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SYNTHETIC CHLOROPLASTS

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Melvin Calvin

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SYNTHETIC CHLOROPLASTS[*]

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Abstract

The principal function of the chloroplast is to capture solar quanta and to store them in some stable form. We are in he process of trying to construct a totally synthetic system that would simulate some of the reactions of the two photosystems which occur in natural chloroplasts. These synthetic chloroplasts will not resemble the natural entitity in detailed construction, as they will contain no protein.

Introduction

The principal function of the chloroplast is to capture solar quanta and to store them in some stable form. All the other functions which can be mentioned are secondary to that one and are present primarily to assist the chloroplast to capture the quantum and store it in some stable form. At the moment, we really do not know which proteins are associated with photosystem I or photosystem II in the quantum converting apparatus of the chloroplast, and it would thus appear presumptious to set about to synthesize all the functions of the chloroplast.

What we are proposing is much more limited: We expect to synthesize an object which will perform the quantum capturing function and the electron transferring function of the natural chloroplast, and that is all. The "synthetic" chloroplast will not replicate itself, will not make protein, will not perform the many other functions which have been attributed to intact live chloroplasts. All the synthetic chloroplast will be able to do is transfer electrons from a low energy state to a higher energy state and, in a sense, that is the primary role of chloroplasts in nature as well.

All of our efforts leading toward this end stem from the ability to understand the functions of a chloroplast. It is my hope that the discussion of synthetic chloroplasts, in terms of physics and chemistry, may provide some ideas about what to look for in nature as well. What I am discussing is really not present in nature as a simple physical entity. It exists naturally merely as a collection of functions. The way these functions are put together in our synthetic system stems from what we think we know of the ntural processes.

A natural chloroplast is shown in the electron micrograph in FIGURE 1, which was taken about 1974. This shows well some of the features of the chloroplast, with the quantum transforming machine constructed of lipid layers which contain particles of various kinds, styles and distributions. The quantum converting process takes place somewhere in that natural machinery. You can see the lipid membrane in the chloroplast, with the protein particles floating in it. The primary function of the lamellar apparatus is to transfer electrons from a lower energy state into a time stable higher energy state. The electrons start in water and eventually end up reducing carbon dioxide; in some cases, under certain conditions, hydrogen generation can occur as well (FIGURE 2).

The fact that the machinery of the natural chloroplast consists of a lipid membrane with particles embedded in it which may or may not penetrate through that lipid membrane, and the fact that we have two quite different quantum processes involved in succession, suggested to us many years ago that the two quantum procsses take place at different sites, either on a macro phase boundary or a micro phase boundary. By macro phase boundary I mean an extended phospholipid membrane, or lipid membrane, and by a micro phase boundary a lipoprotein complex in which each molecule may be surrounded by an insulating lipid layer. Thus, one can think of the electron being transferred across a lipid membrane which is macroscopic, as in a bilipid membrane, or the membrane might be considered as a hydrophobic coat around a protein molecule consisting, for example, of the hydrophobic parts of the polypeptide chain itself.

I believe that the essential feature of natural photosynthesis, i.e. what makes it different from ordinary photochemistry, is the fact that the essential photochemical process is a photoelectron transfer across a phase

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Figure 1. Electron micrograph of chloroplast

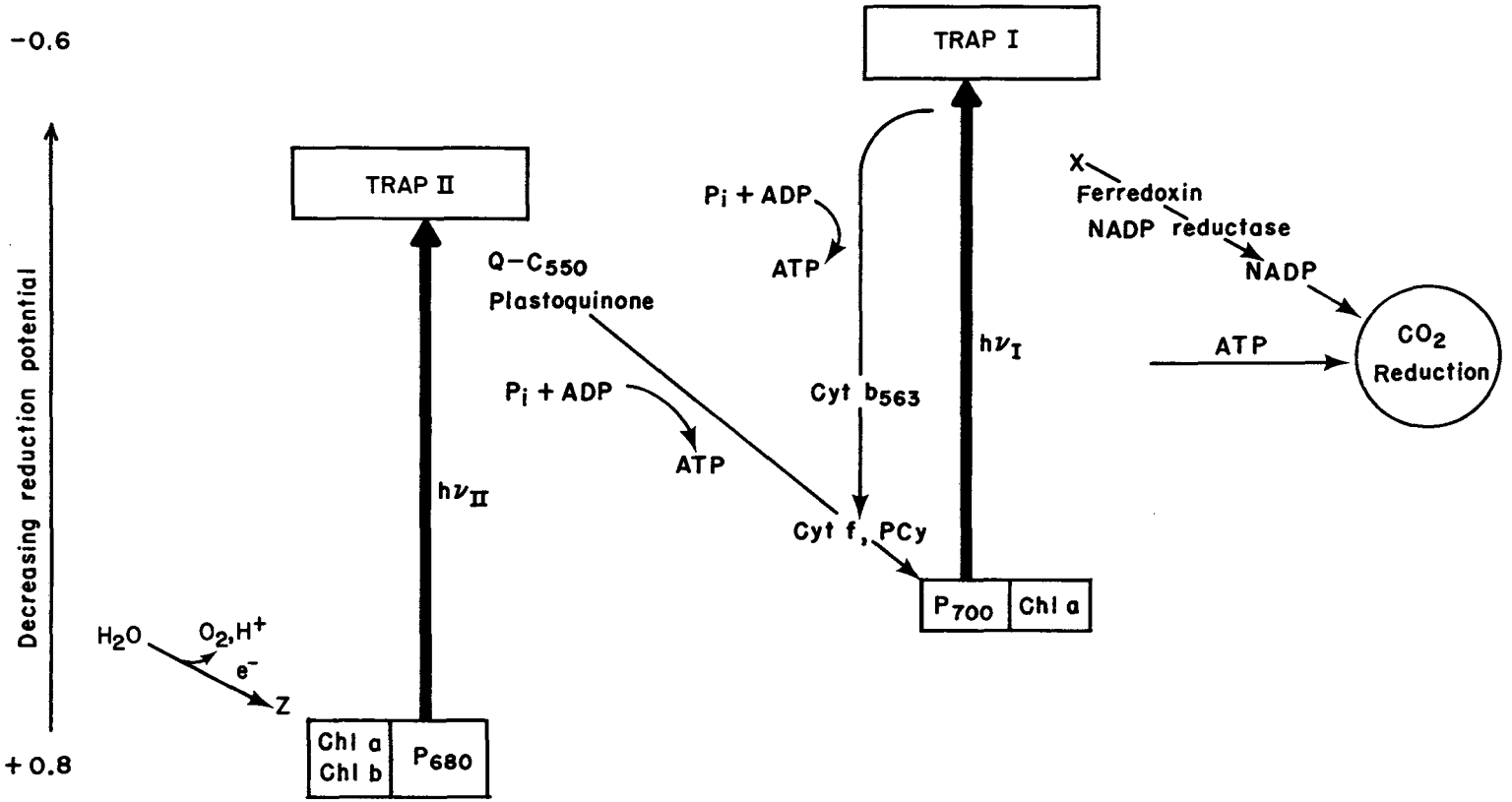

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Figure 2.
Photosynthetic electron transfer scheme

boundary from a water to a lipid phase and/or from a lipid to a water phase. The top part of FIGURE 3 represents a membrane (which could be a macro membrane or a micro membrane) in which the two photo acts (photosystem I and photosystem II) are taking place on either side of the membrane. There is a donor system on the left side an an acceptor system on the right, with corresponding catalysts for the generation of oxygen and hydrogen on each side. The conceptual design of that artificial photosynthetic membrane is the subject of this discussion.

Construction of Micelles

Building such a simple, flat bilipid membrane, with a donor system on one side and an acceptor system on the other, is very complex, because of the technologies involved. I originally thought it might be much easier to build it in the way that nature does, by building vesicles (or liposomes as they were originally called by the biologists). "Vesicle" is the physical chemists' term to describe a simple bilipid sphere which has water on both sides (inside and outside) with two interfaces or two phase boundaries. One phase boundary is present on the outside, water-to-lipid, and another phase boundary is present on the inside, lipid-to-water. Essentially, in constructing vesicles we have rolled up the flat membrane into a sphere. We can consider these spheres as microspheres or liposomes in which the photosynthetic quantum conversion process takes place.

The actual sphere itself can be simplified even further (FIGURE 4). The sphere can be broken down into two parts, the pieces each forming a separate phase boundary. The liposome is thus separated into two parts: one micelle in which one photoact (photosystem I) is accomplished and another micelle in which the other photoact (photosystem II) takes place. The sink

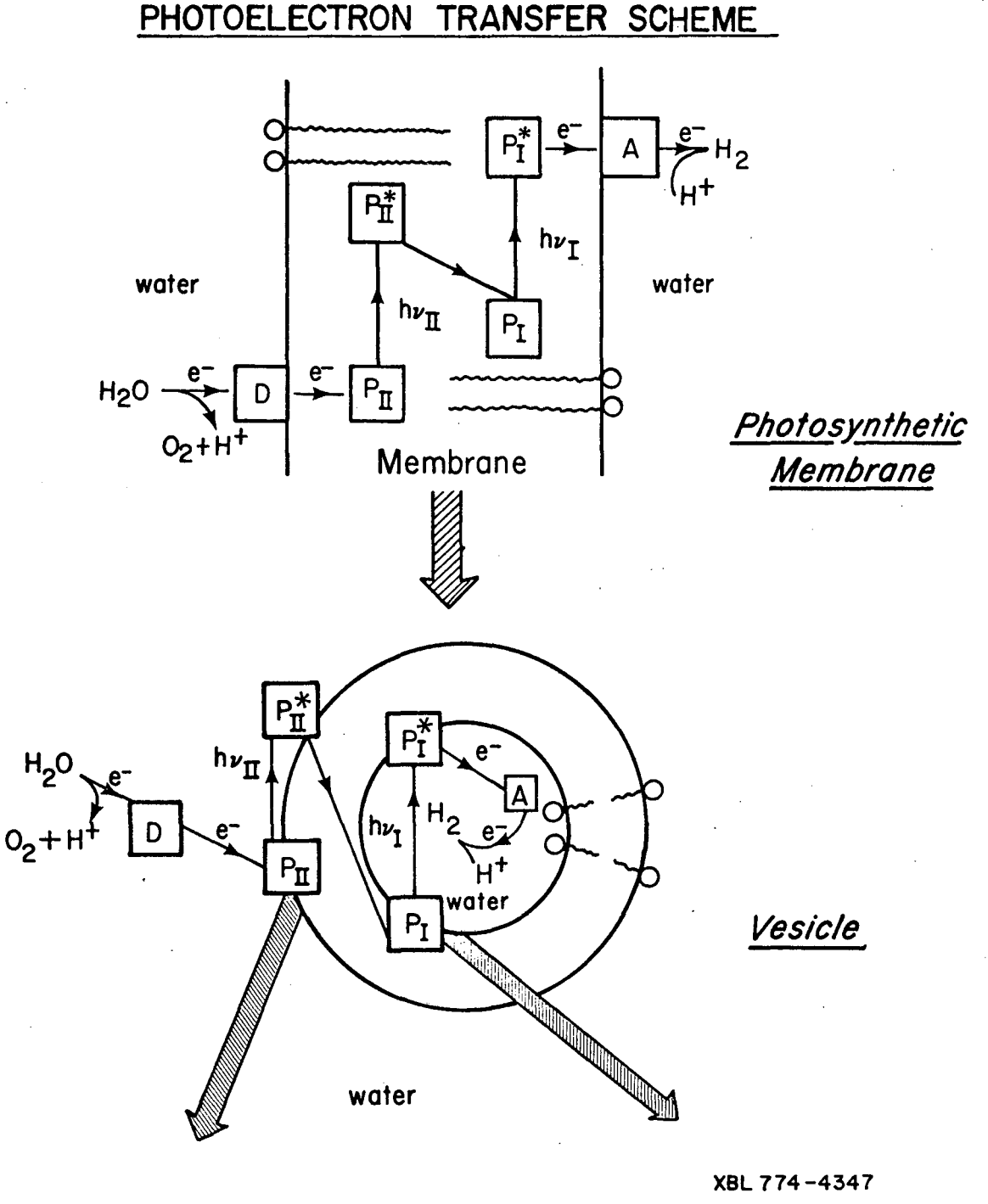

Figure 3.
Photosynthetic electron transfer scheme (vesicle)

PHOTOELECTRON TRANSFER SCHEME

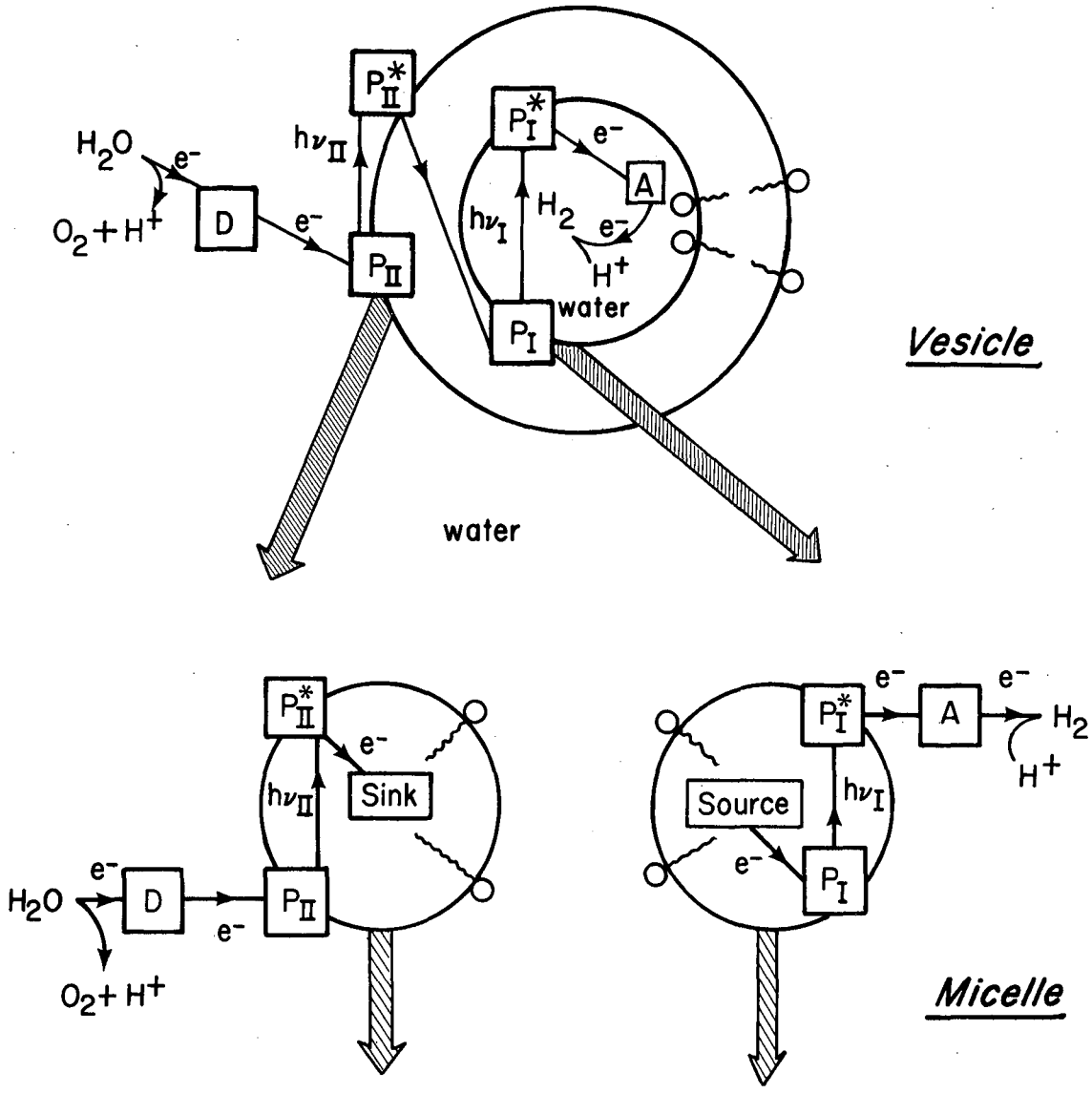

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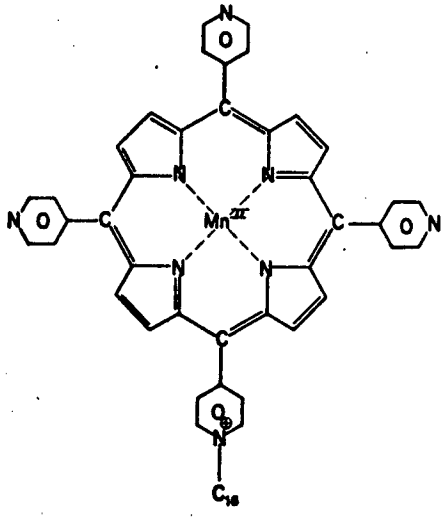
Figure 4.
Photosynthetic electron transfer scheme (micelle)

in one micelle for PS II would in the other micelle be the source for PS I. Thus we can carry out the two processes in two separate experiments and ultimately we can couple the two photoprocesses together.

Dyestuff Selection: We have only recently realized that chlorophyll is essentially a detergent dyestuff with a hydrophilic head and a hydrophobic tail. The important thing about a micelle of this type is that the hydrophilic head of the dyestuff remains on the water interface, while the hydrophobic tail dissolves into the hydrophobic interior of the micelle. We have sought more stable synthetic systems as surfactant dyestuffs, and one relatively easily available chlorophyll analogue which has the capability of being transformed into a surfactant material is tetrapyridyl porphyrin (Fleischer) shown below:



Tetrapyridyl porphyrin, mono C_{16} quaternized derivative

If we quaternize one of the pyridine nitrogens with a C_{16} chain, we create a

surfactant porphyrin. There are, of course, many other possible surfactants similar to this, but we have the most material of this porphyrin now available for experiments.

Our method of operation is to place the surfactant dyes on the synthetic vesicles (or micelles) and try to determine whether or not electron transfer from or two the excited states of these dyes can occur. This had to be an indirect measurement (fluorescence quenching) as we really had no easy electrical or chemical way of measuring single photoelectron transfer. The data for a model system for photoelectron transfer is shown in FIGURE 5 (Frank). We measured the quenching of fluorescence of the sensitizing dye by anthraquinone sulfonate which is a water soluble quinone which has no excited state able to take energy from the porphyrin. The excited state of the anthraquinone is much higher than the excited state of the porphyrin, which absorbs at somewhere around 6000 to 8000 A. There is no way in which quinone can quench the porphyrin fluorescence by energy transfer, and the quenching can occur only by electron transfer. Anthraquinone is a good electron acceptor so we thus have an indirect means of measuring photoelectron transfer by the quenching of the fluorescence of the porphyrin in the phospholipid vesicles using anthraquinone in the water phase. The quenching constant for the porphyrin in a homogeneous medium is shown in the bottom curve of Figure 5. By using as solvent 60% acetonitrile in water, which can dissolve both the porphyrin and the anthraquinone, we were able to measure porphyrin quenching by the anthraquinone as a function of concentration. We then measured the slope of the line to determine the quenching constant for the anthraquinone on the porphyrin in homogeneous medium. In this case, no phase boundaries are present, with everything in solution in a mixed solvent, which resulted in no micellar formation.

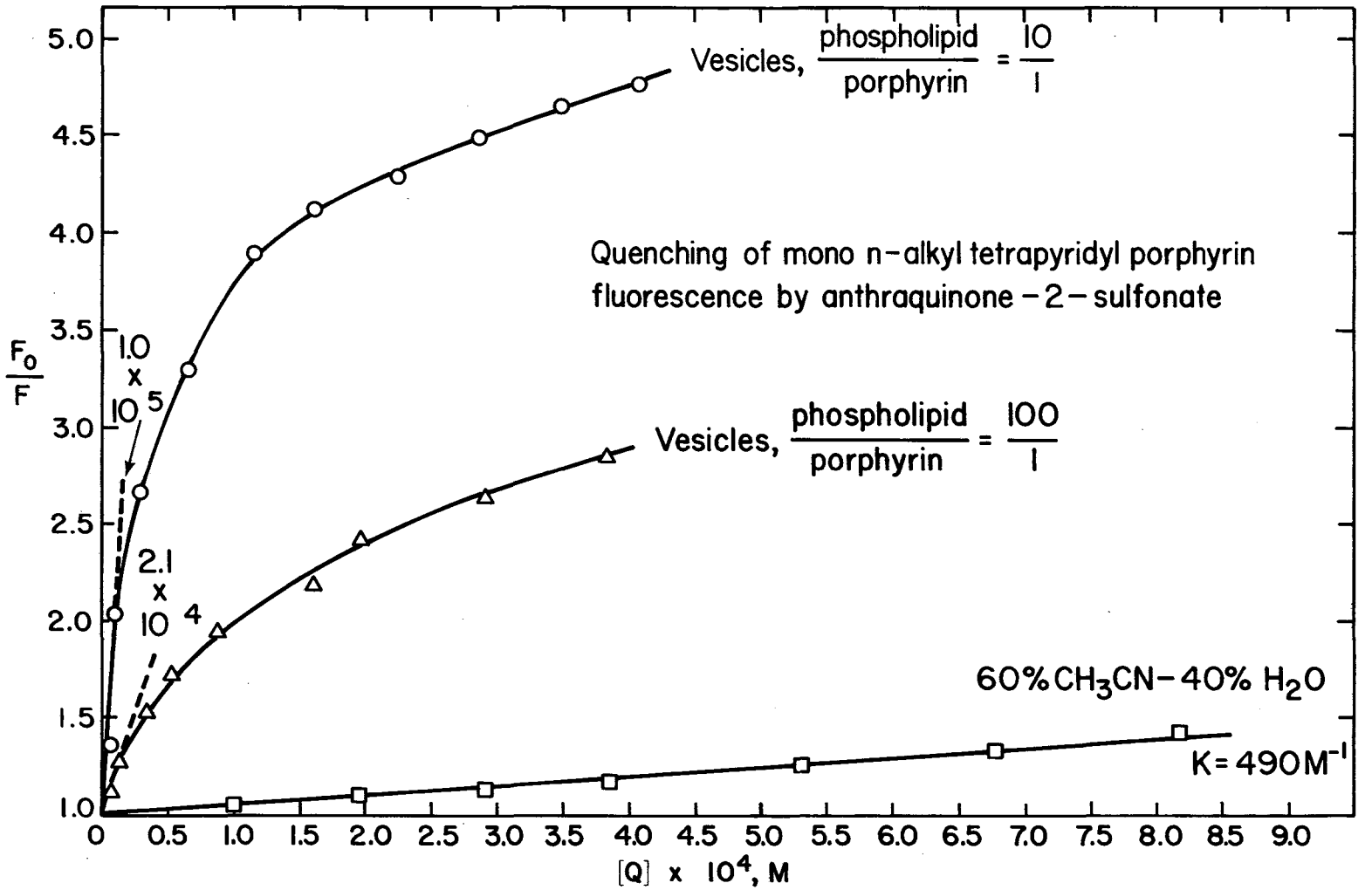
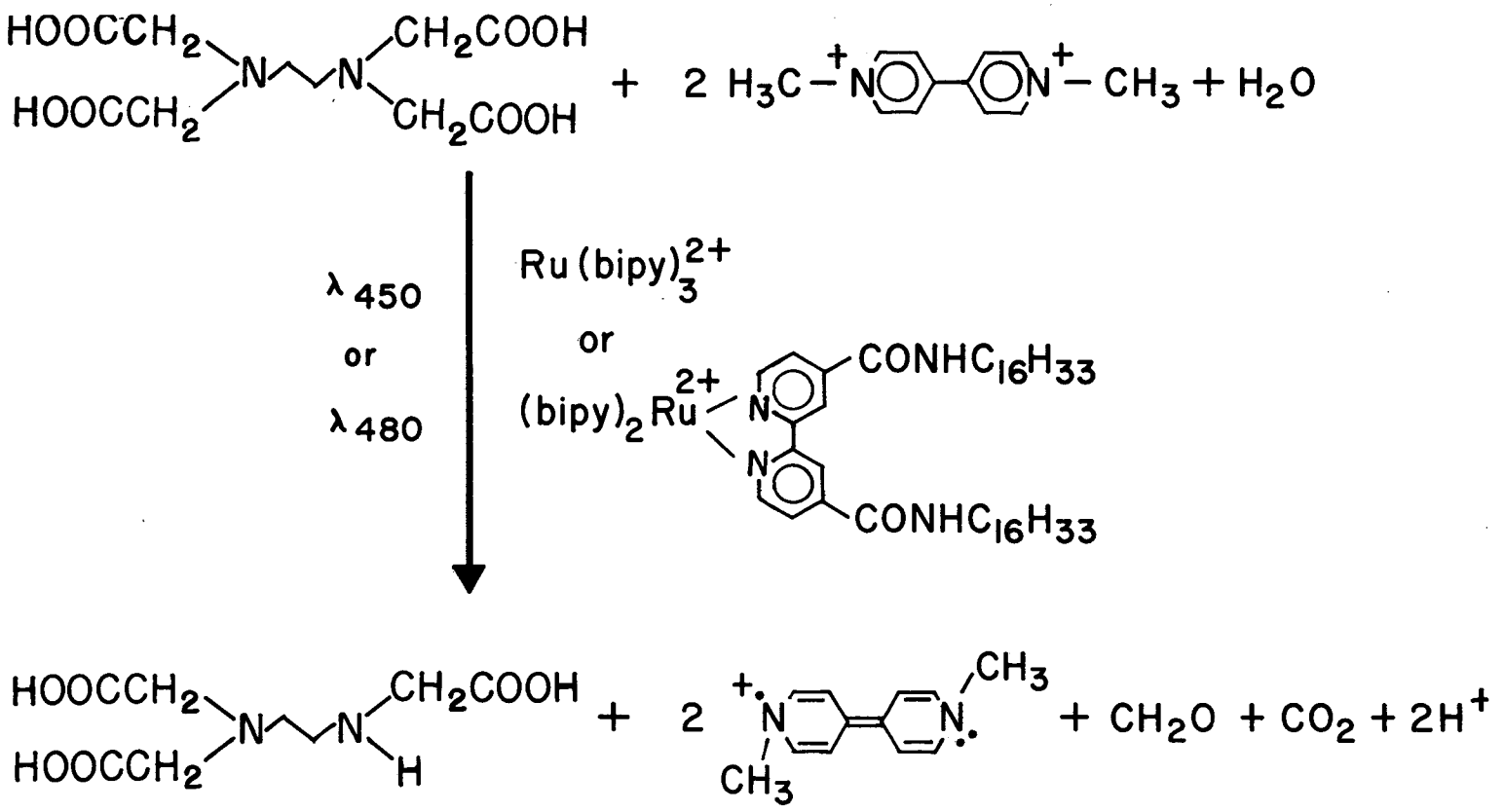


Figure 5.
Homogeneous and heterogeneous quenching

If the porphyin is inserted on vesicles so that it is at the face of a phase boundary, and the quenching constant then measured, it is possible to see that the quenching constant has risen from 490 to $\sim 10^4$; if the phospholipid to porphyrin ratio is decreased from 100:1 to 1:1 (the porphyrin concentration is higher), the quenching constant then rises to 10^5. I took this to mean a confirmation of the original idea, that the excited porphyrin could transfer electrons to a quinone best if the porphyrin is at the phase boundary and the quinone in the water layer adsorbed to that phase boundary.

Photoelectron Transfer

It would be much better, however, if we had a more direct way of measuring photoelectron transfer. There was a report in the literature (Matsuo) by some Japanese photochemists who had sensitized the photoxidation of ethylenediaminetetraacetic acid (EDTA) with methylviologen, that is, photosensitized an electron transfer from EDTA to methylviologen. The chemistry of this direct photoelectron transfer is shown in FIGURE 6. As you can see, electrons are transferred from EDTA to methylviologen, resulting in the oxidation of part of the EDTA, from $-\underset{\underset{N-H}{|}}{N}-CH_2-CO_2H$ and water to CO_2, CH_2O, $2H^+$ -N-H with the two electrons resulting from that oxidation transferred to methylviologen to give two free radicals with a blue color, which is very easily detected. This reaction was first done using the tris(bipyridyl)-ruthenium^{II} complex as the sensitizer. In water solution the quantum efficiency of this reaction is very poor. If, however, we make this sensitizer into a surfactant dye, we could try the same reaction at a phase boundary.



ΔG°~ + 20 Kcal per mole of EDTA

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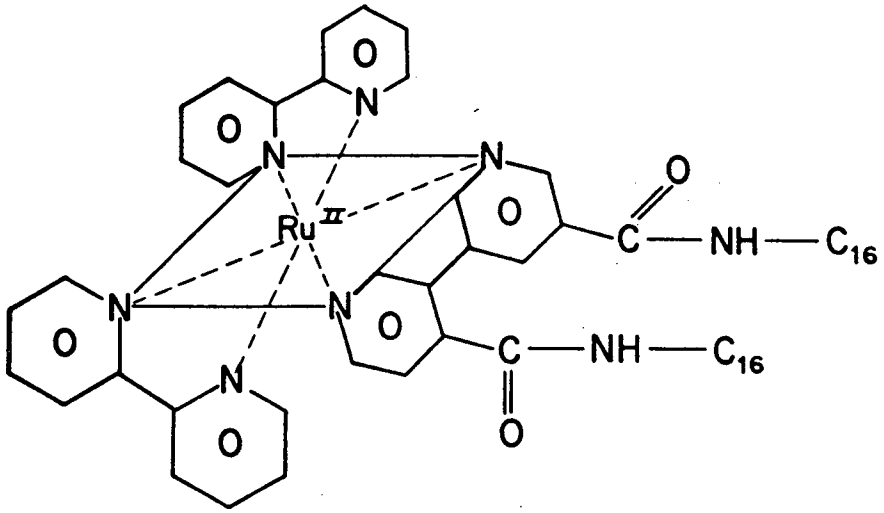
Figure 6.
Photosensitized reduction by methylviologen and EDTA



Surfactant ruthenium complex sensitizer

We constructed vesicles with EDTA on one side and methylviologen on the other, with sensitizers on both vesicle surfaces; see FIGURE 7 (Ford). We first mixed all the vesicle components in an organic solvent--the ruthenium complex together with the EDTA which would go into the spherical liposome. Then the mixture was injected into a large volume of aqueous buffer solution. This produces the vesicle with all its components in the proper place. The ruthenium complex, being the surfactant is on each surface of the vesicle; the EDTA , being water-soluble, is in both water phases (Figure 7) and is removed from the external water phase by gel filtration. At first we thought we would need in the membrane both electron

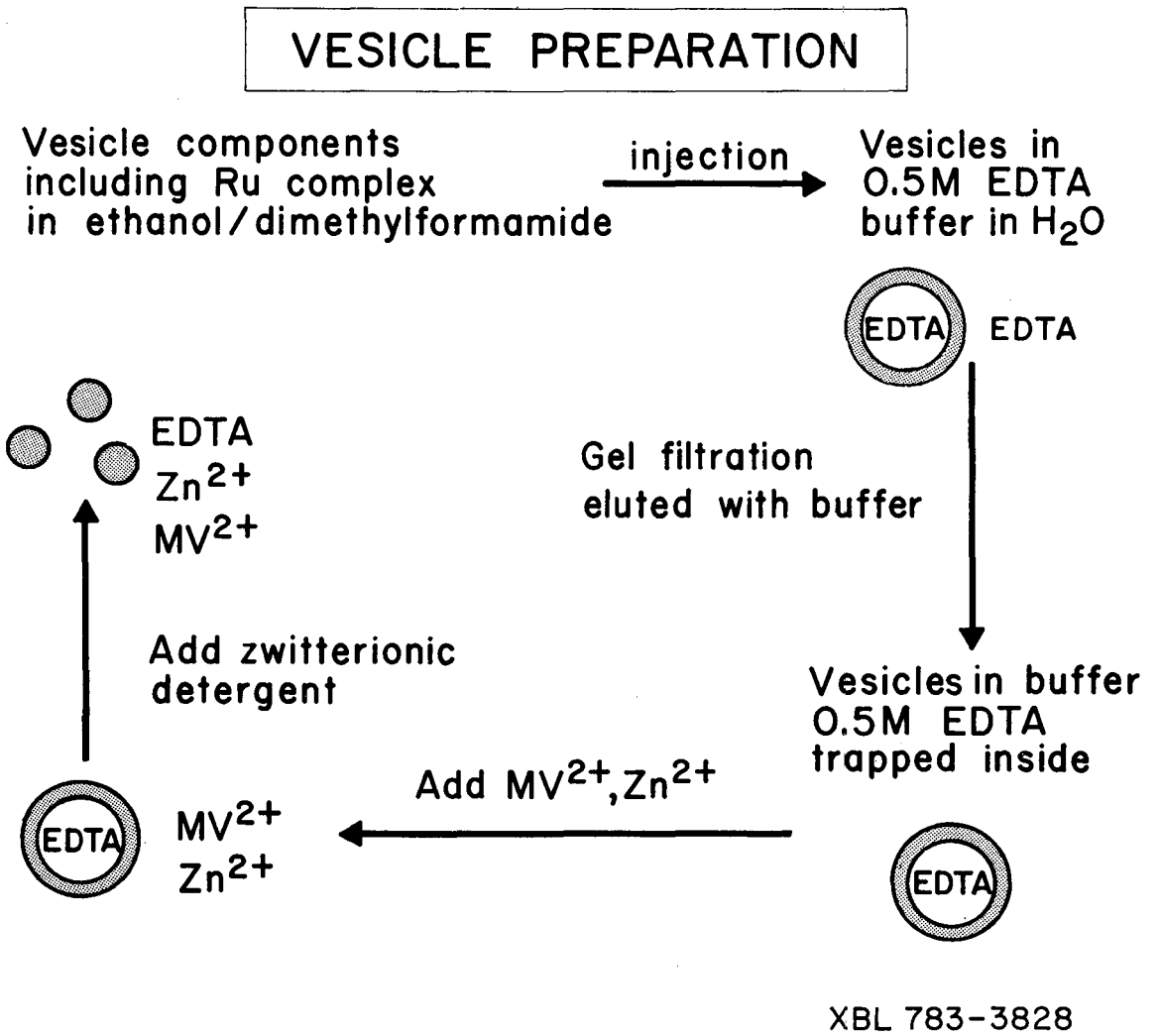


Figure 7.
Vesicle preparation

and proton carriers, that is, a quinone and decarborane, respectively, but we gradually reduced the number of membrane components by taking the carriers out, with the result that the reaction still proceeded (FIGURE 8).

As mentioned above, we first construct the vesicles with EDTA on both the inside and outside. By passing the initial vesicle suspension through a gel filtration, we removed the EDTA and any other small molecules from the outside environment, leaving the vesicles in buffer with EDTA on the inside only (Figure 7). We then added methyl viologen and zinc on the outside of the vesicle, and then, as a further control, we destroyed the vesicles with a zwitterion detergent, which breaks up the vesicle, releasing the methylviologen, the zinc ion and the EDTA into a homogeneous solution.

The photochemistry of the various preparations is shown in Figure 8. In the lower left you can see the photochemistry when EDTA is inside and the methylviologen and zinc are on the outside of the vesicle. The zinc is added on the outside to complex any of the EDTA that might leak out of the membrane. IN the presence of zinc, the EDTA is not oxidizable, it is all bound by the zinc, and there is no reaction at all as shown in the upper right portion of Figure 8. When the detergent has broken up the vesicle so that the EDTA and the zinc can combine, no reaction at all takes place as shown in the lower right. There is very good electron transfer from the EDTA inside the liposome to methylviologen on the outside as shown in the lower left of Figure 8.

We have thus demonstrated that it is possible to transfer an electron from the inside of the vesicle to the outside with the surfactant dyestuff on both sides of the vesicle surface and without additional carriers in the body of the membrane.

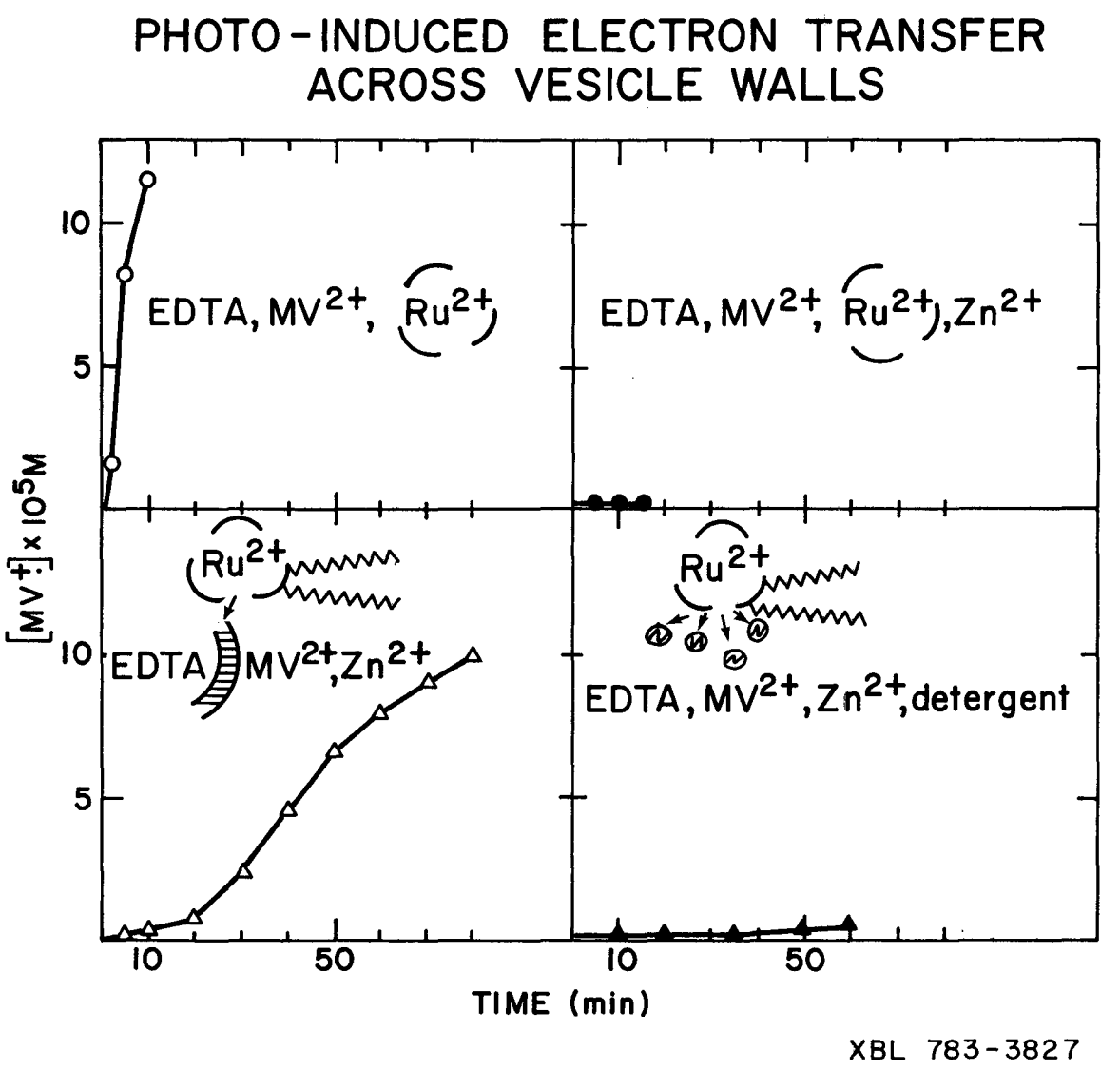


Figure 8.
Photoinduced electron transfe.
across vesicle walls

Electron Exchange across the Membrane. I want to examine in a little more detail what I think the reaction may be, keeping in mind that the membrane contains no electron or proton carriers, just the sensitizer and the phospholipids. The difference between the fast reaction (∇) and the slow reaction (Δ) is shown in FIGURE 9. The fast reaction involves a surfactant electron acceptor (HV) which is isoelectronic with the bulk viologen. Where we have only the dyestuffs on both sides, with methylviologen on the outside of the vesicle and EDTA on the inside, the reaction is relatively slow (Δ). If, instead of placing methylviologen only in the water, we place a surfactang viologen on the liposome as well, the reaction goes much faster. The sensitized electron transfer goes from excited surfactant sensitizer to surfactant viologen acceptor and there is a rapid electron exchange between the reduced surface viologen and the bulk viologen, leaving ruthenium^{III} on the outside surface of the vesicle. Electron exchange across the membrane with ruthenium^{II} on the inside surface of the vesicle then takes place. This electron exchange is very rapid and the inner Ru^{III} then oxidizes the dissolved EDTA, thus resulting in a transfer of electrons through the membrane from EDTA methylviologen.

I had difficulty in believing that the transmembrane exchange, as fast as it is, did not have another quantum involved, one to transfer an electron to the viologen and the other to produce the transmembrane exchange between ruthenium ions. It seems as though it should be a two quantum process. FIGURE 10 shows that the rate is linear with light intensity and therefore the process is not biphotonic. The second electron transfer through the membrane is the simple electron exchange between the two ruthenium complexes on either side of the membrane, which is another isoelectronic exchange reaction. The reaction sequence is as follows:

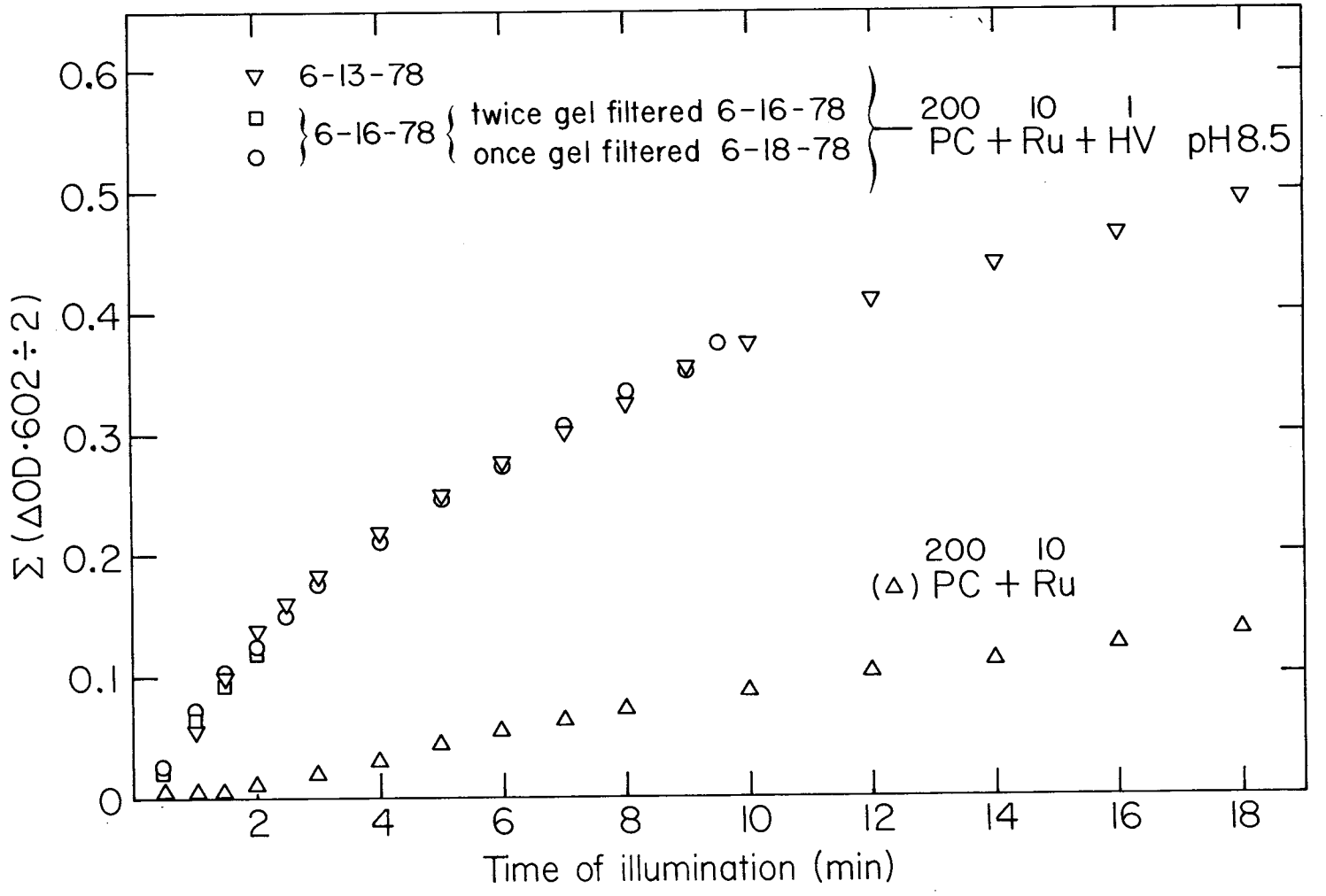


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Figure 9.
Factors in photoinduced electron transfer across vesicle walls

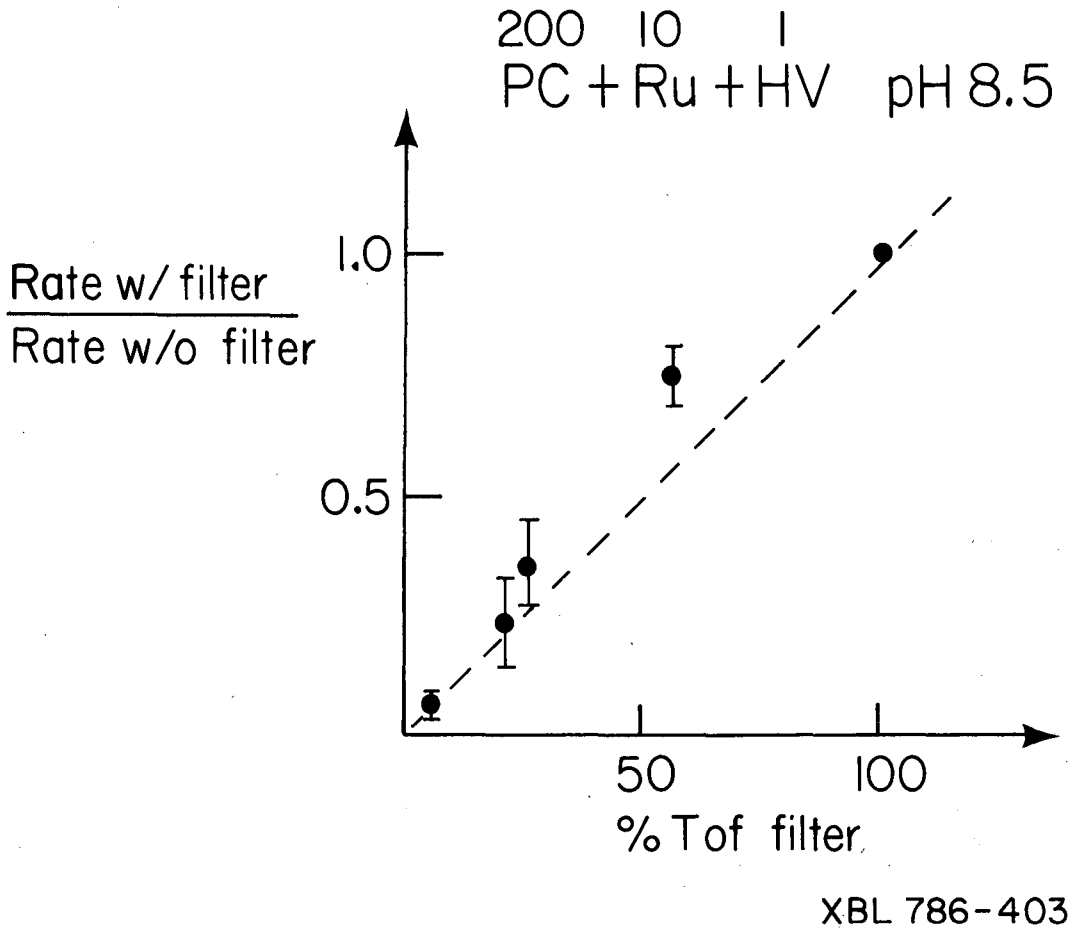


Figure 10.
Light intensity dependence of photoinduced electron transfer

$$Ru^{II}\sim\sim)_o + h\nu \longrightarrow Ru^{II}\sim\sim)_o^* \quad (1)$$

$$Ru^{II}\sim\sim)_o^* + V\sim\sim)_o^{++} \longrightarrow Ru^{III}\sim\sim)_o + V\sim\sim)_o^{+} \quad (2)$$

$$V\sim\sim)_o^{+} + M\text{-}V_{w_o}^{++} \longrightarrow V\sim\sim)_o^{++} + M\text{-}V_{w_o}^{+} \quad (3)$$

$$Ru^{III}\sim\sim)_o + Ru^{II}\sim\sim)_i \longrightarrow Ru^{II}\sim\sim)_o + Ru^{III}\sim\sim)_i \quad (4)$$

$$Ru^{III}\sim\sim)_i + (EDTA)_{w_i} \longrightarrow Ru^{II}\sim\sim)_i + (ox\text{-}EDTA)_{w_i} \quad (5)$$

Reaction (3) proceeds because of the high concentration of the bulk methyl-viologen ($M\text{-}V_{w_o}^{++}$) in the water phase <u>outside</u> of the vesicle. Reaction (5) proceeds because of the high concentration of the bulk $(EDTA)_{w_i}$ in the water phase <u>inside</u> the vesicle. Reactions (3) and (4) are both isoelectronic exchange reactions on or through the vesicle and membrane.

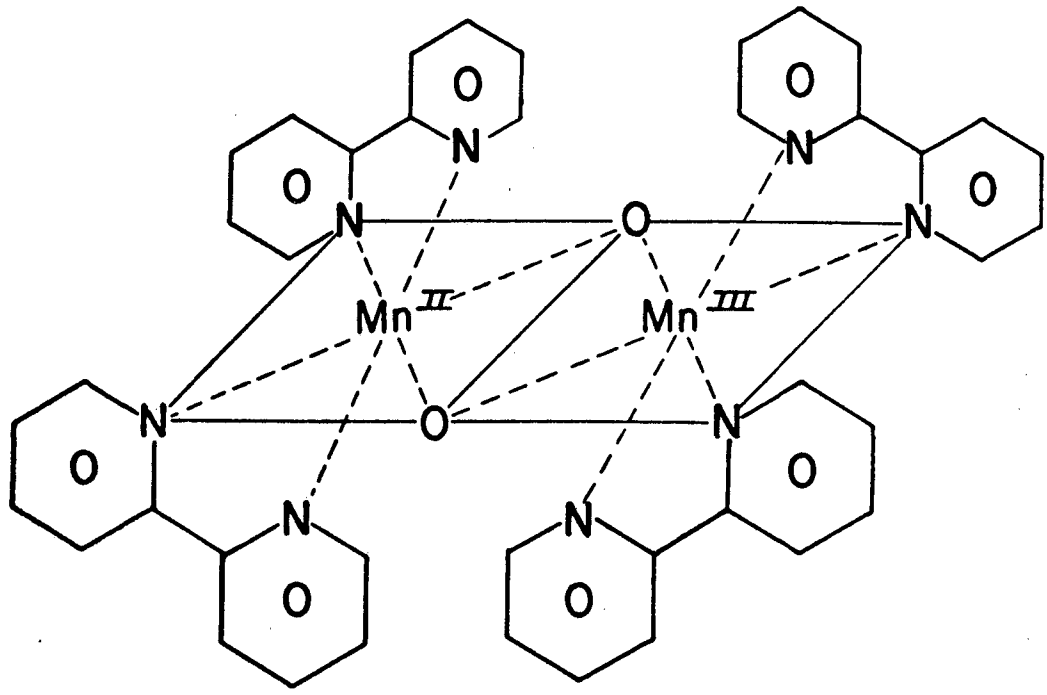
This completes the demonstration that we can transfer photoelectrons through a lipid membrane. At this point we did not really require a quinone carrier. However, eventually we will probably require a quinone electron carrier because a practical device will require a much thicker membrane, and the same thing may be said of the proton carrier.

Having made this demonstration, how can we use this experimental fact to help us design a practical, functional "synthetic" chloroplast? We know that reduced methylviologen in the presence of platinum catalyst will produce hydrogen (Lehn), so in effect we have one-half of the required system separately already. This is not a natural system to be sure. What we need to find is another vesicle to generate oxygen and the hydrogen donor. If we try to encompass two quantum acts on two different vesicles, instead of both quantum acts on one vesicle, and then couple the two different vesicles together, probably via quinone-hydroquinone system, we will be able to create artificially the equivalent of a natural system. In the laboratory we are familiar with the hydrogen evolving system in the natural chloroplast which is accomplished by an iron-sulfur protein (hydrogenase). I think that a synthetic analogue will be available one day soon. Meanwhile, we can fulfill the hydrogen-generating function with a viologen-platinum system or even a soluble rhodium bipyridyl complex.

Manganese Requirement for Photosynthetic Oxygen Production

The other side of the chloroplast requirement is some kind of manganese compound. Manganese is essential as a donor system to move the electrons from water and generate oxygen by photosystem II. What that manganese complex is, nobody knows as yet. In fact, for many years we have been seeking evidence for the nature of the critical manganese. Since it is a four electron process that we have to achieve for oxygen evolution, it seems that we should have at least two manganese atoms involved. We therefore synthesized a binuclear manganese complex bridged by two oxygen atoms.

We thought it might be possible to produce the Mn^{IV}-Mn^{IV} compound by photo-electron transfer of four electrons, two from one manganese atom and two from



the other. The IV-IV compound might be expected to be unstable and decompose into molecular oxygen and regenerate the II-II compound, with this sequence of events ready to repeat. But the binuclear manganese compound failed to generate oxygen. (Cooper). However, the fact that we had this compound available in the laboratory was a very important bridge on the next step.

As I said earlier, we spent many years looking for the manganese complex, and the binuclear compound was one of the guesses. The question

remained, however, what methods can we use to find out what the manganese compound is? Every time we tried to extract the manganese from the chloroplasts, it came out as manganous ion, which indicated that the manganese must be a very loose protein-bound material. What is the environment in the chloroplasts for the protein-bound manganese? Since it is not possible to extract the material intact, because the manganese is so loosely held, how can we explore it? Only one method seemed possible, which was spectroscopy on the fresh chloroplast material. To look for manganese in natural material, particularly when there are only a few manganese atoms for each 500 to 1000 chlorophyll molecules, is not an easy task. However, during the past few years a special spectroscopic method has been developed which made this a possibility. That method is the Extended X-ray Absorption Fine Structure (EXAFS) of manganese atoms, that is, the scatter function of X-ray fluorescence which results from absorption of a high energy gamma ray which is created on the SLAC Linear Accelerator at Stanford. Its high energy gamma (or alpha) rays beamed into chloroplasts excite the manganese. The manganese then fluoresces, and the scattered fluorescence light interferes if there are neighboring atoms close by, very much like an x-ray interference pattern (radial distribution from a crystal powder pattern). In this case only manganese responds when the proper alpha rays are used i.e., those corresponding to k shell absorption for manganese. Thus, with the EXAFS spectroscopic technique it is possible to look at the manganese atoms in the chloroplast even when only a few of them are present in the complex mixture.

The manganese absorption and scattering of photons made on the linear accelerator as they enter the sample are shown in FIGURES 11a and 11b (Klein). The edge absorption (Figure 11a) is characteristic of

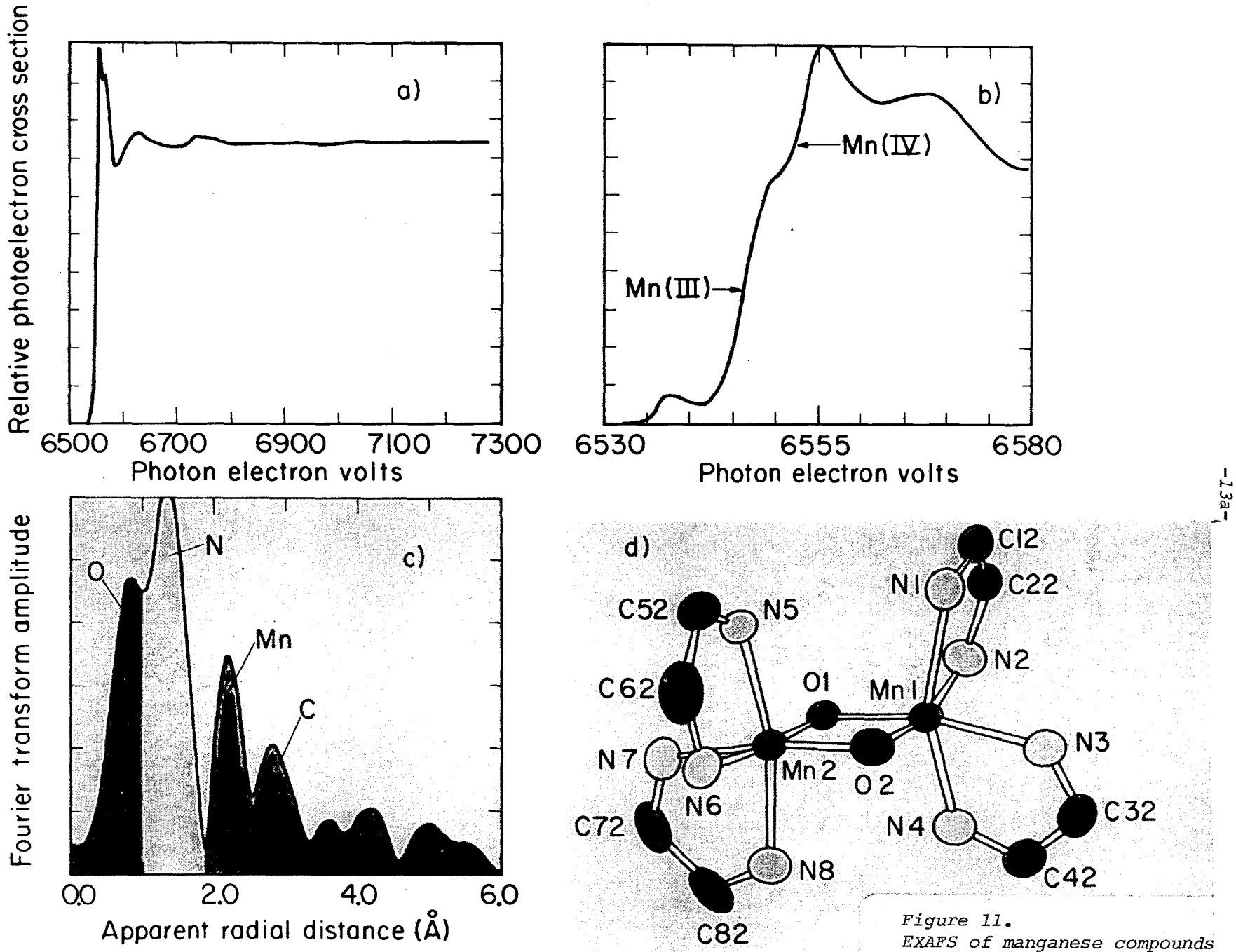


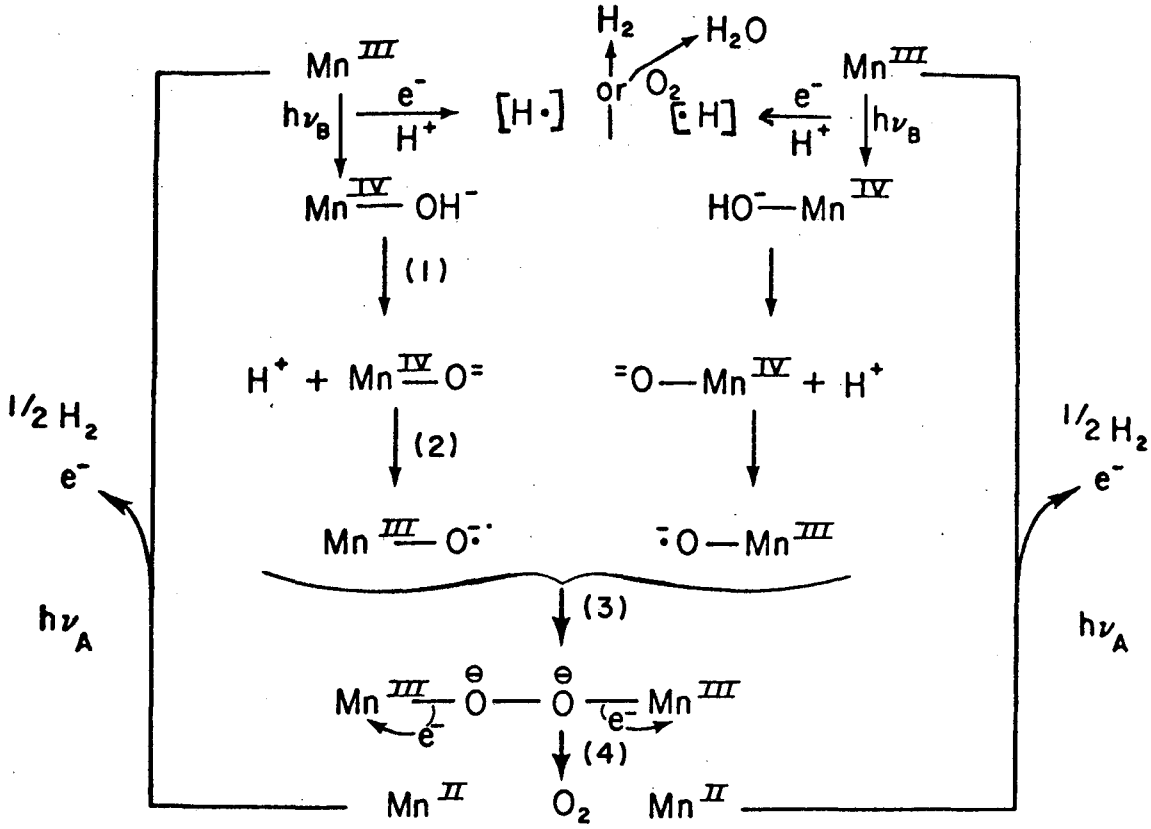
Figure 11.
EXAFS of manganese compounds

manganese atoms and identifies the atom scattering pattern, the extended fine structure (Figure 11b) is due to the environment around them. Only manganese will show absorption at this energy. When you look at this absorption band, you are looking at manganese absorption. The fine structure of the absorption edge (Figure 11b) is the result of interference of the fluorescence which is produced by manganese upon the absorption of those high energy photons. By analyzing the interference pattern, we can determine the environment around each manganese atoms. The radial distribution for the manganese binuclear compound mentioned earlier is shown in Figure 11c. Here are two manganese atoms at ~2.7 A with two oxygen atoms between them and four nitrogen atoms on the outside. That was our model, or calibration, compound. The zero point is one of the manganese atoms and all the atoms close to it are plotted. The closest are the oxygen atoms, then the nitrogen atoms, and then the other manganese atoms. The important thing to recognize is that the very large peak in Figure 11c, about 2.7 A, is in a position corresponding to the distance between these two manganese atoms.

If we perform the same experiment with real live chloroplasts (oxygen producing chloroplasts) instead of "synthetic" chloroplast materials, a very similar result occurs. The nearest neighbor manganese peak is at about the same place, so you know the manganese in the chloroplast is a cluster of at least two atoms and that they are ~2.7 A apart. This is an important piece of information as it is the first time we know for sure that the manganese atoms in the chloroplast exist at least in pairs at about ~ 2 A apart. This experiment gave us the information that we could say for the first time with confidence that the oxygen producing unit of the chloroplast is at least two manganese atoms. We can now hope with more

confidence to find a compound that will produce oxygen. the EXAFS experiments indicate that we should get at least two manganese atoms together.

I now want to tell you about an incomplete but interesting experiment. If we construct the vesicle that I described a moment ago, and instead of surfactant ruthenium compound we make it with the manganese surfactant pyridylporphyrin without anything else in it, the surfactant manganese upon mild illumination goes to the Mn^{II} oxidation state almost immediately. It is reduced upon illumination from Mn^{III} to Mn^{II}. It is difficult to understand this result, keeping in mind that the system is open to air and there is nothing else present but the liposome, i.e., the vesicle and the manganese porphyrin. How can we get from Mn^{III} to Mn^{II} in such a system in the absence of reducing agents? The only way I can see is for photoelectron transfer to occur, with oxidation to Mn^{IV} and the Mn^{IV} can then take electrons from hydroxyl (which is equivalent to absorbed water) and come down to Mn^{III}. Two of these manganese oxygen radicals can come together and presumably liberate oxygen and two Mn^{II} as shown.

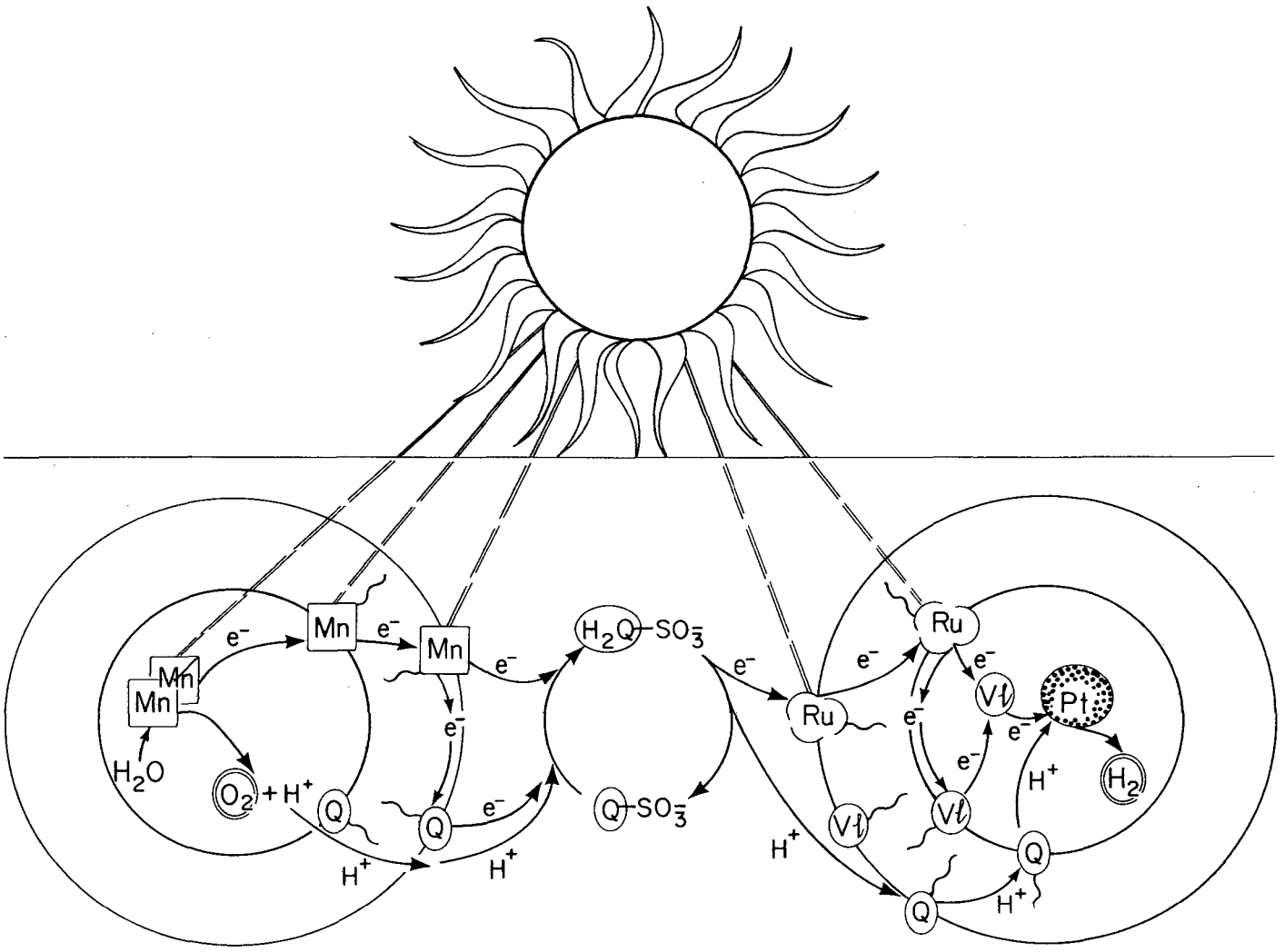


In order that Mn^{II} accumulate, the slowest reaction in the sequence should be the photoreaction $h\nu_B$. So far, we have not found the oxygen, and we may have to modify the vesicle by putting in a water soluble manganese compound that is a surfactant as well, and keep the manganese inside the vesicle at as high a concentration as possible. One might even tie them together in pairs so as to facilitate the dimerization reaction (3) above and accelerate reaction (4).

Structure of Oxygen Generation System

The structure of the still hypothetical oxygen producing vesicle is shown on the left side of FIGURE 12. The structure and composition of the already completed hydrogen vesicle is shown on the right side of Figure 12. The coupling agent between them is a suitably chosen water soluble quinone-hydroquinone redox system. Thus we have a schematic representation of the entire system. Photosystem II is represented by the left vesicle and photosystem I by the right. There is a redox couple such as plastoquinone to connect them. The quinone is the acceptor on the outside of the manganese vesicle and the hydroquinone is the donor on the outside of the viologen-hydrogen vesicle, so that in this way the electron and proton will be transferred from one vesicle to the other, from one reaction site to the other, from photosystem II to photosystem I. Photoelectron transport across a membrane has been demonstrated, and thus the operation of photosystem I with a suitable electron donor can occur.

What remains to be found is the oxygen generating catalyst which in the live chloroplast is at least a dimer of a manganese compound. Just as we have been able to circumvent the need for the natural hydrogenase (an iron-sulfur protein) so it may be possible to reproduce the oxygen generating function in some other fashion. We would, however, retain the ideas of phase boundaries, surfactant sensitizers and electron exchanges already demonstrated. For example, instead of trying to use the manganese compound as both sensitizer and oxygen catalyst, it should be possible to use the ruthenium surfactant system as sensitizer and the water soluble analogue with a platinum oxide surface as the device for accumulating the four electron transfer step intermediates (FIGURE 13).



Schematic for synthetic chloroplasts XBL 7810-4262

Figure 12.
Schematic for synthetic chloroplasts

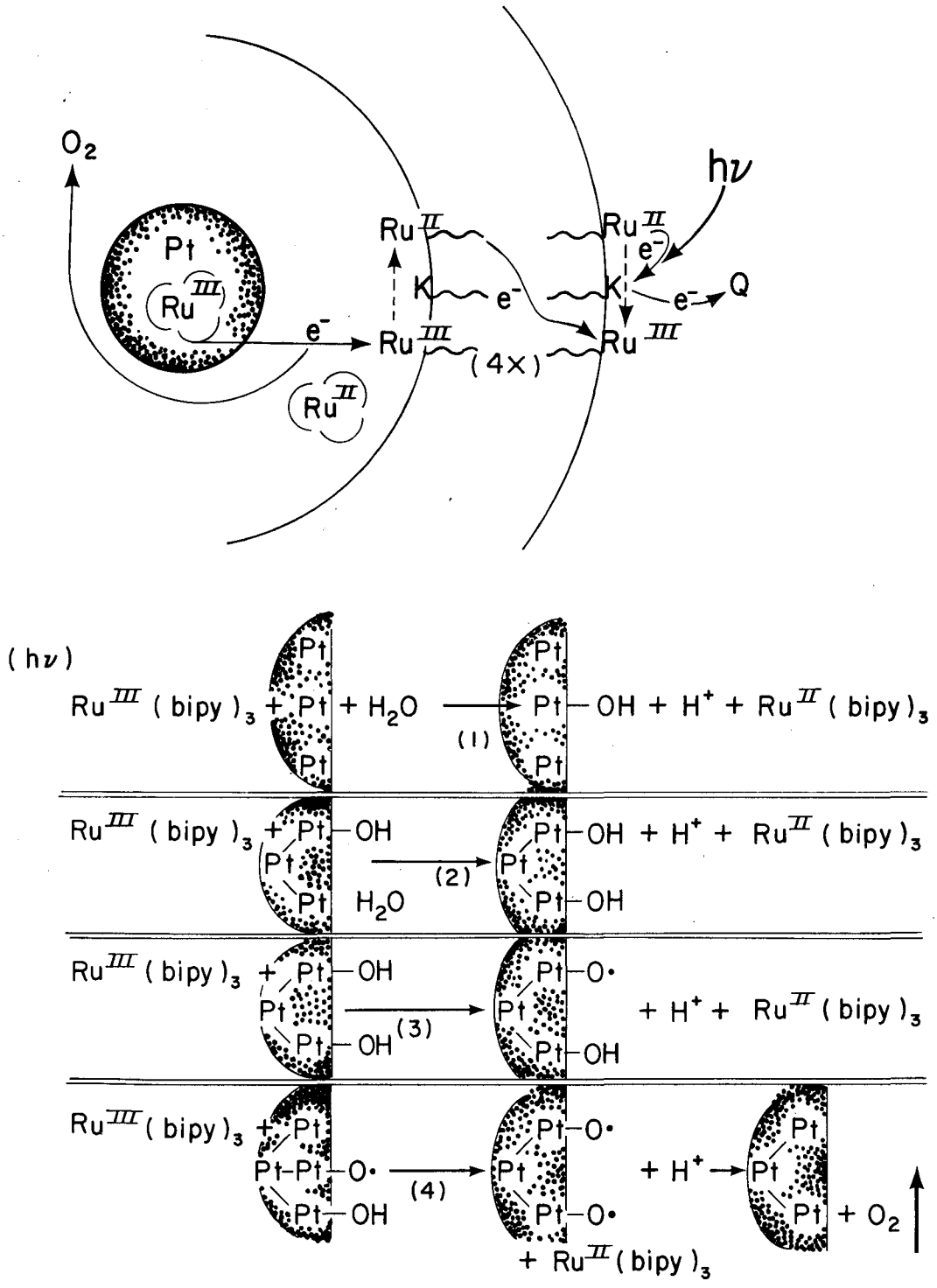
We have already arrived at the stage in which the hollow spheres postulated earlier have been replaced by hollow tubes or fibers built on the same mechanical principles as artificial kidneys or desalinization units. The composition of the fiber will be different and its loading with photosensitizers, electron and proton carriers and hydrogen and oxygen generating catalysts will be similar to the artificial vesicles just described.

Conclusion

I believe we can look forward to the creation of an artificial system for photosynthesis, using the synthetic chloroplasts which have been described. This system will mimic the way in which the green plant takes (four) quanta to generate oxygen on one side and reducing power (either hydrogen or reduced carbon dioxide) on the other side of the membrane. We have extended the experiments to demonstrate directly photoinduced electron transfer from a porphyrin in a micelle to a quinone in aqueous solution by directly measuring the photoreduction of the quinone.

Finally, it is possible to imagine a micellar system in which the photoelectron transfer occurs across the phase boundary, producing the oxidant in one phase and the reductant in the other. This could be followed by an actual physical separation of the phases with the concomitant separation of the potential reactants. These could then be stored separately and be brought together in a suitably constructed physical system to recover the energy of the back reaction in some convenient form and the cycle repeated.

Such systems as have been discussed thus accomplish both of the necessary requirements for a useful solar energy device, namely (i) the



XBL789-4248

Figure 13.
Schematic for oxygen evolution in photosynthesis

capture of the quantum and its conversion to some other energy form and (ii) the storage of that energy for indefinitely long periods with the possibility of its recovery at will in some convenient form. The green plant has always performed these functions in the service of mankind.

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