ROLES OF ORGANIZED MOLECULAR ASSEMBLIES IN ARTIFICIAL PHOTOSYNTHESES*

TAKU MATSUO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University 36, Hakozaki, Fukuoka 812 (Japan)

Summary

As has been verified in biological photosynthesis, organized molecular assemblies (OMAs) are capable of controlling photochemical energy conversion. Charge separation of photoactivated species has been attempted using type I OMAs such as micelles, microemulsions, bilayer membranes and polysoaps. The charge separation is enhanced by molecular diffusion which is aided by local electric field and segregation effects due to microenvironmental compartmentalization. The transport of electrons across the membrane wall of vesicles has been studied in an effort to achieve up-hill energy conversion. The attempts were successful in principle, but in practice considerable improvement of the membrane is required. However, new synthetic amphiphiles have been developed which form bilayers, and stable membranes with variable thicknesses (of the order of 50 Å - 10 μm) have become available. Geometric structures of the membrane may also be modified easily. Both energy transfer and electron transport systems can be constructed using the new bilayer membranes with appropriately immobilized elements. Linked donor–acceptor systems, as represented by porphyrin–quinone, may serve as good photoreaction centres when they are installed on these type II OMAs with immobilized elements. The development of type III OMAs is required for efficient coupling of elementary processes in artificial photosynthesis. The construction of charge pools in OMAs seems to be one of the solutions, as has been demonstrated in several examples such as the cooperative activation of two photoredox systems by the use of OMAs with electron pools.

1. Introduction

The best example of solar energy conversion on the Earth is biological photosynthesis, which is actually carried out by highly organized molecular

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assemblies (OMAs) in biomembranes. In bacterial photosynthesis, for example, highly efficient electron transfer reactions take place successively in the reaction centre complex [1]. The photoexcited bacteriochlorophyll dimer transfers electrons via bacteriopheophytin to the primary quinone Q_I in competition with a decay to the ground state through reverse electron transfer. The charge-separated state is further stabilized by the transfer of electrons from Q_I to the secondary quinone Q_{II}. The distances between the relevant species in this electron transport chain are estimated to be less than 20 Å. Thus, we may define the reaction centre complex as a supermolecule which is neatly constructed for photo-induced charge separation.

The chloroplasts of green plants are also divided into several OMAs, although the structural details are less well understood than those of bacterial photosynthesis. Kinetic studies indicate that the photosynthetic processes are well regulated by the electron transport chain in the OMAs. Thus, Nature has clearly proved that photochemical conversion and storage of solar energy is accomplished by the use of OMAs.

During the last decade, a number of attempts have been made to study the effects of OMAs on photo-induced charge separation and the subsequent conversion of redox pairs into chemically useful material. The attempts may be divided into three categories depending on the degree of organization of the molecular assemblies from a mechanistic viewpoint. The three types of molecular assembly will be discussed in chronological order of development.

2. Charge separation at the phase boundary of organized molecular assemblies

The OMAs of the first type (hereafter referred to as type I OMAs) may be characterized as self-organized systems of rather simple surfactant molecules in aqueous solutions. Micelles, microemulsions, bilayer membranes and polysoaps have been used as type I OMAs in an effort to improve the charge and product separation of photo-induced redox reactions. Numerous studies have been reported and excellent reviews have been published in this field [2]. The specific features of type I OMAs which are relevant to charge separation may be ascribed to the following two factors.

(a) The abrupt change in hydrophobicity across the interface between bulk water and the organic microdomain of the OMA (the microenvironmental effect).

(b) The presence of an electric field gradient vertical to the interface (the electric field effect).

The electric field effect usually predominates over the microenvironmental effect in the charge separation of photogenerated redox pairs, as observed with various micellar systems [3]. Of course, the microenvironmental effect plays a major role in compartmentalization of the photogenerated redox pairs into a separate region of non-ionic surfactant, which is also useful for extending the lifetime of the redox pairs [3]. The relative importance of the above two effects depends on the nature of the redox

products. For an amphiphilic viologen molecule, for example, the photoreduction takes place in bulk water and the reduced viologen is incorporated into a cationic micelle as a result of the increased hydrophobicity, although it still retains single positive charge [4].

From the mechanistic viewpoint, it should be strongly emphasized that charge separation in type I OMAs entirely depends on the molecular diffusion of the relevant species. In homogeneous solutions the probability of survival for the primary redox pair is mainly determined by the cage-escape yield of each component. The cage-escaped redox pairs are still annihilated by reverse electron transfer if they stay in the same solution. Annihilation can easily be prevented if one component of the redox pair is collected by an oppositely charged surface, as observed with type I OMAs.

A typical example is a synthetic bilayer membrane formed by an amphiphilic viologen containing two hexadecyl groups (LEV):

$$CH_3CH_2-N\overset{+}{\bigcirc}\overset{+}{\bigcirc}N-(CH_2)_5\overset{\overset{O}{\|}}{C}N\overset{(CH_2)_{15}CH_3}{<_{(CH_2)_{15}CH_3}}$$
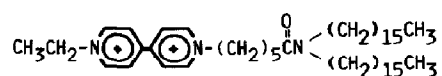
On photoirradiation of aqueous solutions containing zwitterionic propylviologen sulphonate (PSV)

$$SO_3^-(CH_2)_3-N\overset{+}{\bigcirc}\overset{+}{\bigcirc}N-(CH_2)_3SO_3^-$$

and tris(2,2'-bipyridine)ruthenium complex (Ru(bpy)$_3^{2+}$), together with a viologen bilayer membrane, zwitterionic viologen was confirmed to act as a shuttle, providing an efficient electron mediator between the bulk aqueous solution and the bilayer membrane. The quantum yield of viologen cation radicals was close to the net cage-escape yield of the primary redox pair [5]. An analogous example is provided by the use of zinc tetrakis(N-methylpyridinium)porphyrin (ZnTMPyP^{4+})

$$X \equiv -\overset{+}{\bigcirc}N-CH_3$$
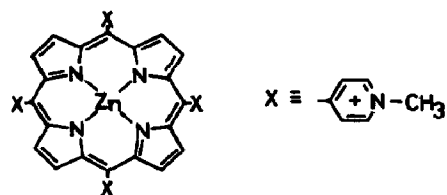
as the sensitizer (Fig. 1). In the presence of 1 mM triethanolamine (TEOA) as the sacrificial reductant the quantum yield for the photoreduction of viologen reached 0.8 on the addition of 10^{-4} M LEV, whereas the corresponding value without LEV did not exceed 0.3 even in 0.1 M TEOA solution [6].

Thus, it is clear that type I OMAs are quite useful for charge separation if the system is appropriately designed. This type of charge separation becomes difficult, however, when the movement of charge carriers is hindered by a highly viscous environment.
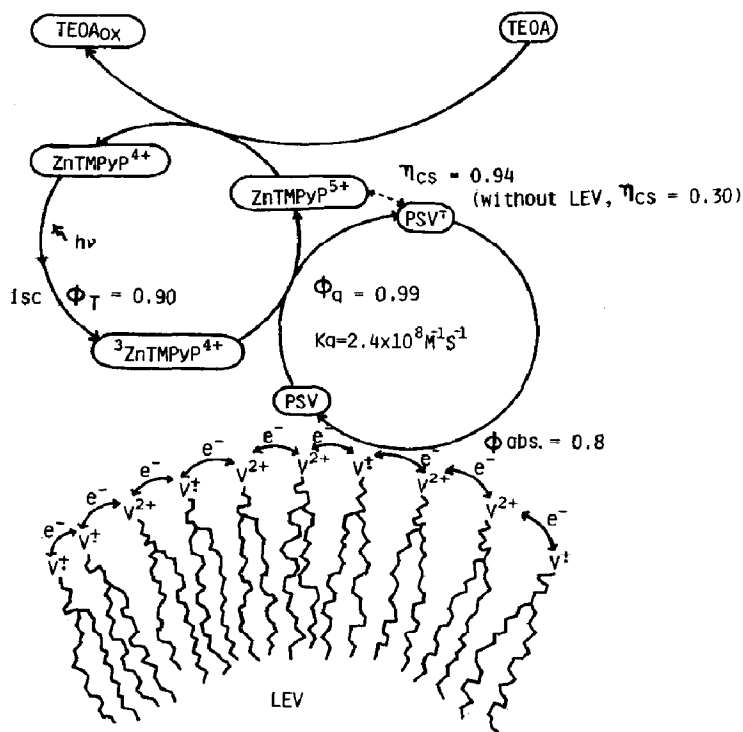
TEOA$_{ox}$ TEOA

ZnTMPyP^{4+}

ZnTMPyP^{5+}

η_{cs} = 0.94
(without LEV, η_{cs} = 0.30)

PSV^T

hν

Isc Φ_T = 0.90

Φ_q = 0.99

$Kq = 2.4 \times 10^8 M^{-1} s^{-1}$

^{3}ZnTMPyP^{4+}

PSV

$\phi_{abs.}$ = 0.8

e^- V^+ V^{2+} V^+ V^{2+} V^+ V^{2+} V^+

LEV

Fig. 1. Schematic representation of the effect of a cationic bilayer membrane (LEV) on the charge separation of the porphyrin(ZnTMPyP^{4+})-sensitized reduction of a zwitterionic viologen (PSV). (The PSV acts as a shuttle, providing an electron mediator between the sensitizer and the LEV membrane.)

3. Electron transport across a membrane wall

In order to achieve up-hill energy conversion, it is essential to use a chemical or physical barrier to prevent the reverse reaction. Membranes are extremely useful for this purpose, as has been verified in chloroplasts. The simplest membranes are organic liquid films [7]. A bilayer lipid membrane on a pinhole has also been used as a model photoresponsive membrane system for energy conversion [8]. The most popular membranes of the first generation are single-walled liposomes (or vesicles) of lipids suspended in bulk aqueous phase.

The study of photosensitized electron transport across lipid vesicle walls was initiated by Calvin and coworkers [9]. The mechanism of photo-induced electron transport across the membrane wall (of thickness approximately 50 Å) has been investigated by several groups [10]. Up-hill energy conversion across the membrane has apparently been achieved by the use of sacrificial reagents. Two-step photoactivation of electron transport across the vesicle wall, as shown in Fig. 2, has also been accomplished [11]. In spite of these valuable findings, lipid vesicles cannot be used as practical OMAs for solar energy conversion since vesicles are not stable for more than one week.
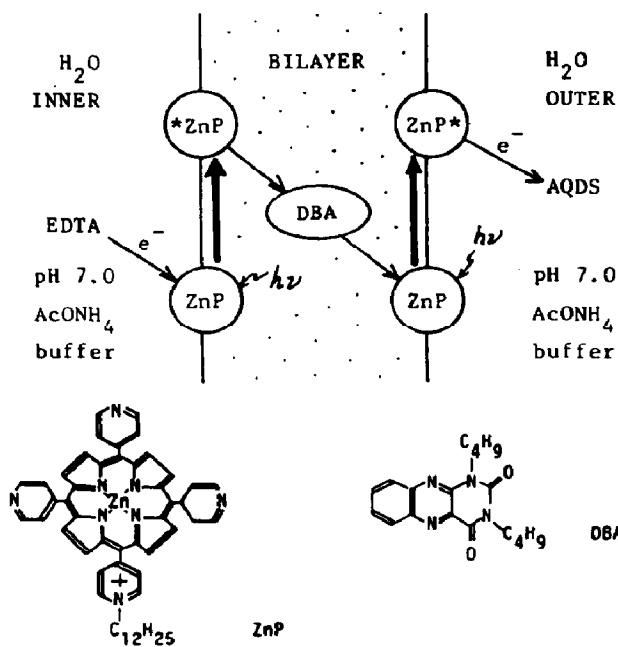
Fig. 2. Schematic diagram of the two-step activation of electron transport across a vesicle wall.

Longer-living vesicles have been prepared using artificial surfactants such as dihexadecylphosphate (DHP) and attempts have been made to use them in photochemical energy conversion [12]. However, the system was disturbed by leakage problems under practical photolysis conditions [13].

4. New generation of synthetic bilayer membranes

In 1977, Kunitake reported that ammonium amphiphiles of double-alkyl chains form bilayer membranes; this report was followed by a number of publications on bilayer-forming synthetic amphiphiles [14]. The structural requirements for membrane-forming amphiphiles are shown schematically in Fig. 3. In general, the alkyl chain is longer than C_8, and the rigid segments are aromatic groups. Bilayer membranes of amphiphiles with fluorocarbon tails are also available [15]. Well-developed bilayer structures have been confirmed by electron micrographs. The introduction of an amino acid residue into the hydrophobic region of the amphiphiles further stabilizes the bilayer membrane structure [16].

Dispersion of the amphiphiles affords multilayered liposomes in bulk water, and single-walled vesicles are obtained on sonication of the dispersion under appropriate conditions. The aqueous bilayer dispersions can be immobilized without losing the bilayer characteristics by casting them onto solid plates [17]. The bilayer membranes can be protected from disintegration in water by covering the surface with a thin film of polymer such as
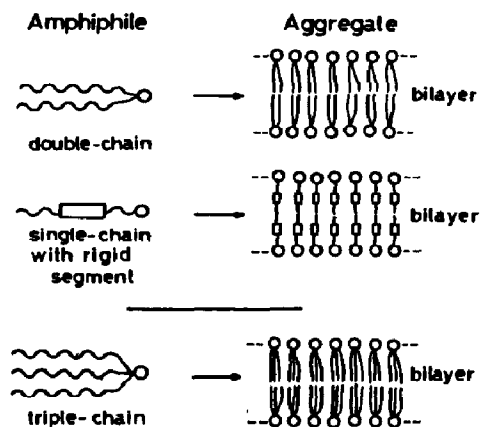
Amphiphile   **Aggregate**

Fig. 3. Structural requirements for membrane-forming amphiphiles: ○, hydrophilic head; ∿∿, flexible alkyl chain; ▢, rigid segment.
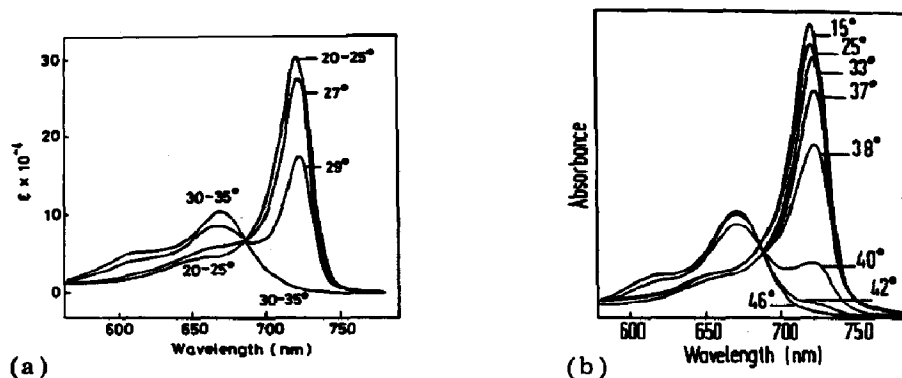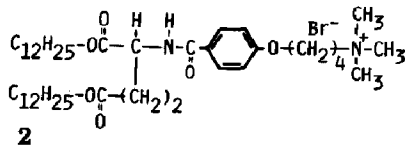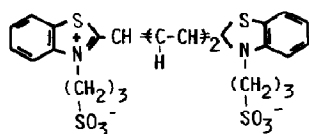

(a)   (b)

Fig. 4. Temperature dependence of the absorption spectra of cyanine dye 1 incorporated into a bilayer system 2

1   2

(a) in an aqueous solution ([1], 5×10^{-6} M; [2], 2.5×10^{-6} M) and (b) in a cast film [17] (density of 1, 2×10^{-8} mol cm^{-2}; density of 2, 2×10^{-7} mol cm^{-2}).

cellulose acetate [18]. Polymerized vesicles with bilayer membrane structures have also been reported by several groups [19]. Thus, we have well-characterized stable membranes with variable thicknesses ranging from 50 Å to 10 μm or more.

Another interesting feature of this new bilayer membrane is the fact that the absorption spectra of chromophores in the membrane show remarkable variation with the change in aggregate structure. For the bilayer membrane formed by ammonium amphiphiles containing azobenzene the absorp-

tion maximum covers a wide region from 300 to 390 nm [20]. Specific spectral variations were also observed with membrane-bound cyanine and merocyanine dyes with an aqueous bilayer solution and a film cast onto glass plate in the same manner (Fig. 4) [17]. Energy transfer and electron transfer in bilayer membranes as prepared by the Langmuir–Blodgett technique have been well investigated by Kuhn and coworkers [21]. For energy transfer, extremely efficient harvesting of energy by one molecule of the guest among 50 000 molecules of the host has been reported. The electron transfer rates decrease exponentially with increasing distance between the donor and the acceptor, and electron tunnelling through the lipid wall (more than 20 Å) has been suggested. Then, an appropriately designed donor–acceptor system in the synthetic bilayer described above is expected to provide an excellent transmembrane electron transport system for photochemical energy conversion. A light-harvesting system should be analogously constructed without much difficulty. The specific feature of these functional membranes is the fact that the relevant elements are immobilized in the membrane. Thus the systems may be defined as type II OMA.

5. Linked donor–acceptor system in organized molecular assemblies

As a model system for the photochemical reaction centre of photosynthesis, a number of studies have been made using a sensitizer–electron acceptor system linked via covalent bonds. A typical example is linked porphyrin–quinone molecules [22]. According to spectroscopy studies by Connolly and Bolton [23], a diamide-linked porphyrin–quinone system yields a charge-separated state which is stable for several hours at cryogenic temperatures. Mataga's picosecond laser photolysis studies of a linked porphyrin–quinone system with an additional quinone in a row (as prepared by Sakata and Misumi) indicated that the charge-separated state can be further stabilized by the transfer of electrons from the first quinone to the second quinone [24]. Moore *et al.* [25] synthesized a carotenoid–porphyrin–quinone system and succeeded in extending the lifetime of the charge-separated state to about 2.5 μs. Thus, it is absolutely clear that linked donor–acceptor systems are useful for constructing photoreaction centres. It is also true that the charge-separated state should be further extended in time and space before the chemical conversion is finally achieved. Coupling of the linked system to bilayer membranes appears to be one of the most promising means of achieving this.

Amphiphilic polypyridineruthenium(II) complexes linked to viologen units (as shown in Fig. 5) have been prepared by the present workers [26]. The linked system can be incorporated into cationic surfactant molecular assemblies such as cetyltrimethylammonium bromide (CTAB) micelles. In contrast, N-hexadecyl-N'-ethylviologen (C16EV(2+)) has been known to yield a micellar system, where viologen units are aligned along the surface [27]. Electron spin resonance spectroscopy studies indicate that a photo-
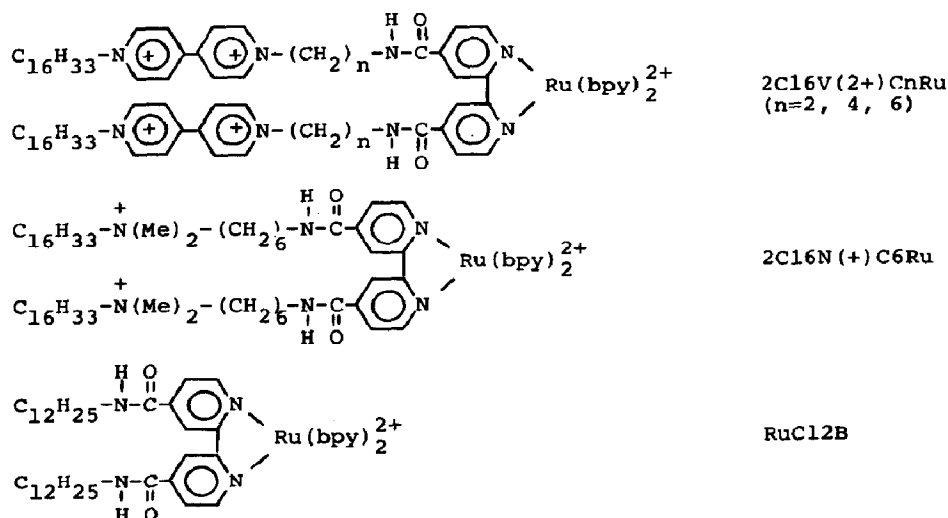
Fig. 5. Molecular structures of polypyridineruthenium(II) complex viologen-linked systems and the reference compounds.

TABLE 1

The effects of the spacer chain of viologen-linked polypyridineruthenium(II) used as a sensitizer in the photoreduction of N-hexadecyl-N'-ethylviologen in cetyltrimethylammonium bromide comicelles using ethylenediaminetetraacetic acid as the sacrificial reagent[a]

Linked system[b]	Number n of methylene chain	Yield ϕ_{rel} of reduced viologen
2C16V(2+)C2Ru	2	46
2C16V(2+)C4Ru	4	280
2C16V(2+)C6Ru	6	511
2C16N(+)C6Ru	6	85
RuC12B	—	100

[a]The concentration of each species is as follows: concentration of ruthenium complex, 20 μM; [C16EV(2+)], 2 mM; [CTAB], 8 mM; [EDTA], 1 mM.
[b]See Fig. 5 for abbreviations.

injected electron in C16EV(2+) micelles migrates on the micellar surface via the exchange of electrons between the viologen units. The polypyridineruthenium(II) viologen-linked systems described above were incorporated into comicelles containing CTAB and C16EV(2+) in the molar ratio of 80 to 20. The ruthenium complexes were photoexcited in the presence of ethylenediaminetetraacetic acid (EDTA), and reduction rates of viologen units were measured. The relative quantum yields for the sensitized reduction of viologen units are summarized in Table 1. The corresponding values for an amphiphilic ruthenium complex without viologen units (RuC12B) and that with quaternary ammonium units are also included in Table 1 as reference systems [28].
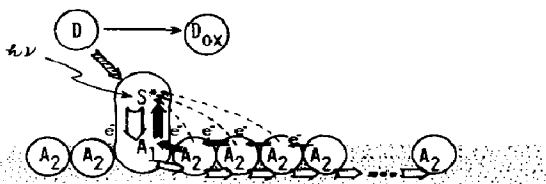
Fig. 6. Schematic diagram of electron transfer processes in an OMA which consists of a polypyridineruthenium(II) viologen-linked system and aligned amphiphilic viologen (C16EV(2+)) on the phase boundary: ⇒, forward electron transfer; ◄ - - -, ◄═, backward electron transfer; (S A₁) , 2C16V(2+)CnRu; (D) , EDTA; (A₂) , C16EV(2+).

For longer spacer chains (*n* = 4, *n* = 6) the relative quantum yield of viologen reduction clearly dominates those of the reference systems. Detailed studies of these systems revealed that the linked viologen is the first electron acceptor, whereas the viologen units in the micellar system (C16EV-(2+)) constitute the second acceptor. The electron on the second acceptor further delocalizes via exchange of electrons over the surface, which competes with the reverse electron transfer as shown schematically in Fig. 6. The reverse electron transfer may be too rapid in the case where *n* = 2, which yielded only small amounts of reduced viologen. Essentially the same results were also obtained with a bilayer membrane system containing C16EV(2+).

The electron transport discussed above takes place along the surface of molecular assemblies. In order to achieve electron transport across the membrane, we have to construct a transverse electron transport system in the hydrophobic region. In this respect, it is very encouraging that Miller *et al.* [29] have found that electron transfer across an insulating barrier as wide as 10 Å can occur very fast (about 100 ps) if conditions are appropriate.

6. Coupling of elementary processes by the use of organized molecular assemblies aiming at new devices for artificial photosynthesis

A very important feature of photosynthesis in higher plants is the fact that the whole chemistry is carried out by the use of multiphoton processes. Cooperation of multiphoton processes is the clue to the splitting of water by visible light. Now that we have reasonable materials and guiding principles for constructing OMAs which are capable of energy transfer and electron transport, we are ready to design type III OMAs for coupling elementary processes. Several examples of attempts to do this will be described below.

Cooperative coupling between two independent photoredox cycles on viologen micelles has been reported by the present workers [30]. One of the photoredox reactions is the reduction of amphiphilic viologen sensitized either by an amphiphilic porphyrinzinc(II) complex or by a polypyridineruthenium complex (RuC12B). The other reaction is the formation of charge transfer complexes between viologen and aromatic donors. A typical exam-
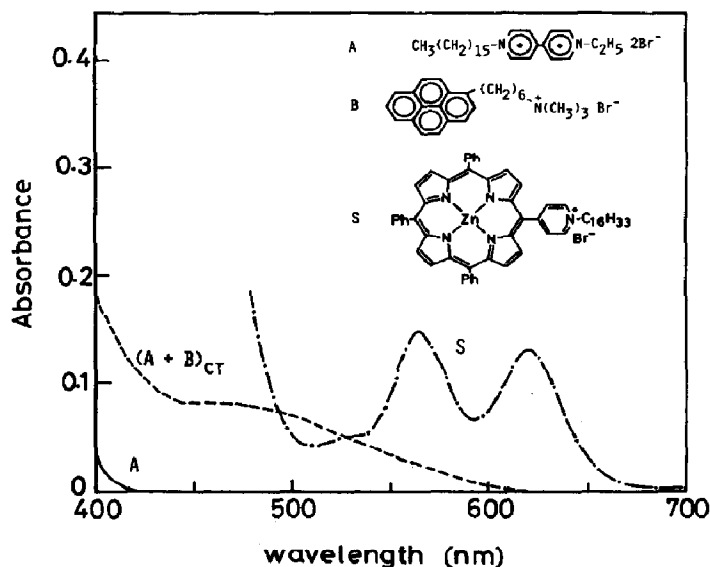
Fig. 7. Absorption spectra of an amphiphilic porphyrinzinc(II) complex and charge transfer complexes between viologen and pyrenyl groups as used in the cooperative activation of two photoredox cycles ([A] = 10 mM; [B] = 0.3 mM; [S] = 20 μM).

TABLE 2

The relative yield $\eta_V\ddagger$ of reduced viologen in the selective or simultaneous excitation of porphyrin and pyrene–viologen charge transfer complexes[a]

System	Solute[b]	λ_{ex} (nm)	Excited species	$\eta_V\ddagger$
1	A	> 470	—	0
2	(A + B)$_{CT}$	> 470	CT complex	22
3	A + S	> 550	Porphyrin	40
4	(A + B)$_{CT}$ + S	> 550	Porphyrin	43
5	A + S	> 470	Porphyrin	100
6	(A + B)$_{CT}$ + S	> 470	Porphyrin and CT complex	175

CT, charge transfer.
[a]The concentration of each species is as follows: [A] = 10 mM; [B] = 0.3 mM; [S] = 20 μM.
[b]See Fig. 7 for notation.

ple of the absorption spectra with solutions containing the relevant species is shown in Fig. 7. The relative yield $\eta_V\ddagger$ for the photoreduction of viologen in the independent redox system was obtained by selective excitation of each sensitizer in the presence of EDTA, as summarized in Table 2. When the solution containing all the components was irradiated with light of wavelength greater than 470 nm (system 6), both the porphyrin and the charge transfer complexes were excited. The $\eta_V\ddagger$ value (175) obtained in this system is 46% larger than the sum of the values for the individual systems. Sensitiza-

$-(CH_2-CH)_n-$

CH_2
N^+
C_4H_9

$-(CH_2-CH)_{0.84}-(CH_2-CH)_{0.16}-$

CH_2
N^+
C_3H_7

CH_2
N^+
$C_{16}H_{33}$

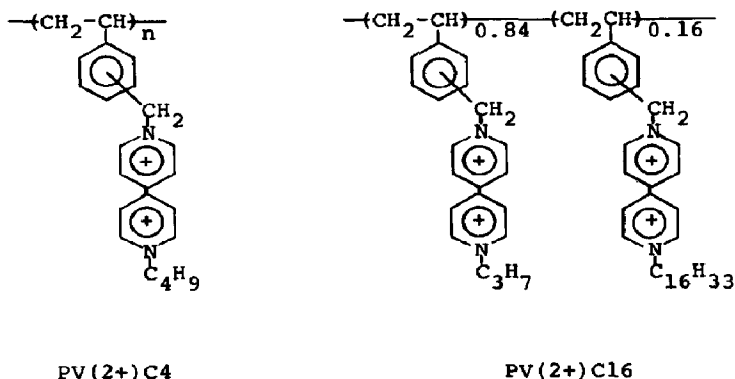PV(2+)C4   PV(2+)C16

Fig. 8. Molecular structure of viologen polymers used as an electron pool.

tion by a polypyridineruthenium complex creates some problems because of the spectral overlap between the metal and charge transfer complexes. After appropriate correction for each absorption, increases in the quantum yield of reduced viologen of two or three times were observed with the solutions where both redox systems were activated.

Kaneko *et al.* [31] have reported an extremely interesting biphotonic effect, namely the complete splitting of water using prussian blue colloids in combination with $Ru(bpy)_3^{2+}$. Light with wavelengths of both 460 and 700 nm was required to generate oxygen and hydrogen molecules in this system. Prussian blue is a polynuclear mixed-valent iron complex and almost all the ruthenium complex is adsorbed onto the surface of the colloids. The photo-excited ruthenium complex is oxidatively quenched by Prussian blue so that the photoliberated electron is stored in the colloids. Light of wavelength 700 nm is required to liberate the trapped electron from Prussian blue as a hydrogen molecule. The oxidized counterpart of the ruthenium complexes generates oxygen molecules at a reaction centre on the colloids. Thus, Prussian blue colloids are functioning as a coupling element of the oxidative and reductive half-reactions of photochemical water splitting. This example indicates that we need electron (or hole) pools as coupling elements in photo-induced redox processes.

The electron pools suggested above were constructed with aligned viologen units on molecular assemblies such as micelles, bilayers and polymers. For the viologen polymer, for example, the photoliberated electron from $Ru(bpy)_3^{2+}$ was delivered to the polymer via zwitterionic viologen (PSV) which acts as a shuttle electron mediator [32]. A series of viologen polymers as shown in Fig. 8 was prepared and the lifetimes of the stored electrons on the polymers were measured by flash photolysis. The longest lifetime obtained with PV(2+)C16 was as long as 1.2 s! On the addition of platinum colloids, the decay of the transient absorption due to the reduced viologen polymer was enhanced, as shown in Fig. 9. A remarkable increase in the decay rate was observed with the 0.5 M H_2SO_4 solution, and the rate was almost independent of the concentration of platinum colloids in the region
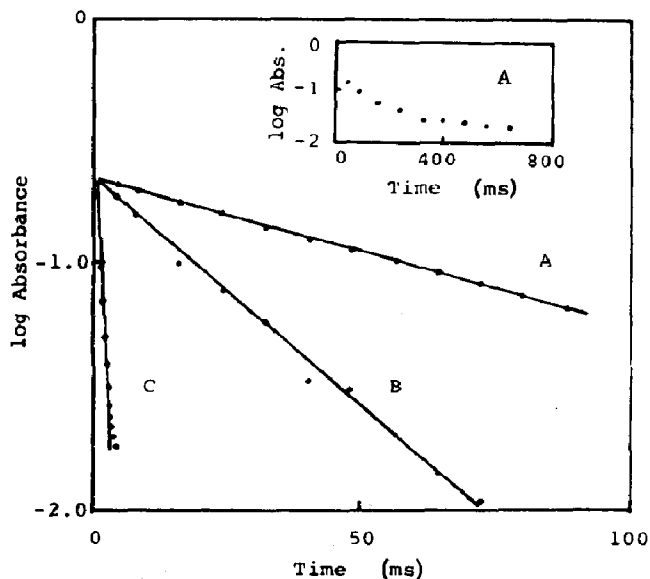
Fig. 9. The decay of the reduced viologen polymer detected at 603 nm under the following conditions [32]: curve A, [$Ru(bpy)_3^{2+}$] = 2×10^{-5} M, [PSV] = 5×10^{-4} M, [PV(2+)-C4] = 5×10^{-4} M; curve B, [Pt] = 5×10^{-5} M, otherwise as for curve A; curve C, as for curve B, except for the acidity (addition of 0.5 M H_2SO_4 solution).

investigated ([Pt] = 3 - 50 μM). Thus, the viologen polymer is thought to play an important role as an "electron pool" which couples the photoredox centre with the multielectron redox reaction site.

The final example is an attempt to use surfactant vesicles as the coupling element for semiconductor-sensitized photoreduction of water [33]. Colloidal CdS loaded with Rh(0) was entrapped in DHP vesicles. Thiophenol (PhSH) was added to the solution and the CdS was irradiated with visible light. Hydrogen gas was generated and the PhSH was consumed. Apparently, the positive holes in the colloidal CdS captured the electron from the PhSH, which was presumably located in the DHP membrane. Thus, a reduction half-cell is constructed using the CdS colloids and a PhSH-impregnated DHP vesicle. If an appropriately designed compound is used in place of PhSH, the vesicle will certainly be useful as a coupling element for the reduction and oxidation half-cells which are located inside the vesicles and outside the vesicles respectively.

7. Conclusion

During the last decade, it has been well established that OMAs are really useful for artificial photosynthesis. Now we have good guiding principles for molecular design and materials to be developed. The problems with light harvesting, photo-induced charge separation and electron transport will be solved before long. The next target must be efficient coupling of the indi-

vidual processes and the installation of good catalysts for multielectron redox processes on the OMA. Considering the extremely rapid progress of the chemistry of OMAs in recent years, we can look forward to a bright future for artificial photosynthesis.

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