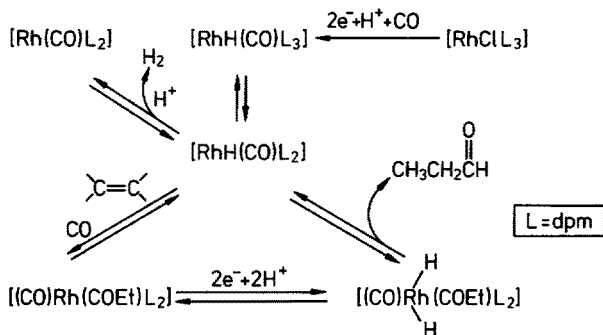




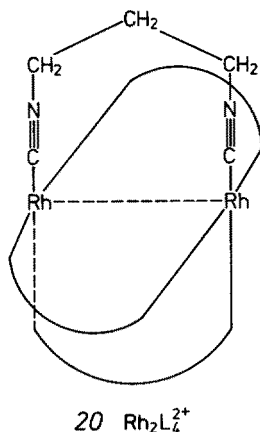
Scheme 3. Suggested cycle for the catalytic functions of $RhCl(dpm)_3^{3-}$ in the photosensitized H_2 -evolution and hydrogenation processes

The homogeneous complex $RhCl(dpm)_3^{3-}$ acts also as hydroformylation catalyst [159]. Upon illumination of the catalytic photosystem $Ru(bpy)_3^{3+}/\text{ascorbic acid}/RhCl(dpm)_3^{3-}$ in the presence of ethylene and carbon monoxide, propionaldehyde is obtained as photoproduct. Similarly, propene yields the hydroformylation product butyraldehyde. The facts that no hydrogenation products are produced in this assembly, and that hydridocarbonyl-*tris*-(diphenylphosphinobenzene-3-sulphonate) rhodium(I), $RhH(CO)(dpm)_3^{3-}$, substitutes $RhCl(dpm)_3^{3-}$ as catalyst in the photosystem to yield the hydroformylation products at similar efficiency, suggest that the homogeneous catalyst $RhCl(dpm)_3^{3-}$ is transformed into a new catalytic species under CO. A possible route for the interconversion of $RhCl(dpm)_3^{3-}$ into the hydroformylation catalyst is provided in Scheme 4.

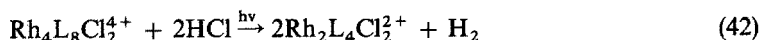
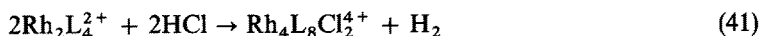
The light-active component of the system can itself generate catalytically active H_2 -evolution species. Polynuclear complexes such as dirhodium isocyanide complexes, $Rh_2L_4^{2+}$ ($L = 1,3$ -di-isocyanide) (**20**), exhibit strong charge transfer absorption bands in the visible region of the spectrum, and photoinduced H_2 -evolution proceeds upon their illumination in acidic solutions [161–163]. Mechanistic studies have revealed that hydrogen is evolved in two steps, a thermal step generating a tetranuclear product, Eq. (41), followed by a photochemical



Scheme 4. Suggested catalytic intermediates formed in the photosensitized hydroformylation processes using $\text{RhCl}(\text{dpm})_3^{3-}$ as homogeneous catalyst



process regenerating the dinuclear component. It is suggested that H_2 -evolution, (Eq.(42)) is triggered by intermediary hydridorhodium species such as $\text{HRh}_2\text{L}_4\text{Cl}^{2+}$. Other polynuclear complexes of molybdenum, rhenium and iridium show similar photophysical and catalytic properties towards hydrogen evolution [164].



5 Carbon Dioxide Fixation in Artificial Photosynthetic Systems

The problematics involved in CO_2 reduction and the different mechanistic routes for CO_2 -fixation were detailed in Sec. 3.2. A further complication involved in

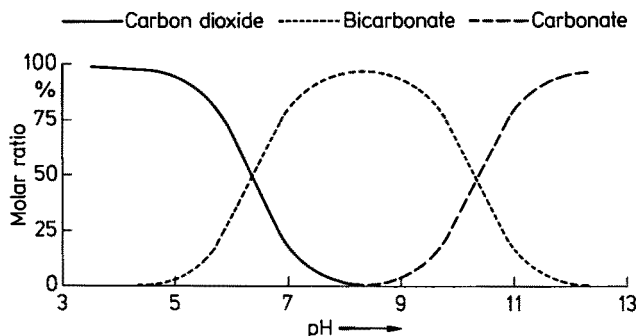


Fig. 26. Molar ratios of CO_2 and its hydrated forms in water (at 25°C and under 1 atm. of CO_2 . Total concentration of CO_2 in water corresponds to 0.76 ml in 1 ml H_2O)

carbon dioxide reduction in aqueous media relates to the different hydration products of CO_2 present in water [165]. The solubility of CO_2 in water at atmospheric pressure (25°C) is 0.76 ml in 1 ml of water. This corresponds to a $11.2\ \mu\text{M}$ concentration. Carbon dioxide undergoes in water hydration to form carbonic acid (Eq. (43)) that undergoes stepwise dissociation to bicarbonate, HCO_3^- , (Eq. (44)), and carbonate, CO_3^{2-} , (Eq. (45)). Figure 26 provides a graphic representation of the molar ratios of CO_2 , HCO_3^- and CO_3^{2-} as function of the pH of the aqueous medium. It is evident that at $\text{pH} < 4.5$ CO_2 is the dominant component, in the range of $\text{pH} = 7.5\text{--}8.5$ bicarbonate is the major form, while at $\text{pH} > 11.5$ only carbonate is present. The formation of different hydrated CO_2 entities introduces versatility in applying heterogeneous and homogeneous catalyst on specific forms, as a function of the pH values of the aqueous medium. Furthermore, the thermodynamic reduction potentials for generating certain products are strongly affected by the source form of CO_2 (hydrated or nonhydrated) as exemplified for the formation of CO (Eq. (46–48)) [166]. In addition, H_2 -evolu-

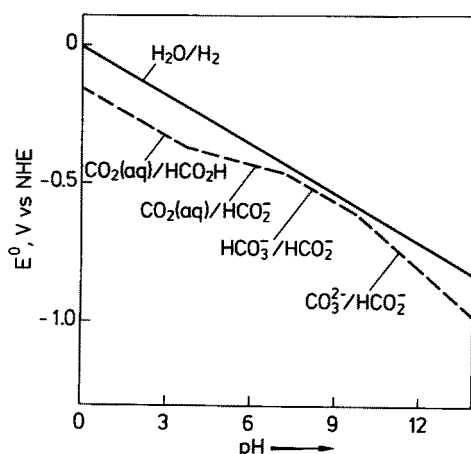
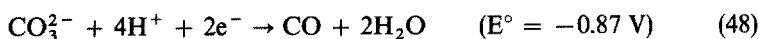
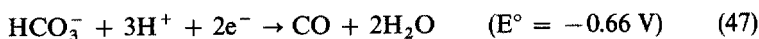
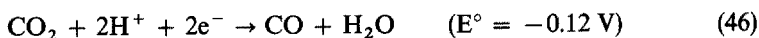
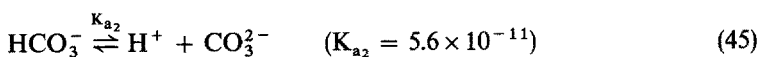
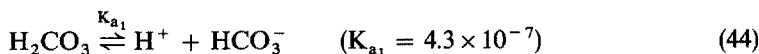
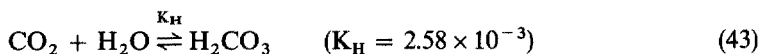


Fig. 27. Reduction potentials of CO_2 and its hydrated forms to formate as a function of pH (---) and reduction potential of water to H_2 as a function of pH (—)

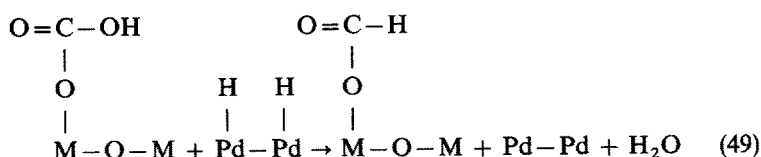
tion from aqueous media acts as a competitive process to the reduction of CO₂ or its hydrated forms. Both processes are pH dependent, but the pH – reduction potential profiles exhibit different dependencies [166]. Figure 27 shows the reduction potential – pH functions for the reduction of CO₂ and its hydrated forms to formate and for H₂-evolution. Thus, three fundamental aspects must be considered in developing artificial photosynthetic CO₂ fixation processes:



- i) Proper and specific heterogeneous or homogeneous catalysts have to be selected for CO₂ or its different hydrated forms.
- ii) The photogenerated ET products must exhibit the proper reduction potentials for reduction of CO₂ or its hydrated form.
- iii) Tuning the pH of the aqueous medium provides a means to thermodynamically control CO₂ reduction and eliminate H₂-evolution.

5.1 Photosensitized CO₂/HCO₃⁻ Fixation Using Heterogeneous Catalysts

Hydrogenation of CO₂ by hydrogen to form formate, over Pd immobilized onto metal oxides such as Al₂O₃, TiO₂ or MgO, has revealed cooperative effects of the support and metal catalyst [167, 168]. It has been suggested that surface hydroxy groups adsorb CO₂, while the Pd catalyst dissociates molecular hydrogen to form Pd-hydride species. Adsorption of carbon dioxide results in the activation of the adsorbate, that undergoes subsequent hydrogenation by surface migration of



hydrides, see Eq. (49). Such mechanism is evidenced by the spectroscopic identification of surface-bound formate intermediates [169, 170]. Accordingly, a palladium catalyst on hydroxy-substituted matrices seems as a potential catalytic assembly for the two-electron reduction of CO_2 to formate.

A photosystem that applies a Pd colloid stabilized by β -cyclodextrin, a cyclic poly-glucose macromolecule, has been developed for the effective photosensitized reduction of $\text{CO}_2/\text{HCO}_3^-$ to formate [171, 172]. The photosystem is composed of deazariboflavin, dRFI (**21**), as photosensitizer and sodium oxalate as sacrificial electron donor (Fig. 28). Illumination of the photosystem in the presence of the Pd- β -cyclodextrin catalyst results in the effective formation of formate, $\phi = 1.1$, and only trace amounts of hydrogen. In the absence of $\text{CO}_2/\text{HCO}_3^-$ the photosystem and catalyst act as an effective photochemical H_2 -evolution assembly, implying that fixation of $\text{CO}_2/\text{HCO}_3^-$ in the system competes effectively with H_2 -evolution. Detailed mechanistic studies have revealed important catalytic functions of the Pd colloid in the reduction of $\text{CO}_2/\text{HCO}_3^-$. The rate of formate production as a function of bicarbonate concentration shows a saturation behavior, suggesting the presence of bicarbonate activation sites on the Pd-catalyst that are saturated at high concentrations of the substrate. Interestingly, the photocatalytic system is inhibited towards formate production in the presence of thiols, acting as inhibitors. Inhibition of formate production is accompanied by H_2 -evolution, a process being retarded in the non-inhibited formate production assembly. In view of these mechanistic studies, a stepwise route for the formation of formate in this photochemical assembly has been suggested, see Fig. 29. Photogenerated methyl viologen radical acts as electron carrier charging the Pd colloid that acts as microelectrode for the production of surface-bound H-atoms (or hydrides). Activation of bicarbonate on the colloid allows its hydrogenation through cleavage of Pd-H bonds. This latter process is faster than the competitive H_2 -evolution process occurring through dimerization of surface H-atoms, and, thus, hydrogen evolution is eliminated. The added inhibitor (thiol) is specifically associated with

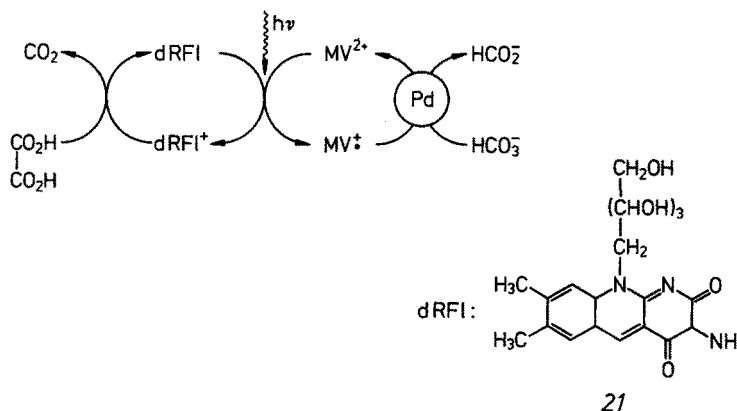


Fig. 28. Photosynthetic assembly for the reduction of $\text{CO}_2/\text{HCO}_3^-$ to formate

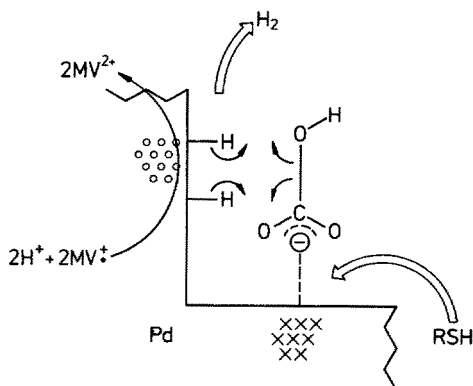
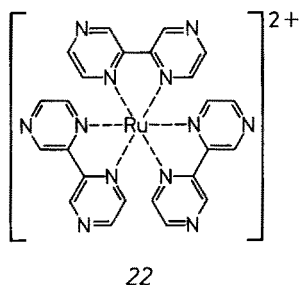


Fig. 29. Schematic functions of the Pd colloid in the activation of $\text{CO}_2/\text{HCO}_3^-$, generation of surface H-atoms and effecting the hydrogenation of activated $\text{CO}_2/\text{HCO}_3^-$

the bicarbonate activation sites. As a result, only the slower H_2 -evolution process takes place in the presence of the inhibitor, as observed experimentally.

Photosensitized CO_2 reduction to methane, CH_4 , through an 8-electron fixation process, Eq. (22), has been accomplished in the presence of Ru- or Os-colloids acting as catalysts [173, 174]. Selection of ruthenium or osmium colloids has been based on the catalytic activities of these metals in the methanation process of CO_2 [175] (hydrogenation of CO_2 by H_2) and electrocatalyzed reduction of CO_2 to methane at a Ru-electrode [176, 177]. An aqueous photosystem composed of Ru(II)-*tris*-bipyrazine, $\text{Ru}(\text{bpz})_3^{2+}$ (**22**), as photosensitizer, and triethanolamine,



TEOA, as electron donor yields upon illumination in the presence of CO_2 and the Ru-colloid, methane as major photoproduct, $\phi = 4 \times 10^{-4}$, and ethylene and ethane at lower yields, $\phi = 7.5 \times 10^{-5}$ and $\phi = 4 \times 10^{-5}$ respectively. In this photosystem, reductive ET quenching of excited $\text{Ru}(\text{bpz})_3^{2+}$ yields the reduced photoproduct $\text{Ru}(\text{bpz})_3^+$ ($E^\circ = -0.86 \text{ V vs. SCE}$) that mediates the reduction of CO_2 to methane and hydrocarbon oligomers (Fig. 30a). Interestingly, the reduced photoproduct $\text{Ru}(\text{bpz})_3^+$ although thermodynamically capable, does not effect H_2 -evolution from the system. On the other hand, a series of photosystems composed of $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer, TEOA as sacrificial electron donor and different bipyridinium electron acceptors (**23**)–(**26**) exhibit non-specificity, and

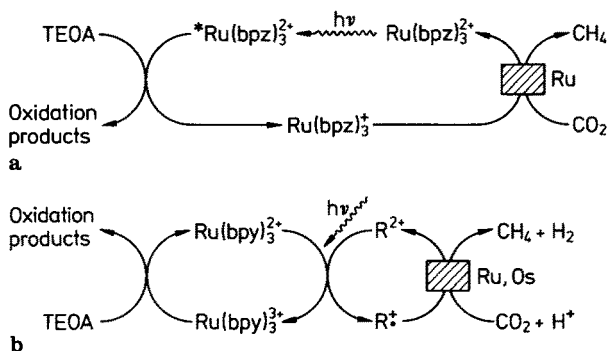
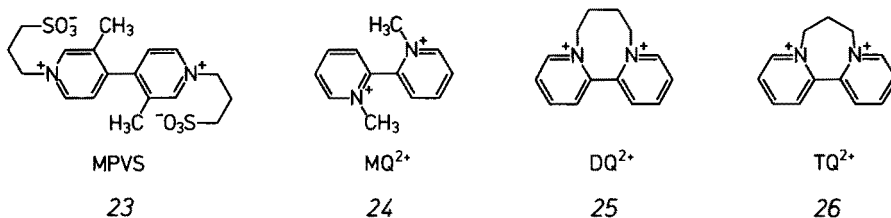


Fig. 30a, b. Photosynthetic assemblies for CO₂ fixation to methane: **a)** A photosystem composed of Ru(bpz)₃²⁺ as photosensitizer and electron carrier. **b)** A photosystem composed of Ru(bpy)₃²⁺ as photosensitizer and different bipyridinium salts, **23–26**, as electron acceptors



upon illumination under CO₂ in the presence of the Ru colloid, CH₄ is formed as minor product, while H₂-evolution is the major photoproduct, see Fig. 30b. Table 7 provides a summary of the quantum yields of H₂-evolution, CH₄-formation and ethylene production from the photosystems applying either Ru or Os as catalysts. The photosensitized ET process operative in these photosystems involves oxidative ET quenching of excited Ru(bpy)₃²⁺ by the bipyridinium electron relays and subsequent regeneration of the photosensitizer through oxidation of TEOA by Ru(bpy)₃³⁺, see Fig. 30b. The resulting bipyridinium radicals act as electron carriers that reduce CO₂ or effect H₂-evolution at the metal catalyst. Comparison of the Ru and Os colloids as catalysts for the photosensitized CO₂ fixation to methane has revealed that the former colloid exhibits superior activity.

Table 7. Quantum efficiencies for CO₂-fixation products and H₂-evolution in the photo-system TEOA/Ru(bpy)₃²⁺/Relay/Ru or Os

Relay	E° (Volt) vs. NHE	Ru-colloid Catalyst			Os-Colloid Catalyst		
		10 ³ φ (H ₂)	10 ⁴ φ (CH ₄)	10 ⁵ φ (C ₂ H ₄)	10 ³ φ (H ₂)	10 ⁴ φ (CH ₄)	10 ⁵ φ (C ₂ H ₄)
MPVS (23)	−0.79	2.6	5.7	1.9	1.9	2.1	1.04
MQ ²⁺ (24)	−0.72	1.7	2.3	0.73	3.0	0.52	0.29
DQ ²⁺ (25)	−0.65	1.8	1.4	1.08	9.2	0.61	0.67
TQ ²⁺ (26)	−0.55	0.28	0.20	0.18	0.64	0.12	0.15

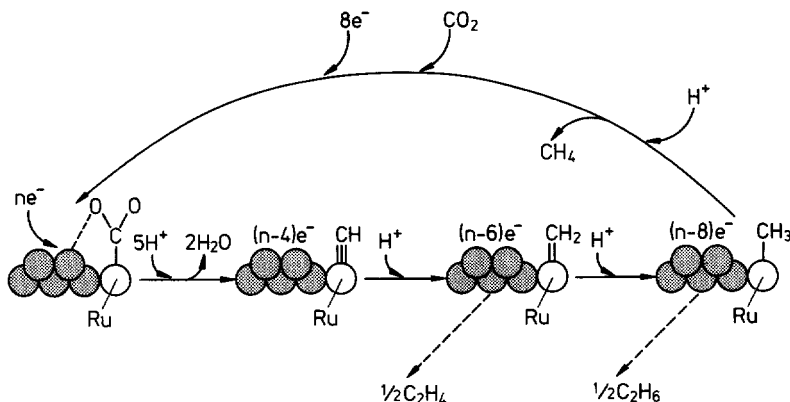


Fig. 31. Schematic functions of the Ru-colloid in the multi-electron reduction of CO₂ to methane

Comparison of the photosystems that utilize Ru(bpz)₃²⁺ or Ru(bpy)₃²⁺ as photosensitizers reveals significant differences; while the system using Ru(bpz)₃²⁺ as photosensitizer exhibits specificity towards CO₂-fixation, the second class of photosystems, applying Ru(bpy)₃²⁺ as photosensitizer, shows non-specific photo-products, and the H₂-evolution process predominates the CO₂-fixation route. Mechanistic studies have suggested that CO₂ reduction and H₂-evolution occurs at different catalytic sites. It has been assumed that the bipyrazine ligand, being a part of the photosensitizer Ru(bpz)₃²⁺ acts as inhibitor for hydrogen evolution, presumably through selective association to the H₂-evolution sites. Introduction of the bipyrazine ligand to the non-specific photosystem, utilizing Ru(bpy)₃²⁺ as photosensitizer, results in the selective blocking of the H₂-evolution process, while CO₂-fixation to methane is not affected. Interestingly, the non-specific performance of the Ru-colloid in the photosystem Ru(bpy)₃²⁺/relay has been rationalized in terms of distinct, separated sites on the metal colloid: One group of sites acts as catalyst for CO₂ activation and reduction, while the other sites are catalytically active in H₂-evolution. Time-resolved studies indicate that fixation of CO₂ to methane proceeds through an ET mechanism followed by protonation steps, rather than by a hydrogenation route. Such a sequential process, where the Ru-catalyst provides the activation sites for CO₂ and acts as multi-electron charge relay (microelectrode), for the reduction of CO₂ to methane, is schematically presented in Fig. 31. Formation of intermediate Ru-carbene and Ru-methyl species is supported by the formation of hydrocarbon oligomers, ethylene, and ethane, respectively, originating from dimerization of the intermediary species.

5.2 Photosensitized CO₂/HCO₃⁻ Fixation Using Homogeneous Catalysts

A variety of transition-metal complexes have been applied as homogeneous catalysts for CO₂-fixation in artificial photosynthetic assemblies. Typical photo-

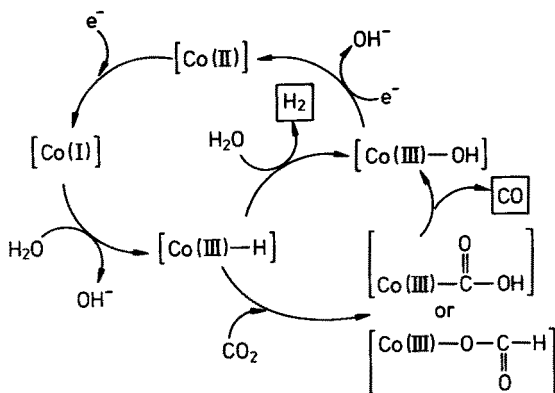
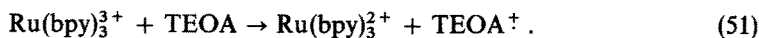
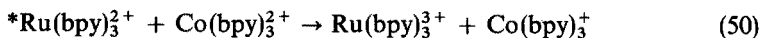


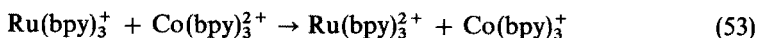
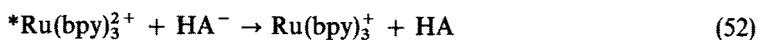
Fig. 32. Schematic catalytic cycle for the reduction of CO_2 and H_2 -evolution by Co(II) -homogeneous complexes

products generated in such systems include CO , formate and concomitant H_2 -evolution. Photosensitized reduction of CO_2 to carbon monoxide has been accomplished in a photosystem composed of Ru(bpy)_3^{3+} as photosensitizer, Co(II) -complex as homogeneous catalysts and various sacrificial electron donors such as triethanolamine, TEOA, or ascorbic acid. The most extensively explored system includes $\text{Co(II)-tris-bipyridine}$, Co(bpy)_3^{2+} , as catalyst [166, 178–180]. Illumination of a photosystem composed of Ru(bpy)_3^{3+} as photosensitizer, Co(bpy)_3^{2+} as catalyst, and an organic solvent-aqueous medium that includes TEOA as sacrificial electron donor results in reduction of CO_2 to CO and concomitant H_2 -evolution. In a closely related system, TEOA has been substituted by ascorbic acid as sacrificial electron donor. Figure 32 outlines a suggested cycle for the formation of CO and H_2 in this catalyzed transformation. The homogeneous Co(II) -complex is reduced in the photosensitized ET process to $\text{Co(I)-tris-bipyridine}$, Co(bpy)_3^+ . This photoproduct subsequently generates an hydrido cobalt species, being the active catalyst in CO_2 -fixation. Carbon dioxide insertion into the hydride species followed by dehydration of the carboxylate intermediate results in CO , while protonation of the hydrido intermediate yields the competitive pathway of H_2 -evolution. Photogeneration of Co(bpy)_3^+ proceeds through an oxidative ET quenching mechanism in the presence of TEOA as electron donor (Eqs. (50 and 51)) or by a reductive ET quenching of the excited photosensitizer in the presence of ascorbic acid, HA^- , as electron donor, (Eqs. (52 and 53)).

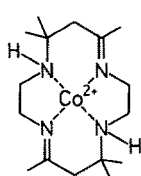
Oxidative ET quenching:



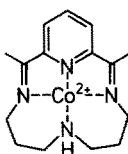
Reductive ET quenching:



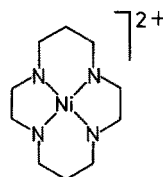
Other Co(II)-complexes that were applied in the photosensitized reduction of CO₂ to CO (and concomitant H₂-evolution) include Co(II)-ethylene glycol dimethyl ether complexes [178], and different tetraaza-macrocyclic Co(II)-complexes such as **27**, **28**. A closely related system, where Ni(II)-tetraaza macrocycle (**29**) substitutes the cobalt homogeneous complexes in the photosystem including Ru(bpy)₃²⁺ as photosensitizer and ascorbic acid as electron donor, has been reported by Tinnemans [181] and Calvin [182].



27



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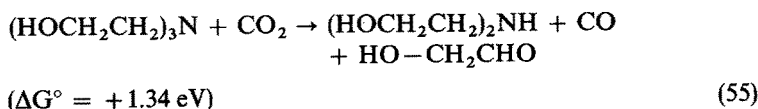
Selective carbon dioxide reduction to CO has been accomplished in a non-aqueous medium that includes tricarbonyl (2,2'-bipyridinium) rhenium(I), *fac*-Re(bpy)(CO)₃X (X = Cl, Br) as light-active component and homogeneous catalyst for CO₂ reduction [183–185]. In dimethylformamide solutions that include TEOA as sacrificial electron donor, photosensitized reduction of CO₂ to CO proceeds with a quantum efficiency of $\phi = 0.14$. Mechanistic investigations have revealed that reductive ET quenching of the rhenium complex (Eq. (54)) yields the catalytic intermediate active in deoxygenation of CO₂. It has been suggested that carbon



monoxide ligand dissociation followed by formation of rhenium-formate intermediate leads to a cyclic process for CO₂ reduction, see Fig. 33. Interestingly, the photosystem generates an isolable structurally determined rhenium carboxylate



complex, *fac*-Re-(O-C-H)(bpy)(CO)₃. The fact that this complex is inactive in cyclic photosensitized CO formation suggests that CO is evolved from a rhenium formate intermediate, formed by the metal-carbon insertion mode of CO₂ into a Re-H intermediate (see Sect. 3.2). Further improvement of this system has been reported through the use of Ru(bpy)₃²⁺ as photosensitizer and [*fac*-Re(bpy)(CO)₃X] as selective catalyst for CO formation. In this photosystem photogenerated Ru(bpy)₃⁺ acts as charge relay for the reduction of the catalyst. The different CO-generating photosystems that include TEOA as sacrificial electron donor represent catalytic assemblies that drive an uphill endoergic CO₂-fixation process, Eq. (55):



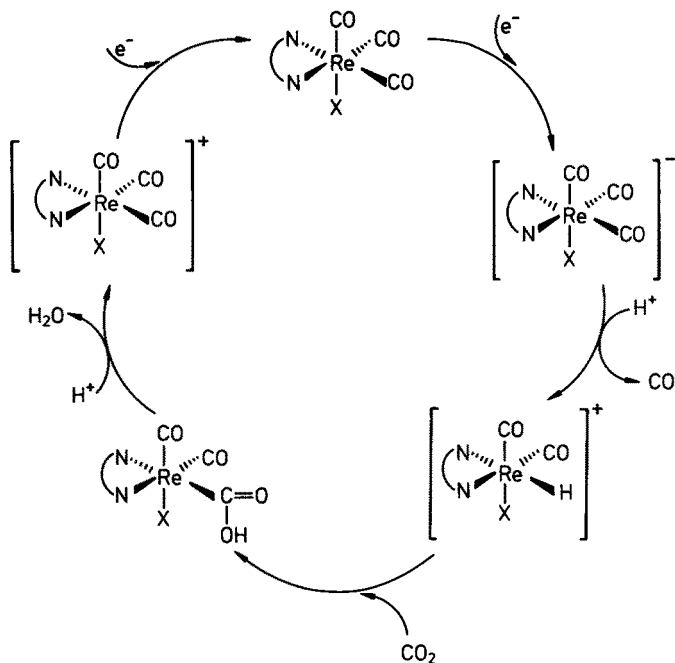
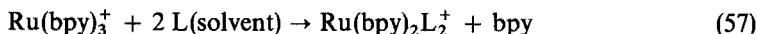
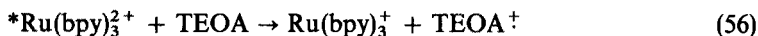


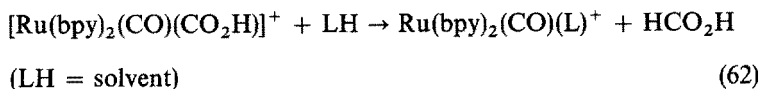
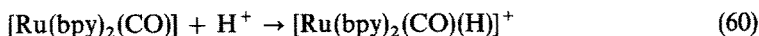
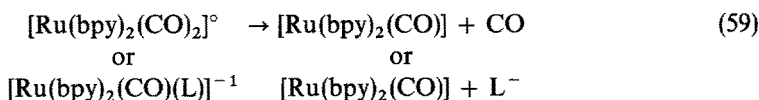
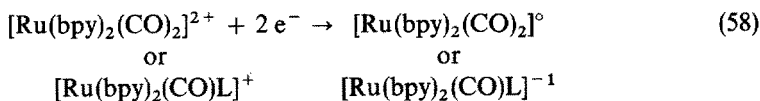
Fig. 33. Schematic catalytic cycle for the reduction of CO_2 to carbon monoxide using $\text{fac-Re}(\text{bpy})(\text{CO})_3\text{X}$ as photocatalyst

Selective photosensitized reduction of CO_2 to formate has been accomplished in organic solvents (dimethylformamide) including $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and triethanolamine as electron donor [186]. It has been suggested that the photogenerated $\text{Ru}(\text{bpy})_3^{2+}$, Eq. (56), undergoes ligand dissociation (Eq. (57)) that ultimately leads to the in situ generation of a selective homogeneous catalyst for CO_2 -fixation to formate. Supporting evidence that a ruthenium-*bis*-bipyridine complex acts as



a homogeneous catalyst for the reduction of CO_2 into formate originates from the fact that dicarbonyl $\text{Ru}(\text{II})$ -*bis*-bipyridine, $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ acts as an effective catalyst [187, 188] for formate production in the $\text{Ru}(\text{bpy})_3^{2+}/\text{TEOA}$ photosystem, $\phi = 0.14$. A possible mechanism for formation of formate in the photosystem including $\text{Ru}(\text{bpy})_2(\text{CO})_2^{2+}$ as catalyst is outlined in Eqs. (58–62). Photogenerated $\text{Ru}(\text{bpy})_3^{2+}$ reduces the catalyst by two consecutive one-electron reduction processes. The latter product undergoes dissociation of the carbonyl ligand and the pentacoordinated, reduced intermediate generates the hydrido-

ruthenium species that undergoes CO₂-insertion and subsequent protonation to formate. Supportive evidence for this sequential route is the fact that chemically generated [Ru(bpy)₂(CO)H]⁺ (the speculative intermediate in the cycle, see Eq. (60)) acts as homogeneous catalyst for the selective reduction of CO₂ to formate using Ru(bpy)₃⁺ as charge relay.



This summary reveals the mechanistic complexity of CO₂-fixation processes using homogeneous catalysts. Formation of CO₂ insertion products into hydrido-metal intermediates could lead to metal-carboxylate or metal-formate species. At this stage it is impossible to elucidate the detailed mechanistic profiles of these transformations. In the photosystem that applies *fac*-Re(bpy)(CO)₃X as catalyst,



rhenium formate, Re(OCH)(bpy)(CO)₃ has been isolated. The inertness of the latter product towards photosensitized CO generation eliminates such species in the catalytic cycle and suggests rhenium carboxylate, Re(COOH), as the catalytically active species. Whether such conclusion can be generalized for other metals, and further elucidation of the origin for formate/CO selectivities in the different photosystems remains a challenging open question in this topic.

6 Biocatalyzed Artificial Photosynthetic Systems

Photosensitized regeneration of an oxidized cofactor, i.e. NAD(P)⁺ or a reduced cofactor NAD(P)H, could provide general routes for oxidative or reductive biocatalyzed photosynthetic transformations (see Sect. 3.2.3). Coupling of the regenerated NAD(P)⁺/NAD(P)H cofactors to enzymes that depend on these cofactors, opens a broad array of feasible photo-biocatalytic syntheses. An alternative approach to couple enzymes as catalysts for artificial photosynthetic

devices involves the design of ET communication between an artificial electron shuttle (electron or hole carrier) and the enzymes active sites. In such cases, the artificial or synthetic shuttle should be recognized by the catalytic assembly. The subject of biocatalyzed transformations through photochemical regeneration of nicotinamide cofactors has recently been reviewed [113]. In this section specific emphasis will be directed to the design of artificial biocatalyzed photosynthetic devices, particularly related to H_2 -evolution and CO_2 -fixation, as well as to the organization of biocatalytic assemblies, where ET communication between the biocatalyst active site and its macroscopic environment is accomplished.

6.1 Photosensitized Biocatalyzed Regeneration of NAD(P)H Cofactors

N,N'-Dimethyl-4,4'-bipyridinium radical cation acts as versatile electron carrier recognized by many redox enzymes (see also Sect. 6.4). It acts also as electron carrier for ferredoxin-NADP⁺-reductase, FDR, and lipoamide dehydrogenase, LipDH, enzymes mediating the reduction of NADP⁺ and NAD⁺ to NADPH and NADH, respectively. Photosystems for the light-induced biocatalyzed regeneration of NAD(P)H cofactors have been assembled [189, 190], see Fig. 34. A photosystem composed of $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer, *N,N'*-dimethyl-4,4'-bipyridinium, MV^{2+} , as primary electron acceptor and $(\text{NH}_4)_3\text{EDTA}$ as sacrificial electron donor has been utilized for the photochemical regeneration of NADPH in the presence of FDR as biocatalyst. In this system oxidative ET quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$ yields $\text{MV}^{\cdot+}$ that acts as electron carrier for the biocatalyst that mediates the formation of NADPH. The quantum efficiency of NADPH formation corresponds to $\phi = 1.9 \times 10^{-2}$, and the rate-limiting step for NADPH production is the photochemical step generating $\text{MV}^{\cdot+}$. A closely related photosystem is used for the light-induced regeneration of NADH. Here, $\text{Zn}(\text{II})$ -*meso*-(*N*-tetramethyl-

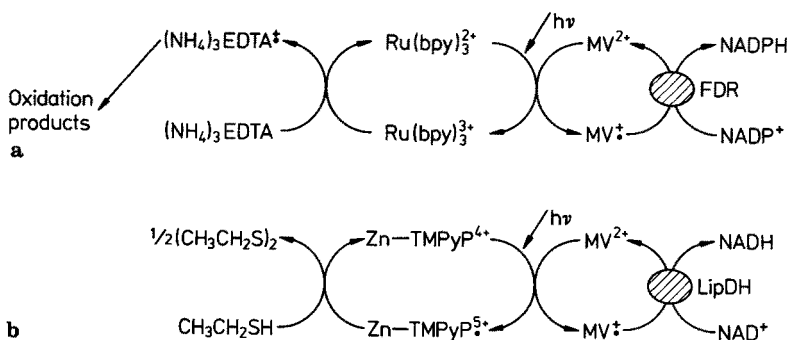


Fig. 34 a, b. Photosensitized regeneration system of NAD(P)H cofactors: **a)** Light-induced regeneration of NADPH using $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and ferredoxin reductase, FDR, as biocatalyst. **b)** Photochemical regeneration of NADH using Zn-TMPyP^{4+} as photosensitizer and lipoamide dehydrogenase, LipDH, as biocatalyst

pyridinium)porphyrin, Zn-TMPyP⁴⁺, has been applied as photosensitizer, MV²⁺ — as primary electron acceptor and mercaptoethanol — as sacrificial electron donor. MV⁺, formed through oxidative ET quenching of the excited Zn-porphyrin, mediates the formation of NADH in the presence of the LipDH as biocatalyst. The rate-limiting step in the formation of NADH is involved with the ET from the electron carrier to NAD⁺. Other light-harvesting compounds that have been applied for the photoinduced regeneration of NAD(P)H are Ru(bpz)₃²⁺ (22) and deazariboflavin, dRF1 (21) [191].

The photosensitized NAD(P)H regeneration systems have been coupled to various biocatalyzed transformation by introducing different substrates and the respective NAD(P)H-dependent enzymes [190]. Figure 35 outlines schematically the various photosynthetic transformations that are driven by the light-induced regeneration of the cofactors. With photochemically regenerated NADPH cofactor, butanone is reduced to 2-butanol in the presence of alcohol dehydrogenase, AlcDH, and α -ketoglutaric acid is reductively aminated to glutamic acid using glutamate dehydrogenase, GluDH, as biocatalyst. Similarly, the photochemically regenerated NADH cofactor has been coupled to the reduction and reductive amination of pyruvic acid to lactic acid and alanine using the biocatalysts lactate dehydrogenase, LacDH, and alanine dehydrogenase, AlaDH, respectively, as well as to the reduction of acetoacetate to β -hydroxybutyrate using β -hydroxybutyrate dehydrogenase, β -HButDH, as biocatalyst. Quantitative characterization of these systems has revealed that the photosensitizer, electron relay and biocatalysts are effectively recycled in the chemical transformations, and that the biocatalysts exhibit high stability in the artificial photosystems. Also, the light-induced NAD(P)H regeneration systems have been coupled to sequential synthesis of amino acids, i.e. aspartic acid, using several enzymes operating in a synchronous route [192].

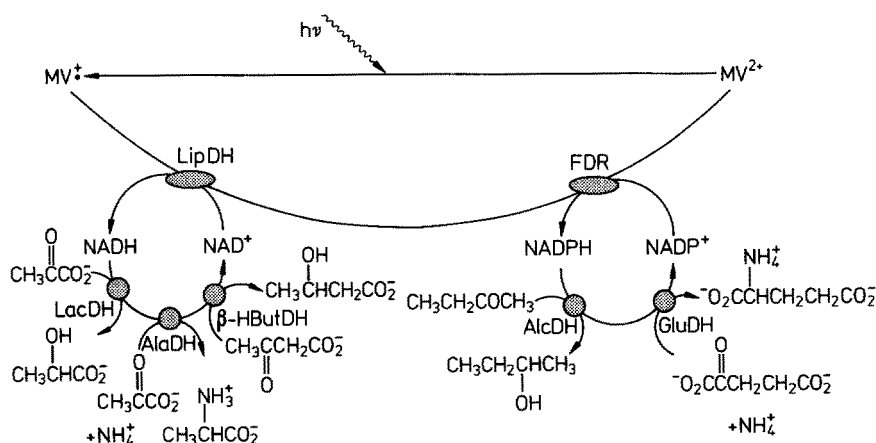


Fig. 35. Light-induced biocatalyzed transformations utilizing photochemically regenerated NAD(P)H cofactors

6.2 Photosensitized Regeneration of $\text{NAD(P)}^+/\text{NAD(P)H}$ with Artificial Catalysts

Non-enzymatic photosensitized regeneration of NADH cofactor proceeds in the presence of different rhodium complexes, such as $\text{Rh(III)-tris-bipyridine}$ or $\text{Rh(I)-tris-triphenylsulfonatophosphine}$ as catalysts [193, 194]. In a photosystem composed of Ru(bpy)_3^{2+} as photosensitizer, $\text{Rh(III)-tris-bipyridine}$ as electron acceptor and TEOA as sacrificial electron donor, NAD^+ is regenerated to NADH. In this system, see Fig. 36a, oxidative ET quenching of Ru(bpy)_3^{2+} yields $\text{Rh(I)-bis-bipyridine}$ that mediates NADH formation presumably through a hydrido rhodium intermediate. Thus, the homogeneous catalyst provides a two-electron charge relay for the regeneration of the biological cofactor. This system has been further improved by substitution of Ru(bpy)_3^{2+} by rhodium(III)-*tris*-(2,2'-bipyridyl-5-sulfonic acid) as electron relay and hydride transfer catalyst [195]. A different non-enzymatic NAD(P)H regeneration photosystem, [191, 194] applies Ru(bpy)_3^{2+} as photosensitizer, ascorbic acid as electron donor and chloro-rhodium-*tris*-triphenylsulfonatophosphine (**19**) as homogeneous catalyst, see Fig. 36b. In this photosystem reductive ET quenching of the photosensitizer by ascorbic acid yields the reduced photoproduct Ru(bpy)_3^+ , Eq. (40), that mediates reduction of the rhodium complex and formation of a hydride intermediate. This hydrido-rhodium species mediates formation of NAD(P)H.

Oxidative regeneration of NAD(P)^+ cofactors can be accomplished by two general routes, see Fig. 37. NAD(P)H might act as an electron donor for an excited photosensitizer, thereby regenerating NAD(P)^+ by a reductive ET quenching mechanism (Fig. 37a). Alternatively, the oxidized photoproduct formed in an

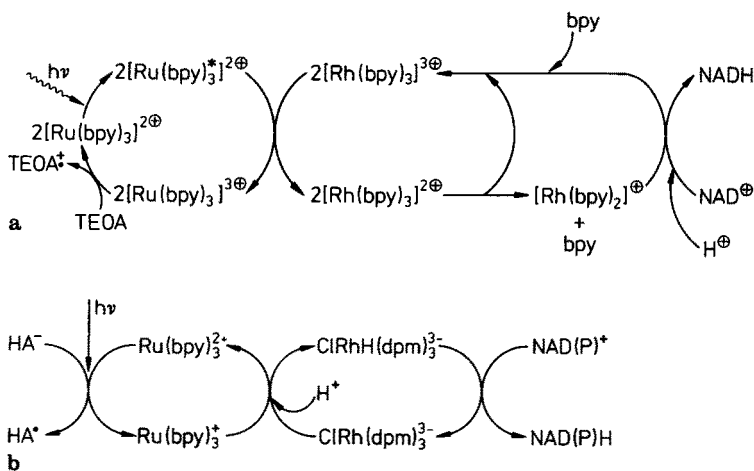
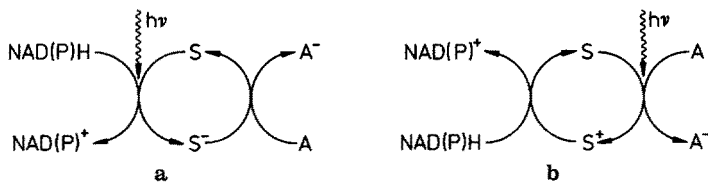
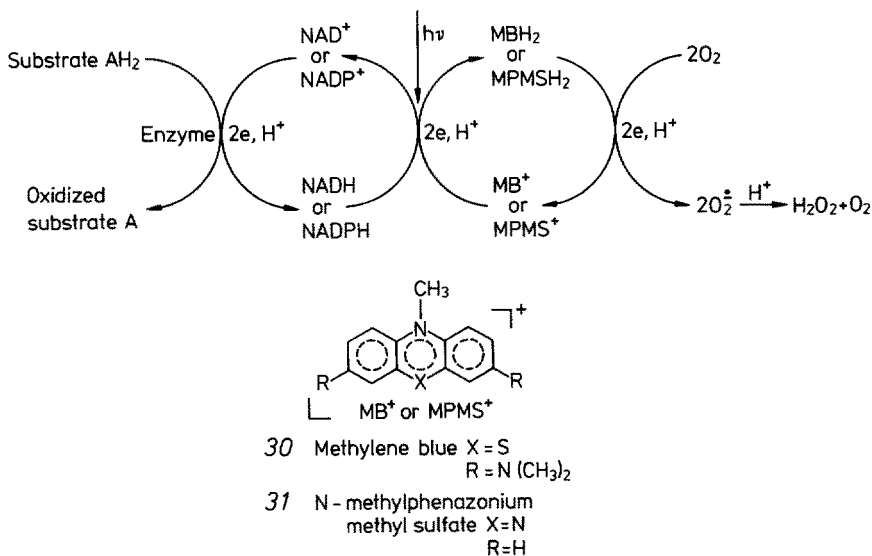


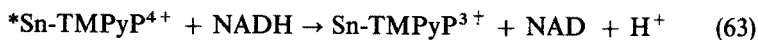
Fig. 36 a, b. Photochemical regeneration of NAD(P)H cofactors through homogeneous catalysis: **a)** by an oxidative ET quenching mechanism using Rh(bpy)_3^{3+} as catalyst; **b)** through a reductive ET quenching mechanism using RhCl(dpm)_3^{3-} as catalyst



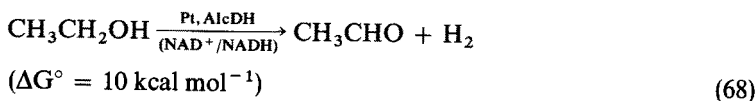
oxidative ET quenching process, Fig. 37b, acts as a hole carrier for the oxidation of NAD(P)H to NAD(P)⁺. Photoregenerated NAD(P)⁺, by either of the mechanisms, can be coupled to biocatalyzed oxidation processes using NAD(P)⁺ dependent enzymes. Organic dyes [196, 197] such as methylene blue, MB⁺ (**30**), or *N*-methyl phenazonium methylsulfonate, MPMS⁺ (**31**), have been applied as photosensitizers for NAD(P)⁺ regeneration through a reductive ET quenching mechanism, see Fig. 38. The quantum yields for NAD⁺ formation using MB⁺ and MPMS⁺ as photosensitizers are $\phi = 3 \times 10^{-1}$ and $\phi = 2.8 \times 10^{-1}$, respectively. Other dyes such as Rose bengal, eosin, thionin, and 2,6-dichlorophenol indophenol act as photosensitizers in similar photoinduced ET transformations. The photoregenerated NAD(P)⁺ cofactors have been subsequently coupled to NAD(P)⁺-dependent enzyme-catalyzed processes: Oxidation of ethanol to acetaldehyde proceeds in the presence of alcohol dehydrogenase, AlcDH, oxidation of lactic acid and alanine to form pyruvic acid is accomplished using lactate dehydrogenase, LacDH, and alanine dehydrogenase, AlaDH, respectively [196, 197].



Cyclic oxidation of organic substrates, with concomitant H_2 -evolution, has been reported through intermediary photoinduced regeneration of the NAD^+ cofactor. The photochemical assembly is composed of $Sn(IV)$ -*meso*-(*N*-tetramethyl-pyridinium)porphyrin, $Sn-TMPyP^{4+}$, as light-harvesting compound, a combination of a biocatalyst and heterogeneous catalyst (a Pt colloid) and the cofactor NAD^+ as electron shuttle [198]. The light-induced transformation operates through the primary reductive ET quenching of $Sn-TMPyP^{4+}$ by NADH (Eq. (63)). The oxidized cofactor is then formed through the sequence of reaction outlined in Eqs. (64–66). In the presence of an organic substrate and the re-



spective enzyme, i.e. ethanol, and AlcDH, the reduced cofactor NADH is chemically recycled and the reduced porphyrin mediates H_2 -evolution in the presence of the Pt colloid, Eq. (67). Consequently, cyclic photodecomposition of the organic substrate occurs, i.e. ethanol, see Eq. (68). In a photosystem including ethanol as substrate, H_2 -evolution proceeds with a quantum efficiency of $\phi = 0.43$ ($\lambda = 550$ nm). Other organic compounds, i.e. lactic acid and alanine are photocleaved in this photosystem to pyruvic acid and hydrogen using LacDH and AlaDH, respectively.



Regeneration of NAD^+ through an oxidative ET quenching process has been accomplished with $Ru(II)$ -*tris*-bipyridine as photosensitizer [191]. In the presence of methyl viologen, MV^{2+} , oxidative quenching of the excited photosensitizer leads to the formation of $Ru(bpy)_3^{3+}$ and $MV^{\cdot+}$. The former photoproduct is reduced by NADH, a process regenerating NAD^+ , while the reduced photoproduct mediates H_2 -evolution in the presence of a Pt heterogeneous colloid. The quantum efficiency for H_2 -evolution and NAD^+ regeneration corresponds to $\phi = 3 \times 10^{-2}$. Upon addition of organic substrates, i.e. ethanol, lactic acid or alanine, and the enzymes AlcDH, LacDH or AlaDH, respectively, dark biocatalyzed formation of NADH from photoregenerated NAD^+ is induced. Table 8 summarizes the quantum efficiencies and turnover numbers of biocatalysts for the oxidation of

Table 8. Ethanol oxidation through photosensitized NAD^+ regeneration in different photosystems^a

Photosensitizer	Quantum Yield (ϕ)	Turnover Number	
		NAD^+	AlcDH
Sn(IV)-TMPyP^{4+}	0.43	86	1.3×10^5
Ru(bpy)_3^{2+}	0.03	8	1.3×10^4
MB^+	0.3	187	$\approx 10^4$

^a Photosystem configuration discussed in text.

ethanol through NAD^+ regeneration by the different photosystems discussed in this section. It should be noted that photosensitized biocatalyzed H_2 -evolution from organic compounds could provide a means for the production of a fuel product from waste biomass materials.

6.3 CO_2 -Fixation through Photochemical NAD(P)H Regeneration

Enzyme-catalyzed decarboxylation processes with concomitant reduction of NAD(P)^+ to NAD(P)H cofactors participate in various transformations of the heterotrophic cycle, i.e. decarboxylation of isocitric acid to ketoglutaric acid in the Krebs cycle. Photosensitized regeneration of NAD(P)H cofactors and the reversible activities of many enzymes could provide a general approach to reverse such decarboxylation reactions. Thus, through coupling photogenerated NAD(P)H cofactors to such enzymes, endoergic carboxylation of C–H bonds (CO_2 -fixation) could be driven. Reversing steps of the heterotrophic cycle by photochemical means could then lead to the production of fuel products.

The biocatalyzed photosystem of NADPH regeneration (Sect. 6.1) has been coupled to the biocatalyzed carboxylation of pyruvic acid and α -ketoglutaric acid

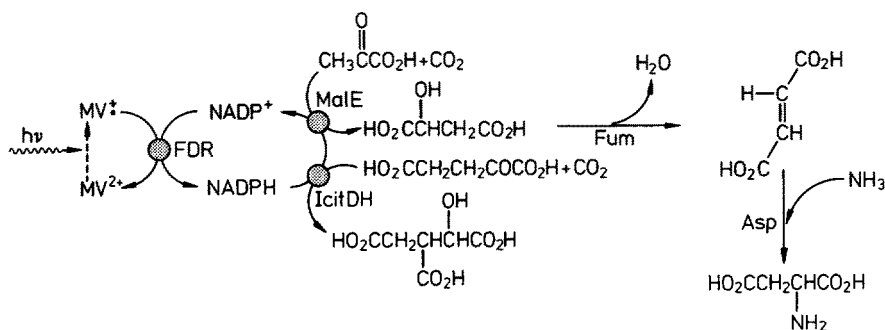
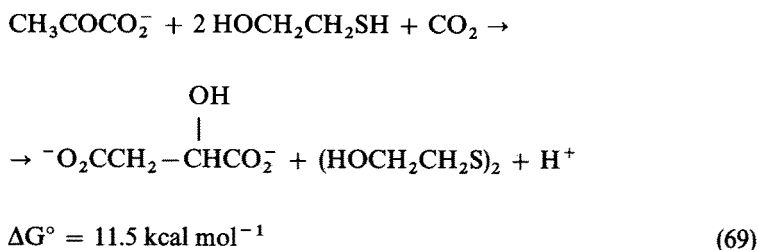


Fig. 39. CO_2 -fixation by coupling carboxylato biocatalysts to the photochemical NADPH regeneration system. CO_2 -fixation products are subsequently coupled to the biocatalyzed photosynthesis of aspartic acid

to form malic acid and isocitric acid using the two NADPH-dependent enzymes [199, 200] malic enzyme, MalE, and isocitrate dehydrogenase, IcitDH, respectively, see Fig. 39. In these photosystems $\text{Ru}(\text{bpy})_3^{2+}$ acts as photosensitizer, methyl viologen, MV^{2+} , is the primary electron acceptor, and 2-mercaptoethanol acts as sacrificial electron donor. Photogenerated MV^+ mediates regeneration of NADPH, using FDR as biocatalyst, and the reduced cofactor is utilized in the secondary carboxylation reactions. The net processes accomplished in these transformations correspond to the reductive CO_2 -incorporation into keto-acids via oxidation of the thiol. Photoinduced carboxylation of pyruvic acid to malic acid, Eq. (69), is endoergic, $\Delta G^\circ = 11.5 \text{ kcal mol}^{-1}$. The possibility to utilize the photochemical NADPH regeneration cycle for carbon-carbon coupling reactions allows the



design of multi-step sequential biocatalyzed photosyntheses. The photosynthesis of aspartic acid from pyruvic acid has been accomplished in a sequential transformation, see Fig. 39, where the primary CO_2 -fixation product, malate, undergoes dehydration to maleic acid, using fumarase, Fum, and the latter product undergoes subsequent amination in the presence of the enzyme aspartase, Asp, to form aspartic acid [200]. Interestingly, this complex assembly, composed of several biocatalysts, a cofactor and an artificial photosystem, operates as an integrated system, and exhibits high stability.

6.4 Biocatalyzed Photosynthetic Systems Mediated by Artificial Electron Carriers

Artificial electron carriers are recognizable by the active sites of different redox enzymes and specifically biocatalysts containing Fe or Mo sulfur clusters as active sites. Bipyridinium radical cations, i.e. methyl viologen radical, MV^+ , exhibit proper electrical and size properties to penetrate into protein structures and to mediate reduction processes at the enzymes active sites.

Hydrogenase, HyD, includes a Fe-S cluster as active site. Photogenerated N,N' -dimethyl-4,4'-bipyridinium radical cation, MV^+ , mediates H_2 -evolution in the presence of HyD [201–203], see Fig. 40. Different photosensitizers such as $\text{Ru}(\text{bpy})_3^{2+}$, Zn-TMePyP^{4+} or acridine orange and sacrificial electron donor, i.e. ethylenediamine tetraacetic acid, EDTA, mercaptoethanol or cysteine, have been

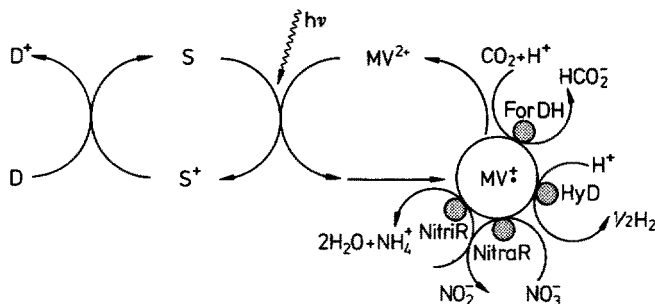


Fig. 40. Biocatalyzed photosynthetic systems mediated by an artificial electron carrier, N,N' -dimethyl-4,4'-bipyridinium radical cation, MV^+ . Photogenerated MV^+ mediates H_2 -evolution, CO_2 reduction to formate and sequential reduction of NO_3^- to ammonia, using Hyd, ForDH and a mixture of NitraR and NitriR, respectively

applied as photosystems for MV^+ formation and H_2 -evolution in the presence of hydrogenase. Also, isolated chloroplasts, where the CO_2 -fixation enzymes are excluded but the light-harvesting chlorophyll centers and ET chain is maintained intact, are capable of inducing the cyclic photolysis of water in the presence of hydrogenase containing bacterial extracts and MV^{2+} as artificial electron carrier [204], see Fig. 41. In this assembly, the electron flow initiated by excitation of chlorophyll centers drives the reduction of MV^{2+} . The reduced relay, MV^+ , acts as electron shuttle mediating H_2 -evolution in the presence of Hyd. The oxidized chloroplast photosystem mediates O_2 -evolution and, consequently, biocatalyzed photolysis of water is induced.

CO_2 -fixation to formate is catalyzed by formate dehydrogenase, ForDH. Photogenerated MV^+ mediates the reduction of CO_2 to formate [200]. Other bipyridinium radicals, such as N,N' -dimethyl-2,2'-bipyridinium or N,N' -trimethylene-2,2'-bipyridinium radical cation act also as charge carriers for ForDH. The photosystem that was utilized for generation of MV^+ and CO_2 -fixation includes $Ru(bpy)_3^{2+}$ as photosensitizer, cysteine as sacrificial electron donor and MV^{2+} as electron acceptor. The net photosynthetic process accomplished in this photosystem (Fig. 40) corresponds to the reduction of CO_2 to formate by cysteine, see Eq. (70). This is an endoergic transformation by ca. $12.5 \text{ kcal mol}^{-1}$.

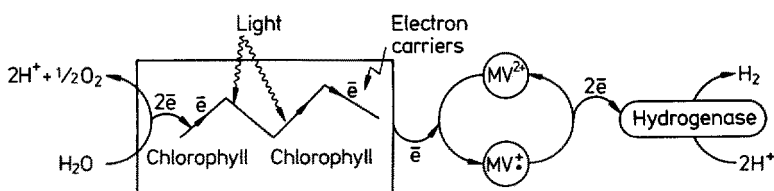
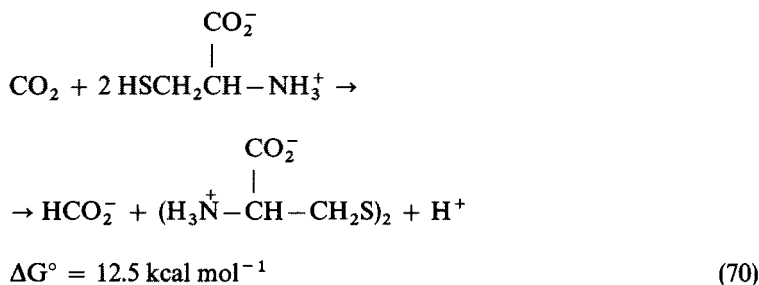
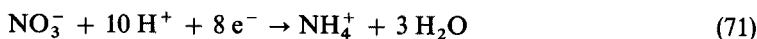


Fig. 41. Cyclic photolysis of water by hydrogenase containing bacterial extracts



Sequential biocatalyzed photoinduced reduction of nitrate, NO_3^- , to ammonia has been accomplished [205] with two enzymes, nitrate reductase, NitraR, and nitrite reductase, NitriR, both activated by MV^+ acting as electron carrier (Fig. 40). This system has important implications in relation to photosynthesis of ammonia. The photosystem itself is composed of $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer, $(\text{NH}_4)_3\text{EDTA}$ as sacrificial electron donor and MV^{2+} as electron acceptor. Photogenerated MV^+ mediates the reduction of NO_3^- to nitrite using NitraR as biocatalyst while the latter photoproduct, NO_2^- , is reduced by MV^+ to ammonia in the presence of NitriR. The overall quantum efficiency for the formation of ammonia, in Eq. (71), corresponds to $\phi = 3 \times 10^{-2}$. This sequential biocatalyzed 8 e^- fixation process of NO_3^- to ammonia highlights the feasibility to apply single electron transfer photoproducts in multi-electron reduction processes using biocatalysts as intermediate charge relays. Table 9 summarizes the quantum efficiencies for the different biocatalyzed photosynthetic transformations using MV^+ as an artificial electron carrier.



Organization of biocatalytic photosynthetic systems in the form of integrated assemblies could provide practical photosynthetic devices. ET-communication of the cofactor or artificial electron shuttle with the enzyme active site proceeds in solution by a diffusional mechanism. An integrated biocatalytic photosynthetic device that allows the continuous light-induced production of fuel materials or

Table 9. Quantum efficiencies for biocatalysed transformations utilizing MV^+ as electron carrier in different photosystems

Photosensitizer	Substrate	Product	Biocatalyst	Quantum Yield (ϕ)
$\text{Ru}(\text{bpy})_3^{2+}$	H^+	H_2	HyD	$\approx 5 \times 10^{-2}$
Zn-TPPS^{4-}	H^+	H_2	HyD	$\approx 3 \times 10^{-2}$
$\text{Ru}(\text{bpy})_3^{2+}$	CO_2	HCO_2^-	ForDH	1.6×10^{-2}
$\text{Ru}(\text{bpy})_3^{2+}$	NO_3^-	NO_2^-	NitraR	8×10^{-2}
	NO_2^-	NH_4^+	NitriR	6×10^{-2}

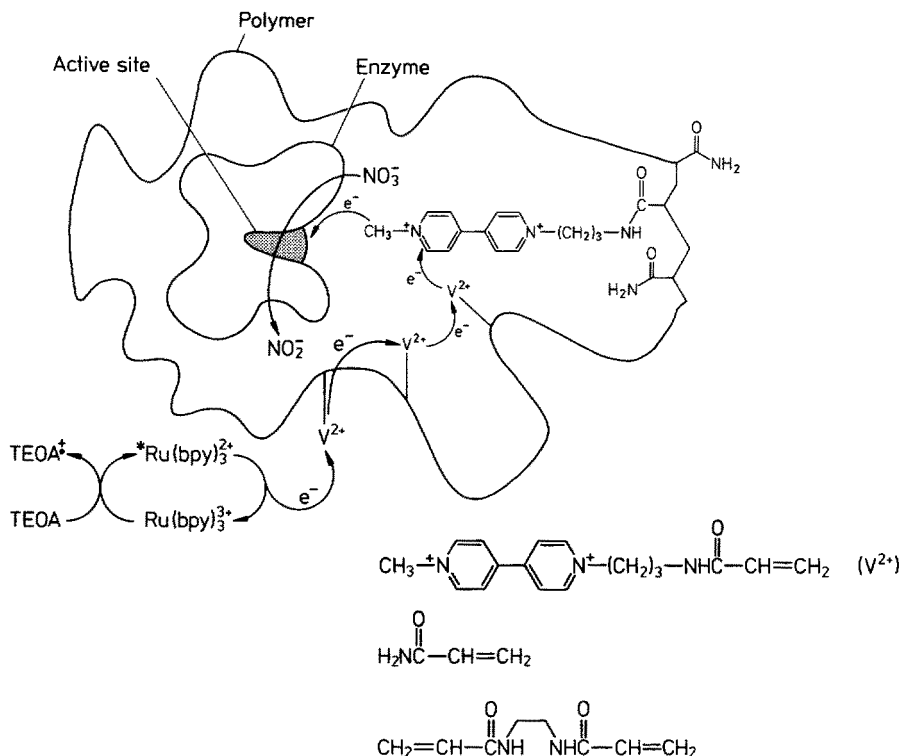


Fig. 42. Photoinduced reduction of NO_3^- to NO_2^- in an organized assembly composed of NitraR immobilized in an acrylamide-bipyridinium redox polymer. ET-communication between the redox polymer and the enzyme active site takes place in the redox polymer-enzyme assembly

valuable chemicals, should be organized in an immobilized configuration. Organization of such immobilized biocatalytic assemblies requires the tailoring of ET-communication between the enzyme active site and its macroscopic environment. The photocatalytic system for the reduction of NO_3^- to nitrite has recently been immobilized into a chemically modified redox polymer, and light-induced electron transfer communication between the polymer backbone and the enzyme active site has been achieved [206]. Nitrate reductase, NitraR, has been immobilized in an acrylamide-acrylamide viologen copolymer, see Fig. 42. Photoreduction of the polymer using $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and TEOA as sacrificial electron donor activates the enzyme towards reduction of NO_3^- to nitrite. Thus, electron-transfer from the reduced polymer to the enzyme active site proceeds without diffusion of the electron carrier. It is suggested that the immobilization of the enzyme, NitraR, into the redox polymer, results in a rigid configuration where proper distances for ET-communication between the redox polymer and the active site are maintained [177].

7 Conclusions, Outlook and Perspectives

Aspects of organization of artificial photosynthetic assemblies and means to couple photosensitized ET reactions with homogeneous catalysts, heterogeneous catalysts and biocatalysts have been reviewed. Organized photosynthetic assemblies could provide universal light-harvesting and fuel-generation systems, man-made devices for removal of environmental pollutants, and novel routes for the production of valuable chemicals. The review has outlined various catalytic materials that can be applied in artificial photosynthetic assemblies. At present it is impossible to impose on a superior class of catalytic materials for the development of artificial photosynthetic devices: Enzymes exhibit high substrate-product selectivities and unique chiral and steric specificities. In turn, the relative stability and synthetic availability of homogeneous and heterogeneous inorganic catalytic materials points to the practical applicability of these catalysts in artificial photosynthetic devices. Ultimately, the selection of the catalytic materials included in artificial photosynthetic systems will depend on the specific chemical transformation, the nature of reacting substrates and the structural characteristics of the requested products. It is certainly implied that future activities are essential for developing all three classes of catalysts. Organization of integrated systems, where photoinduced electron transfer processes are controlled and coupled to new redox catalysts and immobilized enzymes, seems to be a viable approach to harness solar light for useful chemical transformations and fuel generating processes.

The present review has addressed the use of homogeneous light-active compounds (photosensitizers). An alternative approach to impose light-induced electron-transfer reactions involves the application of semiconductor materials [206–211]. Homogeneous catalysts, heterogeneous catalysts and biocatalysts can be coupled to semiconductor light-induced ET reactions, and surface-modified semiconductors by heterogeneous [212–215] and homogeneous catalysts [216] and semiconductor-biocatalytic conjugated systems [217] provide useful photosynthetic assemblies. It is obvious that photo-electrochemical systems and photocatalytic assemblies applying photosensitizers are two complementary interacting approaches for developing artificial photosynthetic systems.

Scientific accomplishments in the field of artificial photosynthesis might have substantial impact in other research activities and could merge into other scientific disciplines. Organized assemblies where ET-communication between redox enzymes and their macroscopic environment occurs are of general interest in designing biosensing devices [218]. Modification of homogeneous catalysts and biocatalysts by light-active components (photochromics) is anticipated to generate light-regulated photosynthetic transformations [219–221]. Such systems could act as information-storage and optical switching devices. Also, organization of donor-acceptor components in polymer matrices is anticipated to generate novel materials of unique nonlinear optical properties [222–224].

8 Acknowledgment

The support of our research activities in Artificial Photosynthesis by the Kernforschungsanlage, Jülich, FRG, Israeli Council for Research and Development, U.S.-Israel Binational Foundation, and Israel Academy of Sciences and Humanities, is gratefully acknowledged. The names of the co-workers who performed the research appear in the list of references. Their skills and enthusiasm enabled the scientific progress.

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Contact and Solvent-Separated Radical Ion Pairs in Organic Photochemistry

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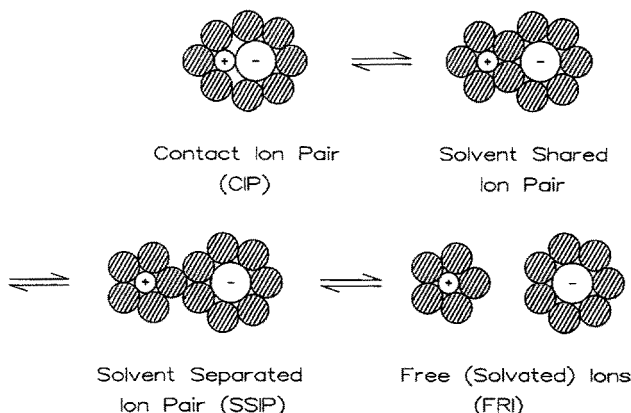
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Radical ion pairs play an important role in photoinduced electron transfer (PET) processes. Several types of them may exist and it will be shown in this article that contact ion pairs (CIPs) and solvent-separated ion pairs (SSIPs) can be differentiated by various experimental methods. Moreover, their controlled formation facilitates the control of chemical reactions. Although this review is by no means exhaustive, it is hoped that interest in the fundamental mechanistic aspects of PET processes in homogeneous media as well as in their synthetic applications will arise.

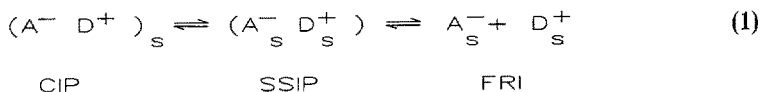
1 Introduction and Definitions

Electron transfer reactions are an extensively studied domain in chemistry [1]. Photochemical excitation is an elegant tool to achieve this type of transformation. Starting with two neutral molecules, a donor (D) and an acceptor (A), an electron transfer reaction between these entities generates charged species. Depending on solvation and degree of dissociation, different types of these have been postulated [2].

Apart from free solvated radical ions (FRI), evidence was gathered for two kinds of ion pairs, which are referred to as tight ion pair (or contact ion pair, CIP) and loose ion pair (or solvent separated ion pair, SSIP) (Scheme 1, Eq. (1)) [3]. It is important to point out that CIP and SSIP are not the only species in solution. There are myriads of spatial cation-anion relationships that lie between them [4]. The SSIP is a pair of two ions of opposite sign with intact solvent shells. This is lacking in the CIP, anion and cation are in direct contact, the whole aggregate being surrounded by solvent molecules.



Scheme 1. Schematic representation of the equilibrium between various types of cation-anion relationships (cf. [4].)



It should be mentioned that Marcus [5] uses the terms inner-sphere ion pair and outer-sphere ion pair for CIP and SSIP, respectively. Depending on the degree of penetration of the solvation shells one may further differentiate between SSIP and “solvent shared ion pairs”. However, a clear experimental assignment has not yet been performed. Therefore, we will use the designation CIP and SSIP

only. Weller [6] states that the classical nomenclature corresponds to his in that CIP is equivalent to “exciplex” and SSIP is equivalent to “radical ion pair”.

Farid uses the term “geminate ion pair” without specification of the solvent interaction. However, modern analytical techniques can sometimes distinguish between the variety of charged molecular species.

2 Experimental Evidence

2.1 Historical Review

Since Bjerrum's [7] introduction of the concept of ion pairing in 1926, a variety of analytical methods has been employed to study the structure and energetics of ion pairs. Szwarc's Book deals with the development of the ideas up to 1972 [3a]. It is also a guiding reference for the different spectroscopic methods that have been employed in the examination of ion pairs.

ESR spectroscopy [8] provided the first direct evidence for ion pairs. Other techniques, including conductance measurements [9], absorption spectroscopy (UV/Vis [10], IR, Raman [11]), and nuclear magnetic resonance [12] have been used as well.

More recently, powerful time-resolving techniques began to evolve. Nanosecond [13] and picosecond [14] flash absorption and emission spectroscopy made it possible to obtain UV spectra of transient species with very short lifetimes.

Together with CIDNP [15] and CIDEF [16], these methods allow for the first time a detailed investigation of the electron transfer process. In some cases, it has become possible to distinguish between CIP, SSIP, and FRI or to study the kinetics of the reorganization of the solvent shell.

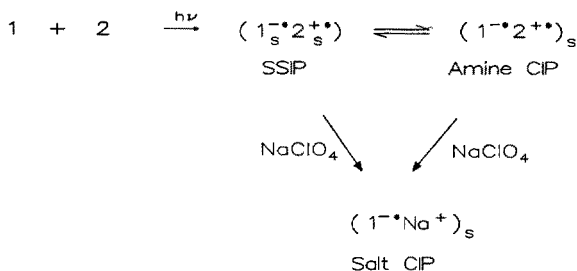
2.2 Flash Photolysis

The conventional flash photolysis setup to study photochemical reactions was drastically improved with the introduction of the pulsed laser in 1970 [17]. Soon, nanosecond time resolution was achieved [13]. However, the possibility to study processes faster than diffusion, happening in less than 10^{-10} s, was only attainable with picosecond spectroscopy. This technique has been applied since the 1980s as a routine method. There are reviews covering the special aspects of interest of their authors on this topic by Rentzepis [14a], Mataga [14b], Scaiano [18], and Peters [14c].

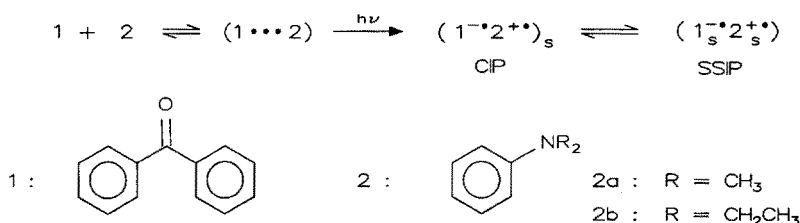
2.2.1 The Benzophenone-Amine System

Concerning the analysis of different types of ion pairs and their discrimination using picosecond absorption spectroscopy, the work by Peters must be emphasized. He studied in great detail the photoreduction of benzophenone by aromatic amines

a in acetonitrile:



b in ethanol:



Scheme 2. Ion pair formation in the photoreduction of benzophenone by amines [19, 22, 23a]

in acetonitrile and observed spectral shifts in the absorption spectrum of the radical anion of benzophenone.

There is evidence [19] that the initial absorption at ca. 720 nm within 25 ps belongs to a kind of SSIP of benzophenone radical anion and dimethylaniline radical cation. This peak shifts during 200–800 ps to 690 nm. The blue shift corresponds to the formation of the thermodynamically more stable contact ion pair, identified according to work by Hogen-Esch and Smid [20]. Finally the ketyl radical is observed at 545 nm after ca. 2000 ps.

The authors draw two conclusions (cf. Scheme 2):

1. Electron transfer in acetonitrile has to occur over a distance greater than the van der Waals radii, because electron transfer happens before the rise of the CIP. First, the SSIP is formed from benzophenone and the amine, separated at least by the encounter distance of 700 pm [21], which afterwards collapses to the CIP.

2. Proton transfer occurs only after formation of the CIP and thus over a rather short distance compared to electron transfer.

Studies of the same system in ethanol [22] showed that this solvent favoured the formation of the CIP ($\lambda = 690$ nm), evolving already 25 ps after photolysis. For this to occur, the amine and the ketone must be cosolvated in the ground state. Indeed, decreasing stretching frequencies of the benzophenone carbonyl by addition of amine indicates ground state complex formation prior to photoinduced electron transfer (cf. Scheme 2). However, 50 to 300 ps after the laser flash, a new

peak appears at 625 nm. This blue shift is attributed to the formation of a new species, the hydrogen-bonded benzophenone radical anion, originating from the disruption of the CIP.

Summarizing these facts, the equilibrium distribution of the ion pair intermediates can be shifted by the choice of solvent or solvent mixture, which stabilizes either CIP of benzophenone and amine (in acetonitrile) or SSIP (in ethanol).

The same authors have studied the picosecond dynamics of ion pair exchange processes leading to a direct observation of the special salt effect as well [23]. While the normal effects of added salt on reaction rates can be explained by polarity changes of the solvating media, the special salt effect requires a molecular interpretation [24]. According to Winstein [25], added salt enhances the rate by undergoing an ion pair exchange with the SSIP. Investigating the kinetics of ion pair formation in the presence of added NaClO_4 or NaI , Simon and Peters [23a] indeed confirmed Winstein's originally proposed mechanism for the special salt effect (cf. Scheme 2). For example, the absorption at 690 nm of the benzophenone-amine CIP which arises within 200 ps is blue shifted to 645 nm after 500 to 1000 ps. This new absorption is assigned to the sodium-CIP.

In following papers, this group reported on various aspects of ion pair dynamics of ketone amine systems, such as hydrogen atom transfer [14c, 26] or the activation parameters for ion pair separation of the trans-stilbene-fumaronitrile CIP [27].

2.2.2 The Ketone-Olefin System

Other donor/acceptor pairs being of synthetic interest are composed of ketones and olefins. Synthetic applications have been reviewed recently. [28, cf. Part IV of this series].

In this account, we will focus on the transient analysis of these systems, which has strongly contributed to a deeper understanding of the diverse reaction modes (Paternó-Büchi, proton abstraction, cycloaddition). In general, aromatic ketones were selected as electron acceptors for reasons of suitable excitation and long wavelength absorption of the radical anion intermediates. Among them, fluorenone 3 is particularly well suited since the concentration, solvent, temperature, and cation radius dependence of the absorption spectra of pairs formed with metal cations are already known [29]. Hogen-Esch and Smid [30, 10] pointed out that a differentiation between CIP and SSIP is possible for fluorenone systems. On the other hand, FRI's and SSIP's cannot be differentiated simply by their UV/Vis absorption spectra, whereas for instance conductance measurements may be successful. However, the portion of free radical ions in fluorenyl salt solutions was shown to be less important [9, 31]

Since the lifetime of fluorenone radical anions lies in the μs -time region, conventional flash photolysis has been used to measure the transient absorption spectra [32]. The effect of solvent and added salts on the reactions of triplet fluorenone and electron rich alkenes is shown in Figs. 1 and 2, respectively.

Whereas the formation of SSIP is favored in polar solvents, only CIP or paramagnetic dimers could be observed in nonpolar media (Fig. 1). However, it should be pointed out that electron transfer can take place even in nonpolar

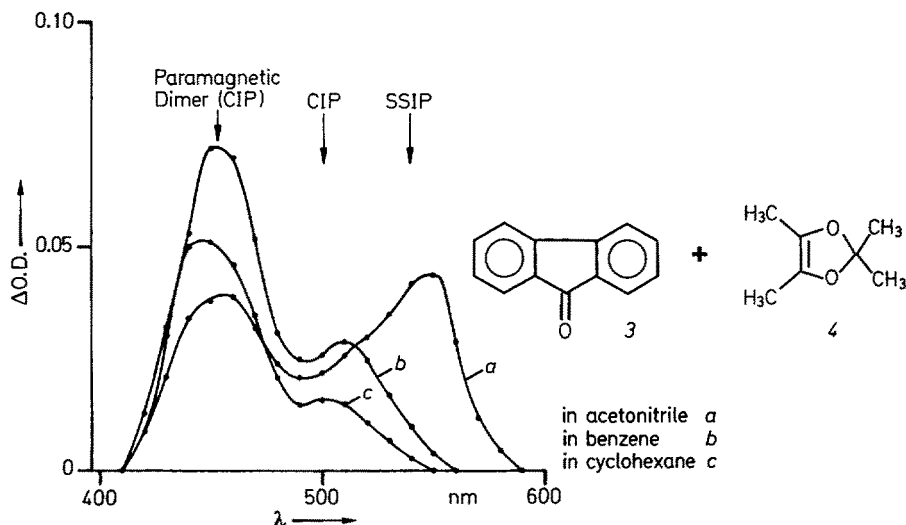
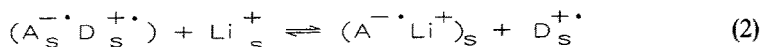


Fig. 1. Transient absorption spectra (ΔOD = absorption difference) 100 μ s after flash photolytic excitation of fluorenone (3) in the presence of tetramethyl-1,3-dioxole (4) in various solvents; a) acetonitrile; b) benzene; c) cyclohexane

solvents like cyclohexane. The addition of lithium perchlorate to solutions of fluorenone and various alkenes in acetonitrile dramatically changes the transient absorption spectra (Fig. 2). Whereas in the absence of salt mainly SSIP's of fluorenone radical anion and alkene radical cation are observed, the hypsochromic shift on the addition of salt indicates the formation of a new intermediate, assigned to a CIP composed of fluorenone radical anion and lithium cation (Eq. 2):



A = Ketone

D = Alkene

As was shown by Hirota and Weissman, the SSIP-CIP ratio increases with increasing radius of the metal cation ($Na^+ < K^+ < Cs^+$, cf. Fig. 2 in Ref. [29a]). Analogously, the increasing fraction of SSIP's going from triethylamine (6) via tetramethyl-1,3-dioxole (4) to tetraethoxyethene (5) may be attributed to an increasing radius of the donor radical cation [32, 33]. The assignment of the 500 nm-transient to the CIP rather than to the ketyl radical of fluorenone (as was reported by Davidson already in 1972 [34]) mainly bases on the thermodynamics of electron transfer and comparative experiments with other proton as well as electron donors (for a detailed discussion see Ref. [33]). It should be noted that quenching of singlet fluorenone by triethylamine (6) did not result in any transient in the μ s time region.

Special Salt Effect

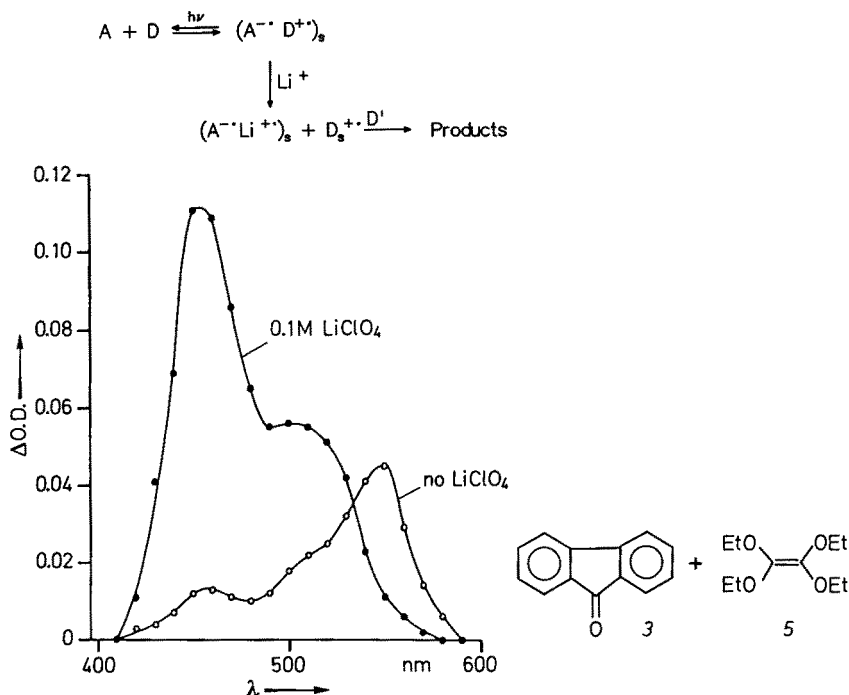


Fig. 2. Dependence of the transient spectra on added lithium perchlorate 100 μ s after flash photolytic excitation of fluorenone (3) in the presence of tetraethoxyethene (5) in acetonitrile. Special salt effect [32].

This corresponds to results reported by Peters [35] who observed the fluorenone radical anion in the presence of diazabicyclo[2.2.2]octane (DABCO) with a half-life of ca. 60 ps. The unusually long lifetime of the transients observed by us can be explained with the formation of radical ion pairs in the triplet state.

The analysis of similar processes with benzophenone (1) and benzil (7) requires a higher time resolution of the experimental setup. Using ns-laser flash photolysis, we observed the formation of radical ion intermediates, depending on solvent polarity, added salts and competing H-abstraction [36]. Summarizing all these experiments, one can draw the following conclusions (cf. Figs. 3–5, see also Ref. [33]):

- (i) Polar solvents favour the formation of the SSIP, but reduce the quantum yield of product formation (oxetanes and ketone-alkene adducts deriving from H-abstraction). This corresponds to similar photoreactions of biacetyl [36, 37]. A detailed discussion of the CIP-SSIP reaction pattern is given below.
- (ii) The addition of lithium perchlorate increases the yield of ketone radical anions (CIP) as well as their lifetime and is caused by the special salt effect (see above).

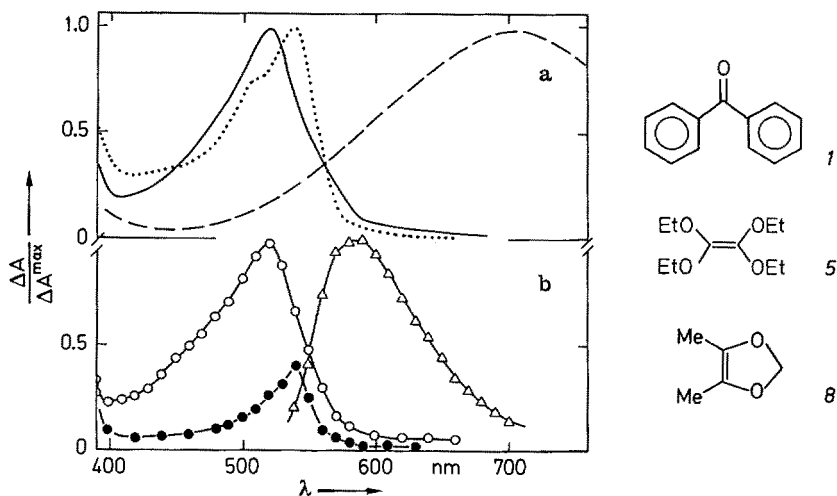


Fig. 3. Absorption spectra with benzophenone (A, 1) in acetonitrile. **a)** of $^3A^*$ (solid line, end of pulse: ≤ 10 ns), of A^*H (dotted line, obtained after 1 μ s in the presence of 2-propanol (≥ 1 M), and of $A^{\bullet-}$ (dashed line, after 100 ns in the presence of tetraethoxyethene (5) (0.01 M), and **b)** in the presence of 4,5-dimethyl-1,3-dioxole (8) (0.02 M) after 20 ns ($\circ$) and 200 ns ($\bullet$); fluorescence (uncorrected) of A^*H for $[8] = 0.2$ M (Δ) (cf. [33, 36])

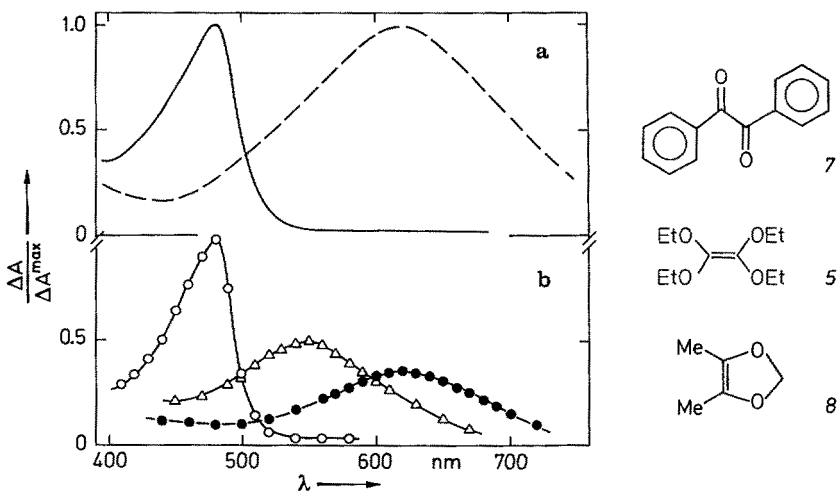


Fig. 4. Absorption spectra with benzil (A, 7) **(a)** of $^3A^*$ (solid line, end of pulse) and of $A^{\bullet-}$ (dashed line, after 100 ns in the presence of tetraethoxyethene (5) (0.01 M) in acetonitrile, and **(b)** in acetone in the presence of 4,5-dimethyl-1,3-dioxole (8) (0.02 M) after 200 ns in the absence ($\bullet$) and presence (Δ) of $LiClO_4$ (0.4 M) (cf. [33, 36])

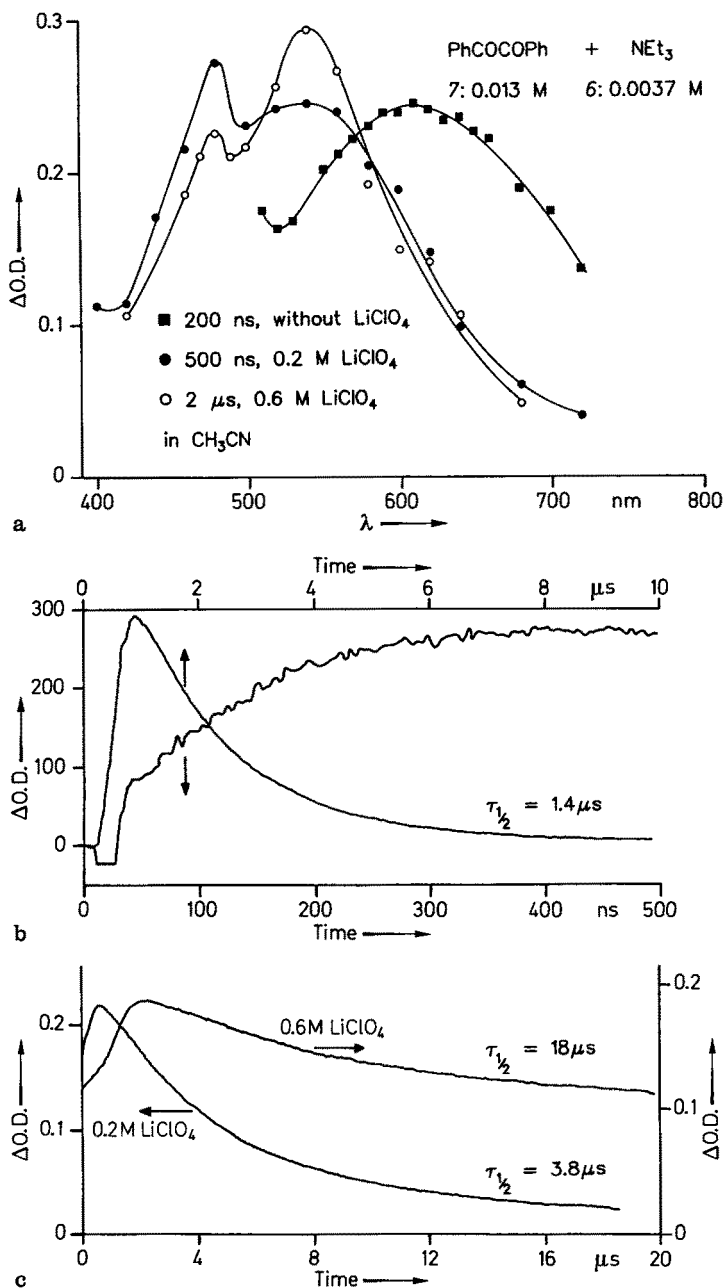


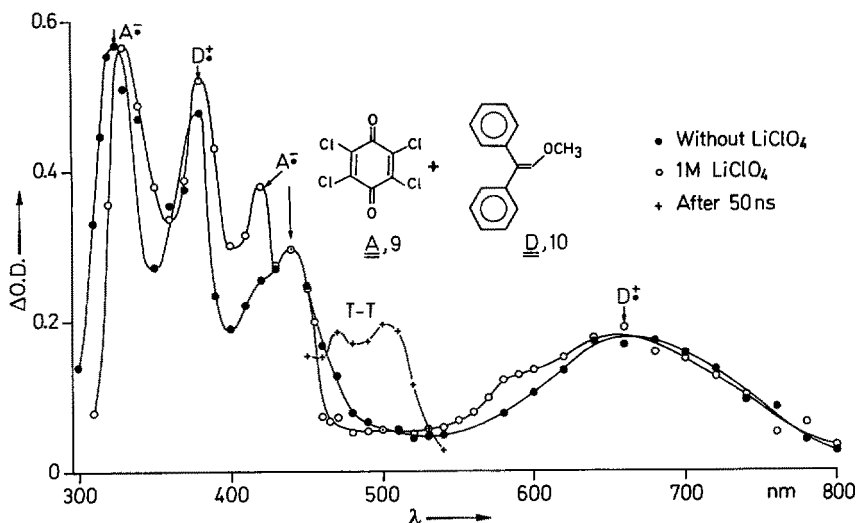
Fig. 5. Absorption spectra with benzil (7) (0.13 M) and triethylamine (6) (0.0037 M) in acetonitrile: (a) in absence and presence of LiClO₄ (b) time dependence of 600 nm transient absorption (formation and decay of A^{-•}); (c) time dependence of the decay of A^{-•} in presence of added LiClO₄ (from Ref. [33], cf. [36])

- (iii) In contrast to benzil, the sensitized reaction with benzophenone does not result in an electron transfer as the major process. Electron transfer can only compete if H-abstraction is hindered (as it is the case for 1,3-dioxole, tetraethoxyethylene and DABCO).

Typical transient absorption spectra are shown in Figs. 3 and 4, exhibiting the effect of alkene structure on the electron transfer – H-abstraction ratio for benzophenone as well as the influence of added salt on the SSIP-CIP ratio for benzil.

Kinetic parameters can be obtained from time resolved measurements. The time profile of the transients (formation and decay) of the photoreaction of benzil (7) with triethylamine (6) in acetonitrile is shown in Fig. 5, together with the influence of added lithium perchlorate on the lifetime of the radical anion intermediates.

In the investigations of the systems so far mentioned, only the kinetics of the long-wavelength absorbing radical anions could be monitored spectroscopically. Simultaneous analysis of both transient species was performed using *p*-chloranil (9) as the acceptor and 2-methoxy-1,1-diphenylethene (10) as the donor [33, 36]. Both the radical anion $9^{\cdot-}$ and the radical cation $10^{\cdot+}$ decay within the same halflife of ca. 1 μ s, as expected for back electron transfer as the major process (Fig. 6). Utilizing the special salt effect (addition of lithium perchlorate) increases the lifetime of both intermediates by a factor of ten.



λ (nm)	$\tau_{1/2}$ (μ s)	
	without LiClO_4	1M LiClO_4
450	0.9	8.9
600	1.3	11.2

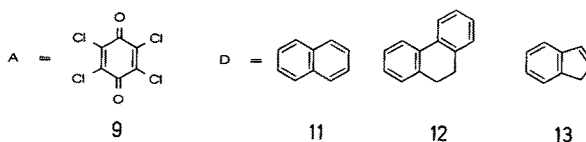
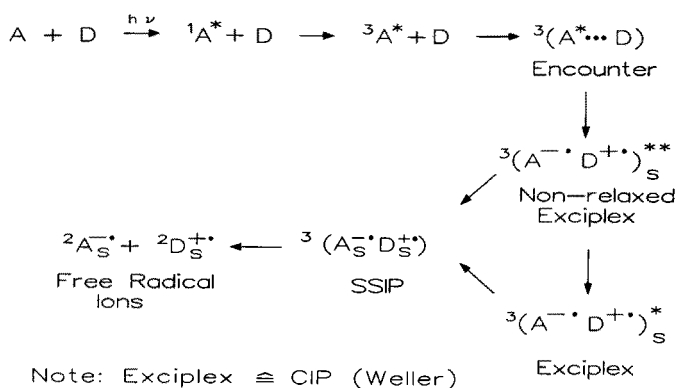
Fig. 6. Transient absorption spectra of chloranil (9) and 2-methoxy-1,1-diphenylethene (10) in acetonitrile, 50 ns (+, T-T = absorption) and 800 ns after the start of the laser flash (from Refs. [1c, 33, 36])

2.2.3 Other Donor-Acceptor Systems

Various groups have contributed to clarify the dynamics of radical ion pairs in PET processes. This account cannot discuss all their results. We rather will try to select some examples which emphasize the specific feature of other donor-acceptor pairs different from those discussed above.

In 1983, Rentzepis published a paper [38] dealing with the charge-transfer interaction of chloranil (**9**) and aromatic hydrocarbons, e.g. naphthalene (**11**). Nanosecond spectroscopy of this system [39] could verify some intermediates of the proposed mechanism [21, 40] (Scheme 3); that is the triplet excited acceptor and the free solvated radical ions ($A^{\cdot-}$)_s and ($D^{\cdot+}$)_s.

Using ps-spectroscopy, Rentzepis and co-workers detected the ground state ion pair (SSIP). However, a red shift in the absorption spectrum of chloranil/dihydrophenanthrene (**12**) mixtures occurring between 75 ps and 600 ps after excitation could be interpreted as the ion pair expanding its diameter. Consequently, the CIP is formed before it diffuses to give an ion pair with less contact (SSIP).

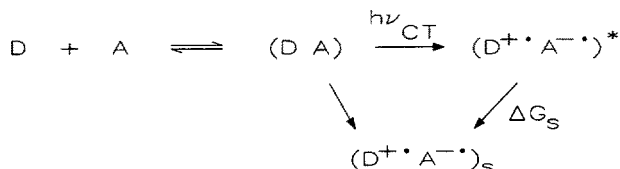


Scheme 3. Photoreduction of chloranil (**9**) with donor aromatic compounds (**11–13**) [38].

The other originally proposed intermediates such as the encounter complex and the non-relaxed exciplex escaped an observation. If present under these particular conditions, their absorption bands possibly may be obscured by the T-T absorption of chloranil.

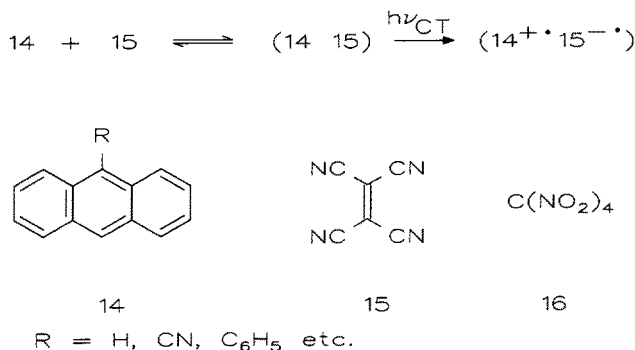
The analysis of other donor (D) and acceptor (A) molecules which form ground state EDA complexes have revealed a deeper insight into the structures and dynamics of various ion pair intermediates. This was first performed in a

collaborative work by Rentzepis and Kochi [41] and was later expanded in a series of investigations by Kochi's group itself. The special features of electron transfer in EDA complexes are presented in Scheme 4 [42]:



Scheme 4. PET in electron donor – acceptor (EDA) complexes; $(\text{D}^+ \cdots \text{A}^-)^*$: „vertical“ ion pair; $(\text{D}^+ \cdots \text{A}^-)_s$: adiabatic ion pair; ΔG_s : free enthalpy of solvation (cf. [42]).

In a first successful approach, Kochi, Rentzepis, and co-workers [41] chose EDA complexes of 9-cyanoanthracene (**14**) and tetracyanoethene (TCNE, **15**) since their charge transfer (CT) absorption bands are well separated from the absorption bands of the monomers. Excitation with a 25 ps laser pulse produced two transient absorption bands near 460 and 750 nm, which decayed simultaneously within ca. 60 ps. As was shown in the chloranil-enoletether system **9**–**10**, cf. Fig. 6), the transients can be identified with the arene radical cation ($14a^+$) and the olefin radical anion ($15^{\cdot-}$), respectively (Scheme 5).



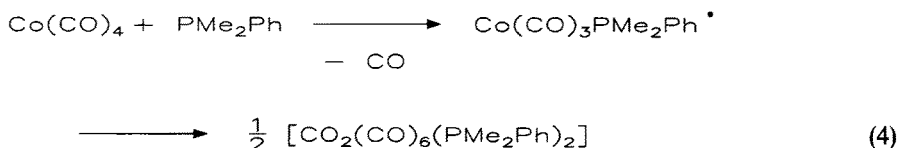
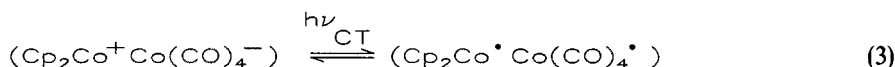
Scheme 5. Charge Transfer Excitation of EDA Complexes [41, 44].

No evidence was found from the picosecond absorption data for an excited state intermediate of the EDA complex. This formulation represents a confirmation of Mulliken's theory, in which CT band excitation of the quite nonpolar ground state produces an ion pair. Accordingly, indene and TCNE form ground state complexes which undergo fast electron transfer on irradiation. However, back electron transfer occurs after relatively long time (ca. 500 ps) via a transient

intermediate arising from single bond formation or a non-equilibrium EDA complex [43]. The same groups have carried out more comprehensive studies on the role of ion pairs in the photoreactions of EDA complexes of 9-substituted anthracenes (14) and tetranitromethane (16) [44].

Just as in the example mentioned above, CT excitation produces a geminate ion pair ("solvent caged species") within few ps, which, however, decays in fast chemical reactions (more about reactions of ion pairs in Sect. 3.4 of this article).

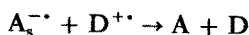
Photoinduced electron transfer in contact ion pairs, which might be seen as charged EDA complexes in this context, have recently been investigated by the same group [45]. In less polar solvents, the cobalticenium salt 17 forms a CIP rather than a SSIP, which, upon excitation into its long wavelength absorption band (520 nm), undergoes electron transfer producing a radical pair (Eq. 3):



Back electron transfer can be effectively obviated by added phosphines (Eq. 4). Recently, even carbocations have been used as electron acceptors in photoexcitations of EDA complexes [46].

For the present, Kochi's extensive work on electron transfer of charge transfer complexes has finished with a generalization of the mechanisms of organic and organometallic reactions basing on the theories of Marcus and Mulliken [42]. Comparison of outer-sphere and inner-sphere electron transfers with the aid of Marcus theory provides the thermochemical basis for the generalized free energy relationship for electron transfer, which is denoted FERET in Kochi's original paper.

Mataga's picosecond spectroscopy studies also focussed on the mechanisms of photoinduced electron transfer and charge separation and recombination processes [47]. Measuring the photocurrent and fluorescence decay with nanosecond spectroscopy, his group found out that the dissociation of the geminate pair of pyrene radical anion and *N,N*-dimethylaniline (2a) radical cation as measured by the rise time of the photocurrent τ_d (e.g., 2 ns in acetonitrile) did not exactly correspond to the fluorescence decay time τ_f (2.3 ns in acetonitrile) of the exciplex of pyrene and 2a. Thus, in this system, the exciplex must be a molecular species different from the geminate ion pair, and, moreover, multiple species of both types may exist. Plotting the charge recombination rate constant k_n for the reaction:



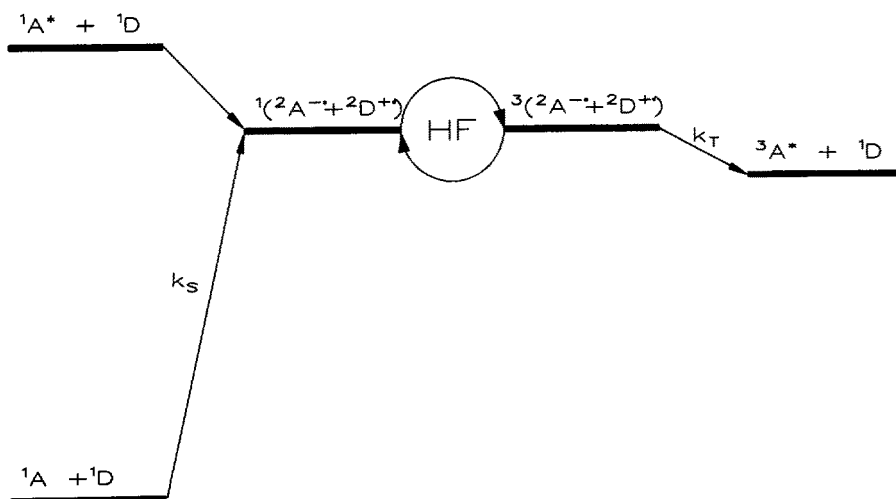
against ΔG_{ip} (the energy gap between the ion pair state and the ground state), Mataga demonstrated the existence of the "Marcus Inverted Region" [48]. More examples of Mataga's extensive work on photochemical charge transfer phenomena using picosecond laser photolysis are summarized elsewhere [14b]. With increasing ΔG_{ip} , k_n dropped, as predicted by Marcus. This was verified for eight different donor-acceptor combinations, however for charge separation reactions as measured by the fluorescence quenching constant, this could not be confirmed. This special topic is discussed in detail by Suppan in Part 4 of this series and is briefly touched in Sect. 3.1 of this article.

In a recent paper, Soumilion and co-workers [49] were able to identify CIP and SSIP in the β -naphtholate anion/alkali cation/tetrahydrofuran system. They found out that with lithium, a CIP is formed whereas with sodium/crown ether, a SSIP results. Using uncomplexed sodium or potassium counterion, mixtures of CIPs and SSIP's were detected. All their conclusions are based on spectral shifts in the transient absorption and emission spectra which were gained using laser flash spectroscopy.

2.3 Magnetic Field Effects, NMR, ESR

In 1976, Schulten, Weller, and co-workers [50] published their first paper on the examination of the effect of a strong external magnetic field on the recombination products of radical ion pairs.

They studied the pyrene/3,5-dimethoxy-*N,N*-dimethylaniline combination in methanol. After the initial laser flash, fast electron transfer occurs resulting first in



Scheme 6. Primary electron transfer of electron donor – acceptor systems in polar solvents (HF = hyperfine interaction) [K. Schulten, A. Weller, *Biophys. J.* 24 (1978), 296].

the exciplex and then in a radical ion pair which can be detected spectroscopically. Deactivation by electron spin alignment occurs from the singlet or triplet ion pair or, after several hundreds of microseconds, from the separated free radical ions (homogeneous recombination, second order). The spin states of the formed recombination products were examined, and triplet excited acceptor was detected spectroscopically. This seemed not unusual after several, μ s, because after diffusion into free radical ions, statistical spin alignment is predicted (that means, 75% triplet and 25% singlet pyrene is produced). However, apart from this slow "homogeneous" process, another recombination mechanism takes place, starting already from the radical ion pair (geminate recombination, cf. Scheme 6). Initially, this has to be in a singlet state, and it was surprising that triplet recombination product arose from the ion pair in a fast (few ns) "geminate" process. Thus electron spin change has to occur in a very fast way. By applying a magnetic field, the degeneracy of the spin states S_0 , T_+ , T_- , and T_0 was lifted and thereby the yield of triplet acceptor was reduced. This clearly showed that the hyperfine coupling, which induces transitions between the degenerate singlet and triplet states is the working mechanism of the fast geminate production of triplet excited pyrene. In a series of papers, Schulten reported on the theory of the magnetic field effect [51], whereas experimental work of solvent, isotope, and magnetic field effects in the geminate recombination of radical ion pairs were performed by the Weller group [52]. All these results were reviewed by Weller [6, 53].

According to the radical pair theory [54], the CIDNP effect results from the competition between a geminate spin dependent radical (ion) pair reaction and the separation of the radicals (radical ions) by diffusion [55]. The free radicals (radical ions) may react with diamagnetic species (e.g. solvent) and accordingly, the escape products have certain nuclear spin states overpopulated. An enhanced absorption or an emission line in the NMR spectrum is observed.

Using time-resolved CIDNP [56], the products of the fast geminate reaction may be detected, too. Obviously, the CIDNP effect is predetermined as an analytical tool for the examination of the structure and energetics of radical ions [57], less for ion pairs.

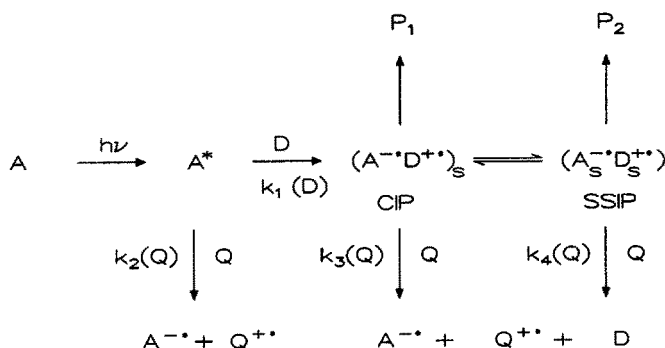
The preferred cage reaction of ion pairs is back electron transfer (see above, magnetic field effect), whereas the free radical ions undergo essentially the same reactions as triplet molecules, apart from complex rearrangements (e.g., the benzonorbornadiene-benzonortricyclene (di- π -methane) rearrangement [58]. Conventional ESR spectroscopy is reviewed by Sharp and Symons in Szwarc's book [8]. It is the only means to identify free radicals in solution positively [59]. In order to overcome the low time resolution, the radicals are produced with repetitive laser flashes at different magnetic field strengths. Using this method, 20 ns can be resolved. This resolution is necessary to observe the CIDEF effect, which reflects, just as CIDNP does, a non-equilibrium population of spin states. CIDEF works with electronic spin states of radicals whereas CIDNP is based on nuclear spin states of products.

CIDEF originates in two independent processes, the triplet mechanism and the radical pair mechanism. The last one arises in spin correlated pairs [60]. The final spectrum gives a direct insight in the working mechanism.

For more information on experimental techniques and medium effects concerning PET and especially radical ion pairs, the reader should consult the Fox-Chanon books [1, Part B]. Solvent and salt effects have been discussed in a special chapter by Santamaria.

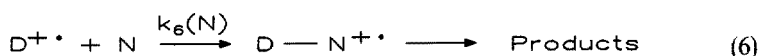
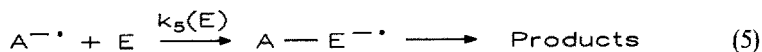
2.4 Indirect Evidence

Besides spectroscopic methods, quenching processes have been utilized to differentiate between various types of radical ion pairs, too. These chemical methods make use of the different reactivities of CIP andSSIP which are caused by the unequal solvation and distance of the charged species in the ion pairs. Depending on the ambivalent character of radical ions, these intermediates may be scavenged either by electron transfer quenchers (Q) or by nucleophilic and electrophilic scavengers (Scheme 7 and Eqs. (5–7)).

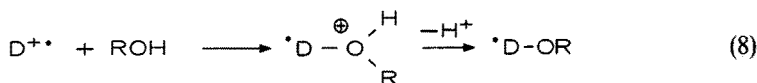
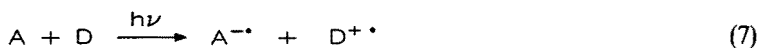


Scheme 7. Quenching of PET processes between A and D by secondary electron transfer (only A is excited); A: electron acceptor; D: electron donor; P: products; Q: electron transfer quencher.

A similar scheme can be designed for PET processes via excited electron donors. However, according to our knowledge, so far only reports on examples shown in Scheme 7 are known. Scavenging by nucleophiles (N) or electrophiles (E) proceeds according to equation 5 and 6 and should also depend on the degree of solvation of the ionic intermediates and competing processes as shown in Scheme 7.



One specific example is the scavenging of radical cations by alcohols (Eqs. (7–10): only one possibility of coupling between A and D is shown in Eq. (10)).



It should be noted that several groups have utilized the nucleophilic scavenging of radical cations by alcohols for synthetic processes [28, 61].

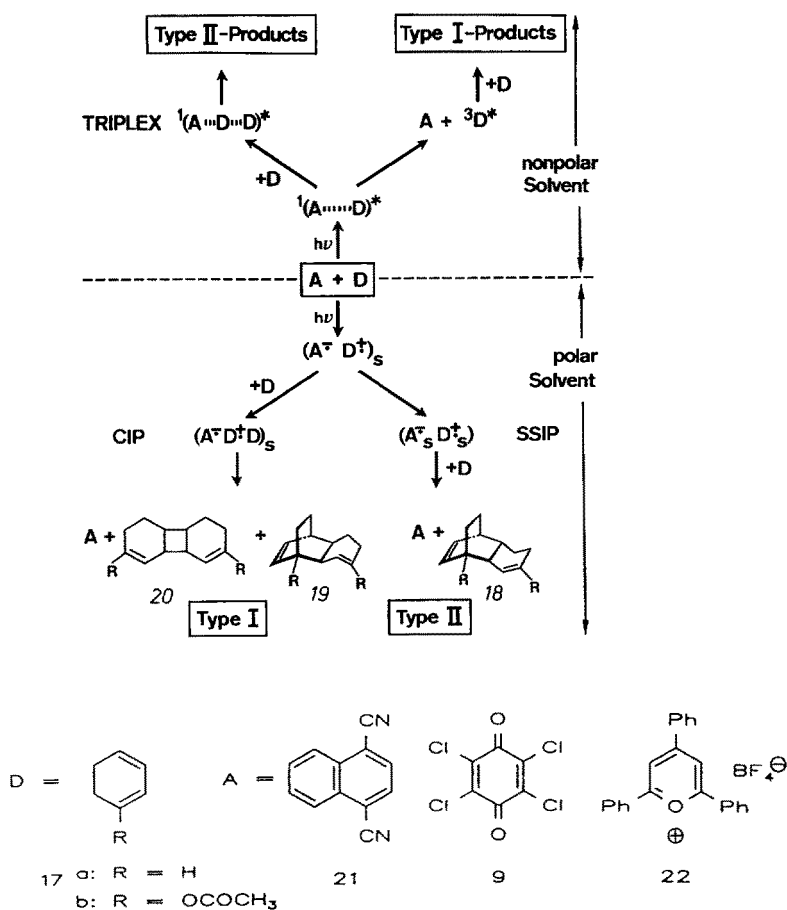
However, in most cases, the detailed mechanism is not yet known, i.e., whether CIP, SSIP or even free radical ions are scavenged by the nucleophile. Arnold and Snow [62] suggest an attack of methanol to solvated olefin radical cations, whereas Mariano observed a highly stereoselective example of a direct scavenging of a radical cation – radical anion pair by methanol [63]. Although this process has received relatively little attention, it is obvious that scavenging of different types of radical ion intermediates is not only possible but may be used to differentiate between the various types of radical ion pairs (CIP and SSIP).

These quenching methods can provide indirect evidence about the involvement of CIP and SSIP in PET reactions. We will briefly discuss the dimerization of 1,3-cyclohexadienes exemplarily, leading either to Diels-Alder products or cyclobutane adducts [37].

Two types of products are observed in these dimerizations, depending on the reaction conditions. In polar solvents (PET conditions), the endo-Diels-Alder adduct **18** is preferred at low concentrations, (Type II). The presence of salts (LiClO₄) also favours its formation. At higher concentrations, however, the product ratio turns to cyclobutanes **20** and the exo-Diels-Alder adduct **19** (Type I). Application of high pressure changes the product ratio in the same way (see below). Since these effects are particularly pronounced in the dimerization of 1-acetoxy-1,3-cyclohexadiene (**17b**), we will discuss the quenching experiments for this case in more detail. Using 1,2,4-trimethoxybenzene (**23**) as electron transfer quencher and ethanol as nucleophilic scavenger, we observed two types of quenching effects (Fig. 7): (a) an almost quantitative quenching of the type II product in presence of ten mol-% of Q and (b) a pronounced (but with ca 50% less efficient) quenching effect of the type I products. Since Q and **17b** quench the fluorescence of the sensitizer (**21**) at the same rate, i.e. nearly at diffusion controlled rate (1.3 and $2.1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$), we concluded that both the formation of type I and type II products involve radical ion intermediates. The different quenching effect, however, may result from different types of intermediates, e.g. from scavenging either CIP or SSIP (or free radical ions), respectively. This rationalization is confirmed by two further experiments:

- (a) the product formation of the PET dimerization of *17b* was quenched to nearly the same extent [using ethanol (40 mol-%) as nucleophilic scavenger], i.e. 90% quenching of the type II product and ca. 60% of the type I products;
- (b) the PET dimerization of 1,3-cyclohexadiene (*17a*) under high pressure up to 2 kbar (200 MPa) favors the formation of type I products instead of the type II product [64], i.e. the endo/exo ratio of the Diels-Alder adducts (*18a/19a*) decreases with increasing pressure in polar solvents with $\Delta\Delta\tilde{V} = +1.2$ to $2.4 \text{ cm}^3/\text{mol}$ (Fig. 8).

These experiments clearly show the involvement of at least two different types of radical ion intermediates which can be designed CIP and SSIP/FRI. The origin of the different reactivity of CIP and SSIP remains unclarified. One speculative explanation may be concluded in analogy to the triplet sensitized dimerization of 1,3-cyclohexadiene, which mainly leads to type-I products, however in different



Scheme 8. PET cyclodimerizations of 1,3-cyclohexadienes [37].

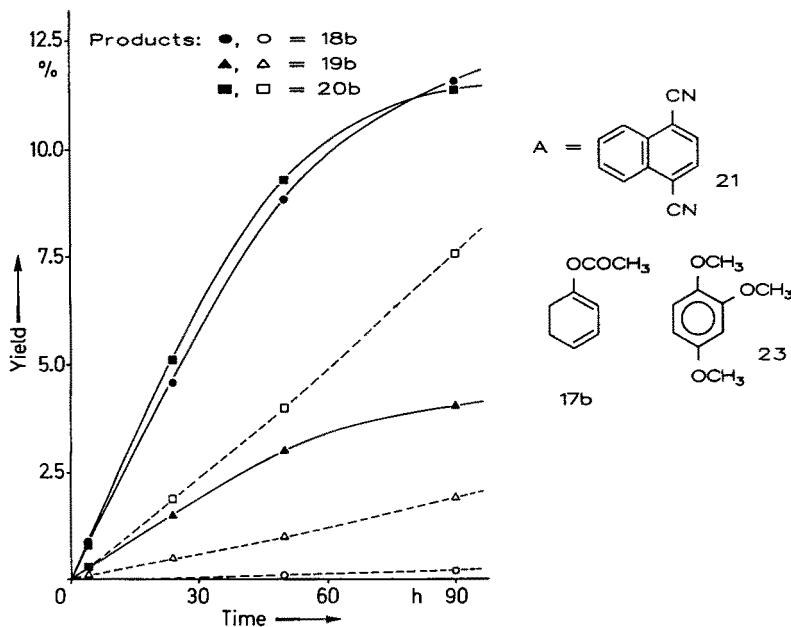


Fig. 7. Cyclodimerization of 1-acetoxy-1,3-cyclohexadiene (*17b*), sensitized by A = 1,4-dicyanonaphthalene (*21*) in the absence and presence of Q = 1,2,4-trimethoxybenzene (*23*) (full symbols: absence of Q; open symbols: presence of Q)

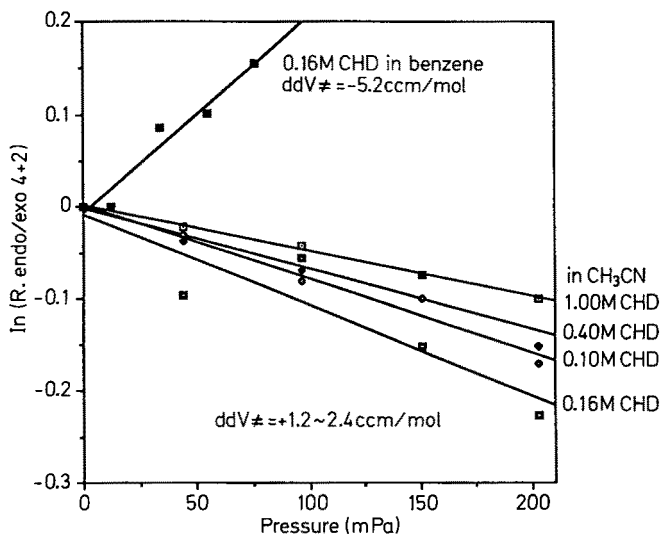


Fig. 8. Pressure dependence of the endo-exo ratio (ln relative endo-exo ratio) in the determination of 1,3-cyclohexadiene (*17a*), sensitized by 1,4-dicyanonaphthalene (*21*) in acetonitrile and benzene [64]

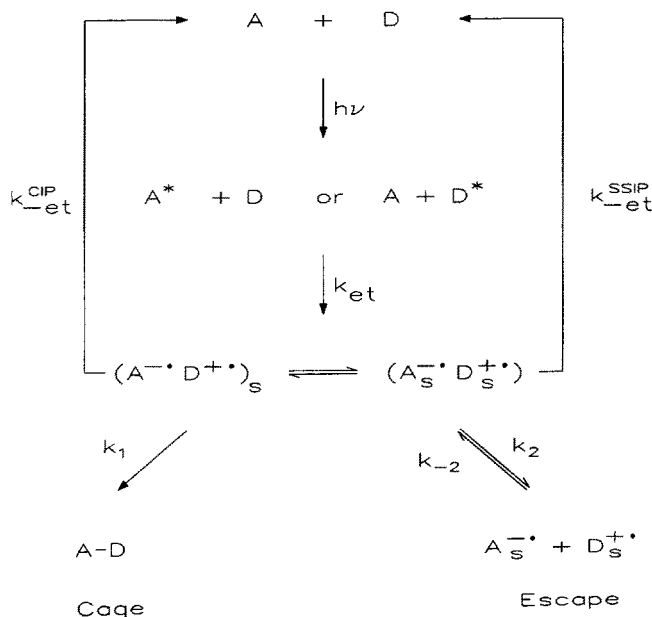
ratios [64, 37]: in this case a direct interception of the CIP by a second donor (*17a* or *17b*) leads to a tight termolecular unit in cage with the radical anion of the acceptor ($A^{\bullet-}$). Fast back electron transfer to the diene radical cation $17^{+\bullet}$ may form a caged radical pair or reverse electron transfer to a preformed dimeric radical cation $17-17^{+\bullet}$ may lead to a biradical. Both intermediates resemble to some extent those of the triplet sensitized dimerization. The different multiplicity (singlet versus triplet), however, may result in different product ratios.

In this context two additional aspects should be noted. First, our high-pressure experiments [64] provided detailed information about the PET dimerization of *17a* in nonpolar solvents which confirm the triplex mechanism (cf. Sect. 4 and Ref. [65]). Second, analogous experiments with triplet sensitizers indicate the existence of a "Marcus Inverted Region" for triplet energy transfer. Third, the mechanism described here for the PET dimerization of dienes resembles that by Mattes and Farid [66] for the dimerization of 1,1-diphenylethene. This latter example will be discussed in more detail in Sect. 3.2 of this article.

3 Reactions of Radical Ion Pairs (Selected Examples)

3.1 Classification: Cage and Escape Processes

The following scheme comprises the generation and fate of radical ions in photochemical processes:



Scheme 9. Cage and escape processes in PET reactions.

The donor or acceptor may be excited photochemically. If a charge-transfer complex (a ground-state electron donor-acceptor [EDA]- complex) is formed, this might be activated specifically at longer wavelength than necessary for the excitation of the free donor or acceptor, leading directly to the CIP (cf. Scheme 4). Depending on the free energy of electron transfer (as calculated by the Rehm-Weller equation [6, 21, 67], charge transfer between the two species (ground state donor/excited acceptor or excited donor/ground state acceptor) takes place. It should be noted that, according to the Weller equation, nothing but the thermodynamics of electron transfer can be estimated, because only the energy difference between the initial and final state of the electron transfer is taken into account. Therefore, calculated ΔG values should be taken with caution for rationalizing PET processes, at least in the " $\Delta G \approx 0$ " region. An evaluation of the kinetics (free enthalpy of activation) is complicated because molecular parameters throughout are not exactly known (with the exception of some well investigated specific systems, especially concerning the "Marcus Inverted Region"). Nevertheless, for a first approach, ΔG may be taken as the driving force of electron transfer, taking into account some specific features such as diffusion control and the "Marcus Inverted Region" [1a].

The electron may be transferred back in the radical ion pair yielding either the starting material or an adduct $A-D$ (cage process). Alternatively, the ions diffuse apart and perform their characteristic reactions (escape process).

3.2 Back Electron Transfer

Theoretical considerations by Marcus [48b, c] and later by others [68] have led to the prediction that the rate constant of electron transfer is a function of the free energy. k_{et} is low for weakly exergonic processes, it goes through a maximum with increasing $(-\Delta G)$ and falls again for strongly exergonic reactions.

The initial rise of the rate was confirmed soon (e.g. Refs. [21, 69], whereas the left branch of the parabola could not be detected until recently ($\Delta G > -0.5$ eV). In a series of communications [70–74], Gould, Farid, and co-workers account on their investigations of back electron transfer in laser flash generated radical ion pairs in homogeneous solution.

As acceptors, they used 9,10-dicyanoanthracene (DCA) or 2,6,9,10-tetracyanoanthracene (TCA), the donors were methylated benzenes or naphthalenes. The D/A pair was designed to give radical ion pairs on irradiation. In order to determine Φ_{sep} , they monitored the quantum yield of dimethoxystilbene radical cation formation [70], which intercepts the free radical cation of the donor exclusively. Assuming a constant k_{sep} from earlier studies [66b], they indirectly obtained k_{-et} according to Eq. (11):

$$k_{-et} = \frac{k_{sep} (1 - \Phi_{sep})}{\Phi_{sep}} \quad (11)$$

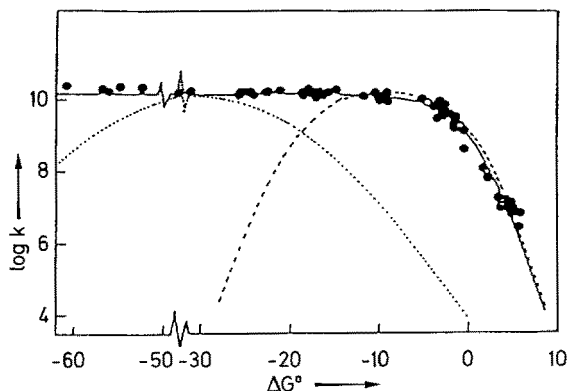


Fig. 9. Plots of $\log(k[M^{-1} s^{-1}])$ for fluorescence quenching of excited states [21, 40]. The *solid* curve is a Rehm-Weller plot and the *broken* one a Marcus plot, both with $\lambda = 9.6 \text{ kcal mol}^{-1} = 40 \text{ kJ mol}^{-1}$. The *dotted* curve corresponds to a Marcus plot with $\lambda = 38 \text{ kcal mol}^{-1} = 159 \text{ kJ mol}^{-1}$ (λ = reorganization energy, ΔG^0 = corrected standard free energy change of electron transfer) – taken from Ref. [1b]

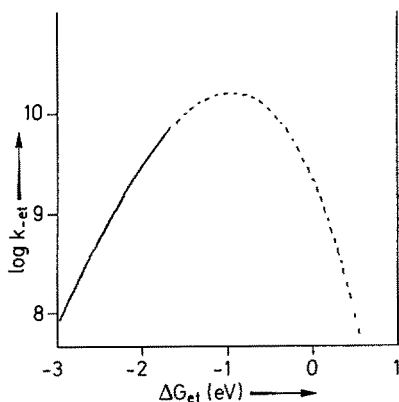
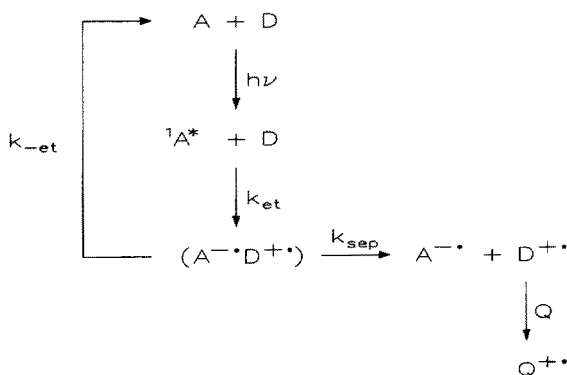


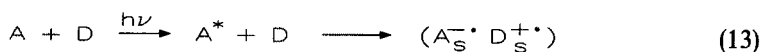
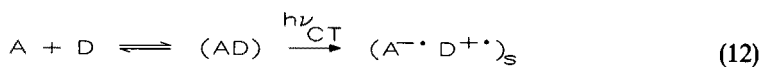
Fig. 10. Dependence of $\log k_{-et}$ of return electron transfer within ion pairs ($A^{\cdot-} D^{\cdot+}$) in acetonitrile on the free energy change (*solid line*: experimental) – according to Ref. [70]. A = 9,10-dicyanoanthracene, 2,6,9,10-tetracyanoanthracene; D = aromatic hydrocarbons



Scheme 10. Simplified reaction scheme of PET processes of electron donor (D) and acceptor (A) molecules; Q: 4,4'-dimethoxystilbene (cf. [70]).

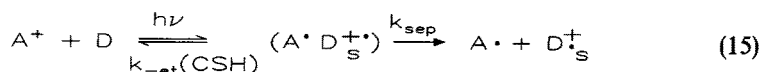
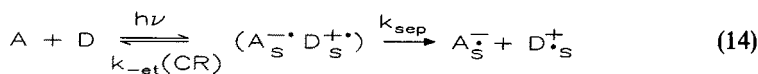
Plotting $\log(k_{-et})$ versus $-\Delta G$ (the free energy of electron transfer of the D/A pair concerned), they found direct evidence for the Marcus Inverted Region: all points lay on the left side of the parabolic curve predicted by theory (cf. Fig. 9.). The following paper [71] dealt with the influence of the structure of the donor on the shape of the parabola (one ring donors [benzenes] gave lower Φ_{sep} 's and correspondingly higher k_{-et} 's at similar ΔG 's than the two ring donors [naphthalenes, biphenyls, fluorene]). This effect was ascribed to both larger electronic coupling and larger total reorganization energy for the one ring donors compared to those for the two ring donors, indicating differences in the matrix coupling elements and the degree of solvation between the ion pairs. The latter feature was thoroughly described in a paper dealing with back electron transfer from CIPs and SSIPs [72].

The CIP was formed upon irradiation of the ground state CT complex between TCA and the donor, whereas the data for the SSIP stem from selective irradiation of the electron acceptor as described in the preceding paper in this series (Eqs. (12) and (13)).



Comparing k_{-et} (CIP) and k_{-et} (SSIP) (cf. Scheme 9) revealed that the former rate constant is much more dependent on the reaction exothermicity. This again can be ascribed to the electronic coupling which is recognizably higher in the CIP compared to the SSIP due to the shorter distance of the charged species (CIP: ca. 350 pm, SSIP: ca. 700 pm). In addition, the solvent reorganization energy also depends on the separation distance and differs by ca. 1 eV for both ion pairs. The deuterium effect on the rate of electron transfer was investigated in the fourth paper [73]. k_D ($= k_{-et}$ for deuterated electron donors) was compared with k_H . It turned out that increasing $-\Delta G$ caused an increasing isotope effect, that means, k_D decreased in comparison to k_H . Interestingly, methyl deuteration lead to an equal effect as perdeuteration of the benzene donor, whereas ring deuteration (and H at the methyl group) did not result in a measurable isotope effect. This was explained with frequency changes of the rearranged vibrational modes and with a reduced extent of hyperconjugation due to the stronger C-D bond in the intermediate CT complex.

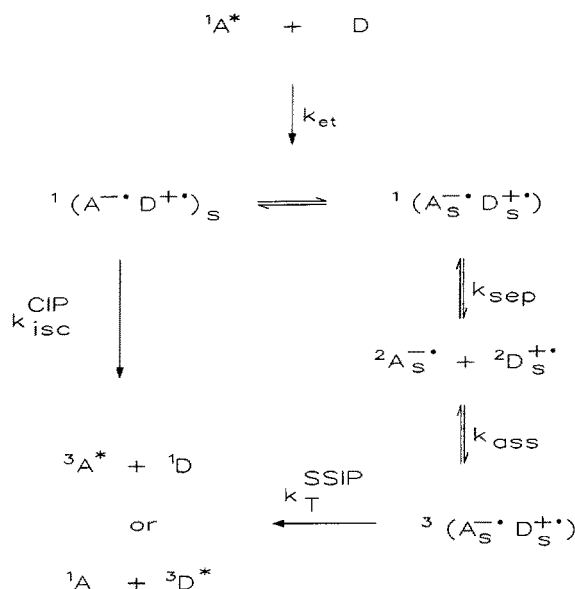
Still the last paper [74] by this group turns from charge recombination (CR) to charge shift (CSH) reactions, using a cationic acceptor (*N*-methylacridine, MA)



$(k_{-et})_{\text{CSH}}$ is more dependent on $-\Delta G$ than $(k_{-et})_{\text{CR}}$. This is in contrast to Mataga's predictions of a more pronounced Marcus Inverted Region of CR reactions compared with CSH reactions and can be ascribed to a smaller solvent reorganization energy for the charge shift reaction. Although the origin is not yet clear, these findings for the SSIP remind to some extent of conclusions obtained by Marcus for electron transfer reactions in the CIP [75]. Meanwhile, other reports have confirmed the Marcus Inverted Region for homogeneous electron transfer reactions. For example, E. Vauthey and co-workers [76] performed an analogous study with 9,10-dicyanoanthracene and diverse electron donors and determined the ion yield directly using photoconductivity measurements.

3.3 Triplet Formation

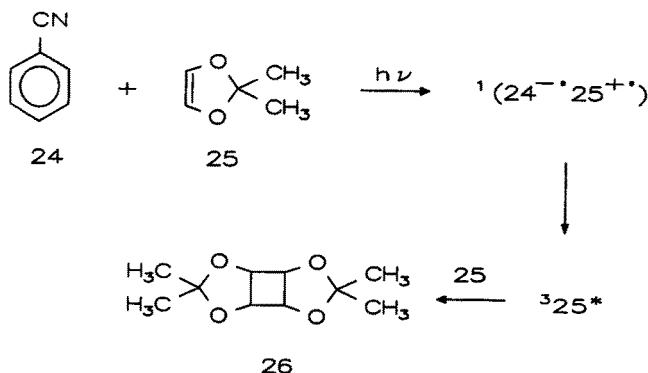
According to the pioneering work of Weller and coworkers, back electron transfer in radical ion pairs can proceed by two different mechanisms [53a], i.e. a slow homogeneous recombination (second order) and a fast geminate recombination (first order). Both may lead to triplets of either the donor or the acceptor, depending on the energetics.



Scheme 11. Intersystem crossing in radical ion pairs [53].

Triplet formation is favoured by back electron transfer when the energy of the radical ion pair is higher than the triplet energy of one of the starting compounds Farid et al. [77] have reported such an example in the PET reaction

of 1,2-diphenylcyclopropene-3-carboxylate. In nonpolar solvents, it reacts with 9,10-dicyanoanthracene to form the *exo*-Diels-Alder adduct via a luminescent exciplex, whereas in acetonitrile, the cyclopropene dimerizes to give an anti dimer (back electron transfer – triplet mechanism). Another example is shown in Scheme 12 [78].



Scheme 12. Photoreaction of benzonitrile with 2,2-dimethyl-1,3-dioxole [78].

With benzonitrile in nonpolar solvents, the 1,3-dioxole derivative 25 forms the dimer 26, which earlier was shown to be a typical triplet product [79]. Weaker donor olefins, such as 1,3-dioxole, enol ethers, and cyclopentene mainly form cycloadducts with benzonitrile due to unfavourable energetics of electron transfer [80, 81].

3.4 Ion Pair Separation

According to the topic of this article (which is mainly devoted to radical ion pairs), the process of ion pair separation will not be discussed in detail, although it belongs to the important reaction channels, offering specific reactions of radical cations and anions, respectively (cf. Scheme 1, 3, 8, and 9). Various groups have been concerned with this process, which is also termed “ionic photodissociation”, according to Masuhara and Mataga [82]. Mataga’s as well as Weller’s group [21, 53a] have fundamentally contributed in the early days of PET. More recent results stem from other groups and the reader may be referred to Sect. 2 of this article, as well as to the other contributions of this series (e.g., PET in Organic Synthesis).

The following criteria govern the process of ion pair separation [1c]:

- a) the free enthalpy of PET (Weller equation, eq. 16 with $E_{1/2}(D)/E_{1/2}(A)$ = oxidation/reduction potential of the donor/acceptor, ΔE_{excit} = electronic excitation

energy of A or D respectively, and ΔE_{coul} = coulomb interaction energy of the charged species $A^{\cdot-}$ and $D^{\cdot+}$,

$$\Delta G = E_{\frac{1}{2}}^{\text{Ox}}(D) - E_{\frac{1}{2}}^{\text{Red}}(A) - \Delta E_{\text{excit}} + \Delta E_{\text{coul}} \quad (16)$$

- b) solvent polarity (ΔE_{coul} in Eq. (16)),
- c) salt effects (e.g., special salt effect, cf. Eq. (2)), and
- d) last but not least chemical reactions which may compete with the association of the free radical ions.

One common feature of all these aspects is the control of back electron transfer. Other points may be of great importance, e.g., pressure effects [64], membrane effects (cf. Fox-article), and complexation [83].

3.5 Chemical Reactions of Radical Ion Pairs

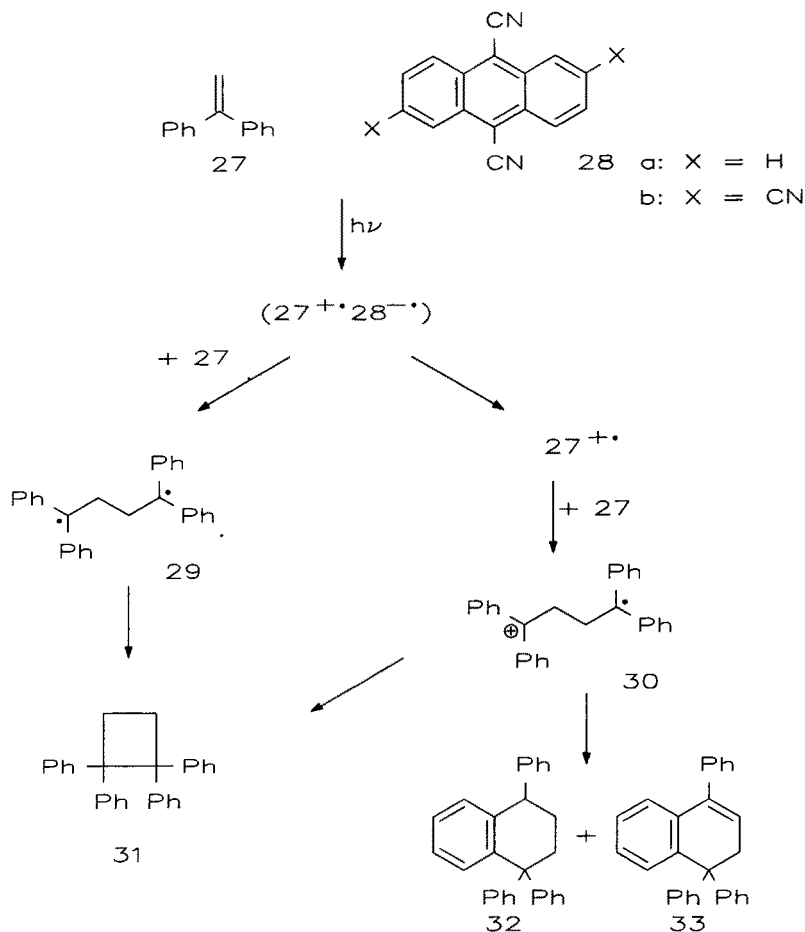
So far, we have mainly focussed on spectroscopic features of radical ion pairs as well as on evidence resulting from indirect methods. Apparently, the diverse reactivities of the CIP and theSSIP have been discussed in detail as shown for the dimerization of the 1,3-cyclohexadienes (see Sect. 2.4). A large number of reports of the last decade concern reactions of radical ion pairs in which, however, only occasionally the mechanism has been elucidated. Therefore we will restrict ourselves only to few meaningful examples.

In a paper of 1986, Mattes and Farid demonstrated the influence of the formation of an ion pair on the periselectivity of the photoreaction of 1,1-diarylethenes with electron acceptors in acetonitrile [66b].

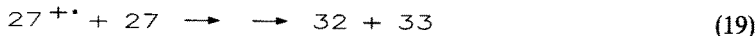
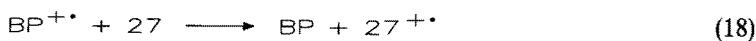
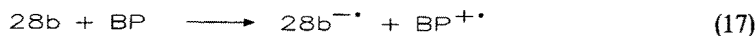
Irradiating 9,10-dicyanoanthracene (A) with 1,1-diphenylethene (D) results in an ion pair $A^{\cdot-}/D^{\cdot+}$ which may be trapped by another donor molecule to give a caged dimeric radical cation $D_2^{\cdot+}$ with $A^{\cdot-}$, or, alternatively, separates into free ions. $D^{\cdot+}$ may then be trapped by D, resulting in the separated dimeric radical cation $D_2^{\cdot+}$. However, the caged dimeric radical cation undergoes fast back electron transfer to give the caged diradical $D^{\cdot}-D^{\cdot}$ which exclusively leads to 1,1,2,2-tetraphenylcyclobutane. The separated dimeric radical cation may cyclize via the 1,4- or the 1,6-path, leading to the cyclobutane again, or, predominantly, to the tetrahydro- or dihydronaphthalene derivatives instead (see Scheme 13).

This supposition was backed by the addition of biphenyl, which bypasses the formation of the radical ion pair ($27^{\cdot+}/28^{\cdot-}$) according to Eqs. (17–19) and consequently suppresses the formation of 31.

As in the dimerization of 1,3-cyclohexadienes (Sect. 2.4), the concentration dependence confirms the proposed mechanism in this case, too. Other acceptors, which favor ion pair separation, support the formation of the escape products 32 and 33. For example, with the pyrylium salt 22 as acceptor, the cage/escape ratio ($31/32 + 33$) decreases from 0.65 to 0.04 compared to the PET reaction using 9,10-dicyanoanthracene (28a) as electron transfer sensitizer [84]. This behaviour



Scheme 13. Electron transfer sensitized dimerization of 1,1-diphenylethene (27) via radical ion pairs or free radical ions [66].



BP = biphenyl

seems reasonable, since 22⁺ is reduced to 22 after the initial electron transfer, leaving no Coulombic attraction.

Kochi studied the selective excitation of preformed ground-state charge transfer complexes [85]. Irradiation of the long wavelength band of these species results

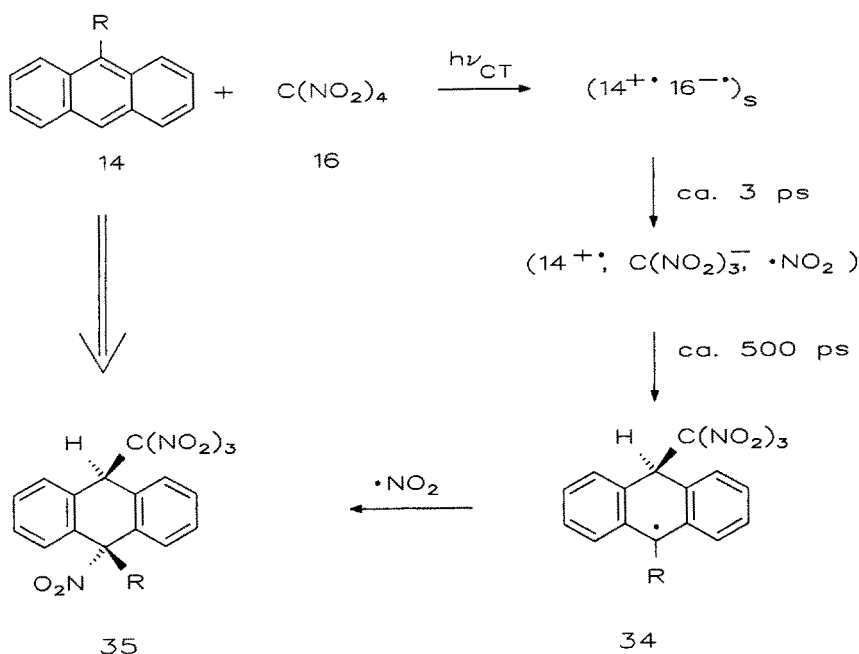
in electron transfer and formation of the CIP. However, depending on the donor and the acceptor, back electron transfer is too fast (< 60 ps) to allow the evolution of finite concentrations of the CIP (Scheme 5) [41, 43].

This is the case in the system anthracene donor – tetracyanoethene (TCNE) acceptor [86]. Replacing TCNE for tetranitromethane, donor-acceptor addition (in this case aromatic nitration) occurs [44b, 87].

Here again, irradiation in the long wavelength absorption bands of the CT complex of *14* and *16* results, in accordance with the Mulliken theory, in a fast electron transfer (< 25 ps) with the formation of a radical ion pair. Due to its spontaneous fragmentation to the trinitromethide anion and NO_2 within few picoseconds, the primarily formed CIP is not observed. The geminate ionic intermediates (arene radical cation and trinitromethide anion) undergo cage recombination to produce hydranthryl radicals *34* in less than 500 ps. The photoproducts derive from addition of NO_2 to *34* with an overall high quantum yield.

This mechanism also holds for the photochemical osmylation of arenes through irradiation of a preformed arene/ OsO_4 CT complex. This reaction finally results in the formation of vic-diols [88].

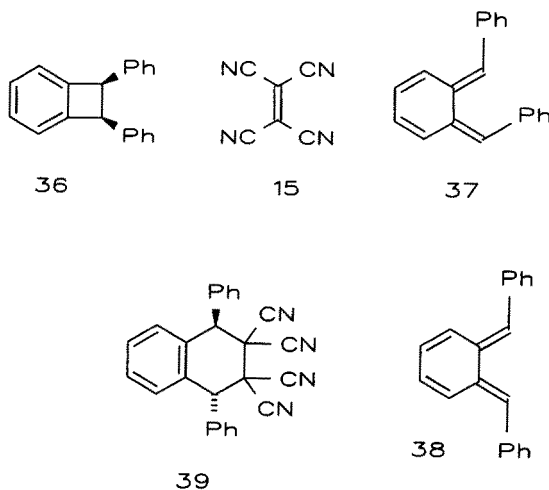
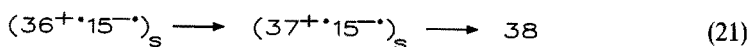
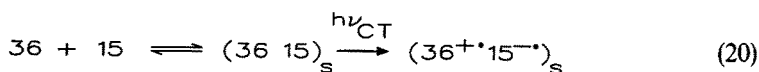
Another reaction happening upon irradiation of the CT band of an EDA complex is the cycloreversion of the dianthracene donor in the dianthracene – TCNE complex after irradiation [89]. Interestingly, this EDA complex exhibits two well



Scheme 14. Ionic coupling within a CIP and radical coupling via free radicals in photoreactions of anthracenes (*14*) and tetranitromethane (*16*) [44b, 87].

resolved CT bands and the striking wavelength dependent quantum efficiency for cycloreversion has been analyzed in terms of two different ion pairs. For more examples, see for instance [90–93]. In all these cases, efficient back electron transfer is suppressed by the lability of the donor, which escapes from the CIP via a chemical reaction.

The electron transfer photochemistry of benzocyclobutenes in the presence of dienophiles exhibits another interesting feature of CIP reactions [93]. For example, charge transfer irradiation of the EDA complex composed of 1,2-diphenylbenzocyclobutene (**36**) and TCNE (**15**) leads to the CIP ($36^{+\bullet}15^{-\bullet}$), of which $36^{+\bullet}$ spontaneously ring-opens to the *o*-xylylene (**37**) radical cation, followed by the collapse of the new CIP (Eqs. (20, 21)), leading to the Diels-Alder adduct **39** in high yield and with high efficiency.

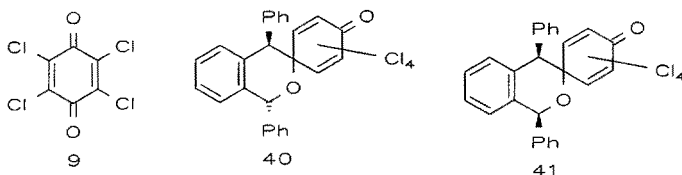
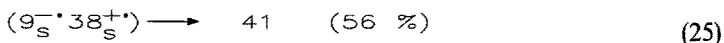
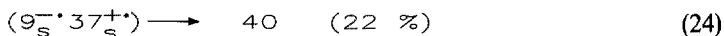
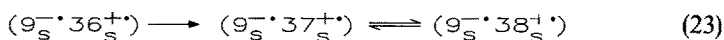
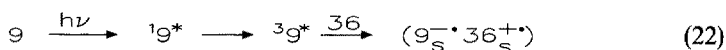


Further studies on the stereochemistry of these processes indicate an allowed conrotatory ring opening for the benzocyclobutene radical cation, similar to the neutral process (there is no evidence for **38** as intermediate either uncharged or as radical cation). However, diffusional quenching by means of chloranil (**9**) as acceptor leads to SSIP's (Eq. (22–25)).

Due to the longer lifetime of the arene radical cation in the SSIP, $37^{+\bullet}$ undergoes isomerization to $38^{+\bullet}$, yielding after return electron transfer and collapse of the reactive intermediates the Hetero Diels Alder adducts **40** and **41** in a ratio of ca. 1:2.5. There is also experimental evidence for some participation of an ion pair annihilation leading directly to **40** and **41**.

As mentioned above, the reviewers could extend the list of examples concerning the diverse reactions of CIPs and SSIPs. The reader may be referred to the other

contributions to this series, as well as to recent reviews published by other active groups [1, 28, 57, 63, 94–100].



4 Triplexes

In 1966, Walker, Bednar, and Lumry postulated the formation of a 1:2 excited complex state in the system indole-pentane- butanol [101]. Two years later, Beens and Weller found fluorescence emission at 475 nm from an excited complex composed of two molecules of naphthalene and one of 1,4-dicyanobenzene. They postulated the unsymmetrical structure ($DD^{+\cdot} A^{-\cdot}$) from the solvent dependence of the wavelength of the peak maximum (high dipole moment in contrast to DAD structure) [102]. Later, several other groups detected such termolecular species. For a review on earlier contributions, see Ref. [103].

In the following years, several groups postulated the involvement of triplexes in various photochemical electron transfer reactions [104].

Dörr, Lewis, and co-workers found evidence through quenching experiments and flash spectroscopy for a triplex in the system trans-stilbene – amine – benzene – [105]. They quenched singlet excited trans-stilbene with various mono- and diamines and found a steric effect on the quenching constant.

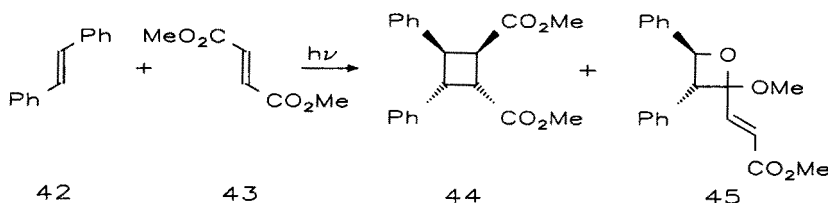
The α , ω -diamines (dabco, diaminoethane, -propane and -butane) quenched the stilbene fluorescence more efficiently than the monoamines, depending on the chain length between the amino groups. This was ascribed to the formation of cyclic radical cations, with a N-N three electron σ -bond. In this case, an exciplex between diamine and stilbene is formed.

Diaminobutane gives rise to a strain free six membered ring radical cation, and this substance therefore quenches more efficiently than diaminopropane or -ethane. Consequently, monoamines form open chained species after electron transfer. The

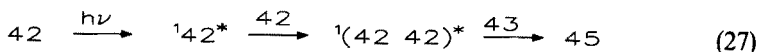
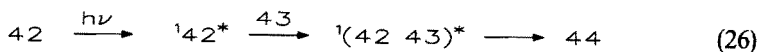
exciplex which is formed from stilbene and an amine molecule is trapped by a second amine. This triplex formation does not take place with sterically hindered amines, e.g., ethyldiisopropylamine, which therefore exhibits a low quenching efficiency. That's why the authors suppose both N-atoms of the triplex to lie on the same side of the double bond of the stilbene moiety.

The following paper in the same journal [105b] deals with the same system, this time studied in acetonitrile solution. Here, a CIP (or an exciplex) is formed, which dissociates to the SSIP (which may be quenched by a ground state amine) or reacts otherwise. No triplex formation is observed in the polar solvent.

In this context, an earlier paper of Lewis and co-workers [106] should be emphasized. They found a striking difference in the selectivity of the [2 + 2]-photoaddition of electron poor olefins to stilbene, depending on the reaction conditions (Scheme 15 and Eqs. (26, 27)).



Scheme 15. PET reaction of *trans*-stilbene with dimethyl fumarate.

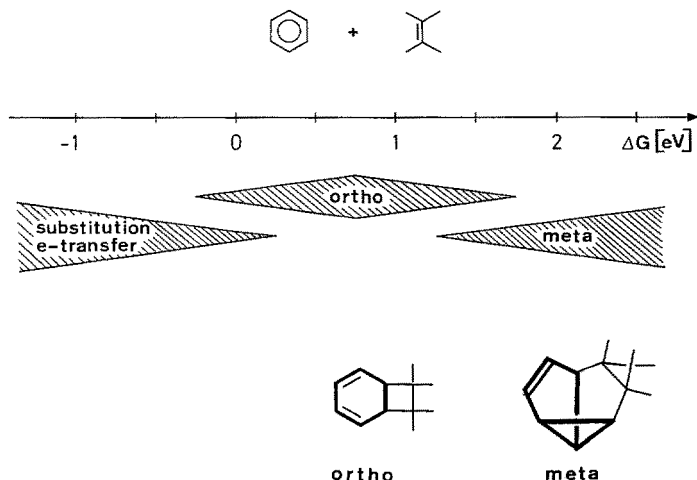


In nonpolar solvents, the cyclobutane **44** is the only product upon irradiation of *trans*-stilbene/dimethyl fumarate mixtures. Exciplex emission, the detection of a weak ground state complex, as well as the stereospecificity of the cyclobutane formation support the proposed mechanism outlined in Eq. (26).

On the other hand, the formation of the oxetane **45** is accompanied by the quenching of the excimer fluorescence with **43** (Eq. (27)).

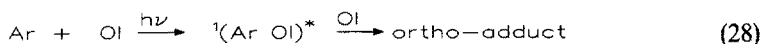
Further evidence for different reactivities of exciplexes and termolecular complexes was also found in photocycloadditions of olefins to aromatic compounds [107]. Depending on the degree of charge transfer, the reaction course turns from *meta* to *ortho*-cycloaddition [78, 80] (cf. Scheme 16).

Whereas it is accepted for many cases that *meta*-adducts are formed via exciplexes of singlet excited arenes and ground state olefins [108], the mechanism of *ortho*-adduct formation still requires further investigation. However, we have shown for the benzene – 1,3-dioxole system, that a second olefin molecule is



Scheme 16. Mode selectivity as a function of free energy of electron transfer in photoreactions of benzene with olefins [1c, 78, 80].

required for product formation (Eq. (28)):



Ar = benzene

Ol = olefin (1,3-dioxoles)

Whether the role of the second olefinic partner is catalytic or a triplex intermediate is involved is not yet clear. The role of triplexes in photoreactions of aromatic compounds with olefins may be even more complex. For example, excited biphenyl forms both a fluorescent dual and triple exciplex with 2,3-dimethyl-2-butene [120]. The possibility of these two pathways of deactivation can explain the inefficient photocycloaddition in the particular case of ${}^1\text{biphenyl}^*/\text{cyclopentene}$ [121].

In 1983, Jones et al. [104] reported on the photosensitized [4 + 2]-cycloaddimerization of 1,3-cyclohexadiene. They found evidence for a tight complex as an intermediate of the Diels-Alder adducts rather than free radical cations. These findings extended an earlier work of Libman [109] but, however, left a decision open pro or against a triplex intermediate. In a series of papers, Schuster and coworkers elegantly extended these preliminary discoveries to its generalization as the "Triplex-Diels-Alder Reaction".

In benzene solvent, Calhoun and Schuster [110] proposed this intermediate with 1,3-cyclohexadiene and 1,4-dicyanonaphthalene as sensitizer. The same group expanded this mechanism to other substrates in benzene solution, e.g., 1,3-cyclohexadiene-indene [111], cyclopentadiene-indene [65], 1,3-cyclohexadiene-enol

ethers [112], 1,3-cyclohexadiene-methylstyrenes [113], and 1,3-dienes — acetylenes [114].

With high indene concentration, high yields of 1 : 1 photoadducts of indene and 1,3-cyclohexadiene are formed in benzene solution. This concentration dependence was established with 1,4-dicyanonaphthalene as sensitizer, whereas with 9,10-dicyanoanthracene no such observation was made.

Additional quenching experiments (1,3-cyclohexadiene quenches both 1,4-dicyanonaphthalene fluorescence and 1,4-dicyanonaphthalene-indene exciplex fluorescence) further supported the triplex mechanism outlined in Scheme 8. In addition, experiments under high pressure conditions also confirm the triplex mechanism for nonpolar or weakly polar solvents [64]. However, no unequivocal proof for the triplex intermediate in these reactions exists.

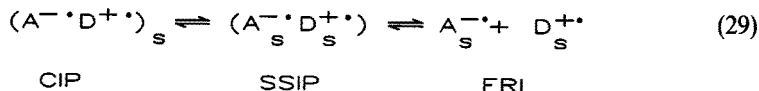
So far, only examples of A-D-D triplexes have been discussed. One example of an emissive A-D-D' triplex was recently reported by Pac and co-workers [115]. Excited singlet 1,4-dicyanonaphthalene forms exciplexes with benzene derivatives whose emission is quenched by a variety of aromatic olefins. This quenching is accompanied by the appearance of new emissions at longer wavelengths which has been assigned to a A-D-D' triplex with e.g., A = 1,4-dicyanonaphthalene, D = benzene, D' = 2-methylstyrene.

Trichromophoric systems having the structure $R_2N-(CH_2)_n-NH-(CH_2)_m-Ar$ generally form either normal exciplexes involving only one amine function or triple exciplexes incorporating both amines in a linear arrangement (A-D-D) [116]. Nonlinear triple exciplexes with an unusually high fluorescence quantum yield have recently been observed between anthracene and two anchored amines of an anthraceno-cryptand [117]. Just as exciplexes, triplexes are important intermediates in a variety of photoreactions [1c, 118], too.

The future impact of instrumentation will certainly bring more information about these supermolecular intermediates which might be termed "multiplexes" [119] or, in analogy to inorganic systems, "excited-state organic clusters" implying some ordered structure.

5 Conclusions

This article has summarized the current stage of the role of radical ion pairs in photoinduced electron transfer (PET) processes, reflecting the personal view of the authors. Consequently, this review is by no means exhaustive. In addition, several topics had to be excluded due to the limited space. In any case, it was intended to show that radical ion pairs are similarly important as reactive intermediates in PET processes as was earlier demonstrated for ion pairs [3], and, moreover, that various types of them may exist (Eq. (29)):



Their controlled formation can be utilized to control the course of the chemical reaction. In this context the chiral discrimination of PET processes of a chiral electron acceptor and (pro)chiral electron donors is of special interest. We have observed such a discrimination in case of the isomerization of 1,2-diarylcyclopropanes [122] and, for the first time, in case of a bimolecular PET process, e.g. the dimerization of 1,3-cyclohexadiene in presence of (+) and (–) 1,1'-binaphthalene-2,2'-dicarbonitrile as chiral electron acceptors [123]. Experiments in the same field are undertaken by Schuster and Kim and have been published recently [124]. So far the enantiomeric excesses are small (ca. 15% [124] in toluene at –65 °C) but future efforts will certainly give more information about the applicability of 'catalytic' asymmetric PET reactions. Consequently, the conditions which govern the formation and the fate of radical ion pairs are of central importance both for a better understanding of the mechanism and for synthetic applications.

Just as other photochemical disciplines, this is a topic of interdisciplinary character, which covers basic problems of physical chemistry as well as preparative applications of organic and inorganic chemistry. Since the nature of the medium also has an important influence on biochemical processes, mutual implications from both photobiology and photochemistry may have a strong impact on future developments, too. In this context, photochemistry is developing from a molecular to a supermolecular discipline which certainly belongs to one of the most fascinating fields of the 1990s.

6 Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft, the Minister für Wissenschaft und Forschung, NRW, the Graduiertenförderung des Landes NRW, and the Fonds der Chemischen Industrie for their generous support of this research.

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