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Simulating Photosynthetic Quantum Conversion

MELVIN CALVIN

Laboratory of Chemical Biodynamics, University of California, Berkeley, California 94720

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Our approach to the problem of simulating photosynthetic quantum conversion is to study the way in which the living organism achieves many of its physical and chemical transformations. We are trying to select the essentials of what we have learned over the past 30 years of the mechanism of how the living organism achieves the quantum conversion process, i.e., the reduction of carbon dioxide and various other physical and chemical processes, and apply this knowledge to devise synthetic (or artificial) systems to achieve the same result. We have come to these systems and conclusions not as theoretical organic chemists or physical chemists but rather from the point of view of those who are trying to understand how the living organism accomplishes this biological process. Thus, we have found it necessary to devise micellar systems and coordination or complex systems for this purpose, largely because the operation of the natural system suggests it.[1-5]

Our work in biomimetic chemistry began with the relatively limited knowledge we had of how the green plant converts the sunshine into chemical energy. Although we know how the green plant converts carbon dioxide into carbohydrates and hydrocarbons,[6] we do not yet know in fine detail how the quantum is converted into the first stable chemical forms which can perform the various steps involved in CO_2 reduction. We do know, however, that it does involve a two-quantum process: photosystem I and photosystem II. This quantum conversion system involves two separate quantum acts: first (PS II) is an excitation of an electron in one pigment system to an excited state, followed by the electron transfer from this state down through a number of steps, or pigments (plastoquinone, cytochrome *f*, etc.). Eventually the electron reaches a hole left in another pigment system by another quantum (PS I). The excited electron from PS I travels down to a trap, which is probably bound ferredoxin, an iron–sulfur protein,[7] to free ferredoxin and NADP (nicotinamide adenine dinucleotide phosphate) reductase and reduced NADP which then drives the carbon reduction cycle. The process is shown schematically in Figure 1.

In the plant, these two processes or steps are taking place simultaneously in time but are separated in space. In chemistry, however, one could find additionally systems in which these steps would take place in the same space but separated in time. My discussion at this time will be confined to our efforts to set up the physical system in which these two quantum acts are separated in space, so that the oxygen-generating system will be in one place and the hydrogen, or reducing, system will be in another place, rather than two different kinds of chemical steps taking place at different times.

Development of the Concept of Artificial Photosynthesis

I wish to lead you through a sequence of thoughts which will, hopefully, lead to actions which will allow us to construct with entirely synthetic materials a system to accomplish at least one of the two photoprocesses that occur in natural photosynthetic systems. The lamellar, or membrane, system on which are situated protein molecules that contain the pigments involved in the photoprocesses actually performs all of the photochemistry connected with quantum conversion. There are at least two different and distinct sides to these membranes. The current dogma[3,8] states that one of the quantum reactions takes place on one side of the membrane, with the other occurring on the other side. Figure 2 indicates an artificial photochemical cell modeled on one concept of the photosynthetic mem-

Melvin Calvin is University Professor of Chemistry, Professor of Molecular Biology, and Director of the Laboratory of Chemical Biodynamics at University of California, Berkeley. He was born in St. Paul, Minn., and received the Ph.D. degree from the University of Minnesota in 1935. Following 2 years of postdoctoral research at the University of Manchester, he joined the faculty at Berkeley. His research covers a wide spectrum of interests, including such diverse topics as metal chelate compounds, the molecular basis of learning, and solar energy conversion. Dr. Calvin was awarded the Nobel Prize in Chemistry in 1961 for his establishment of the sequence of chemical reactions involved when a plant assimilates carbon dioxide.

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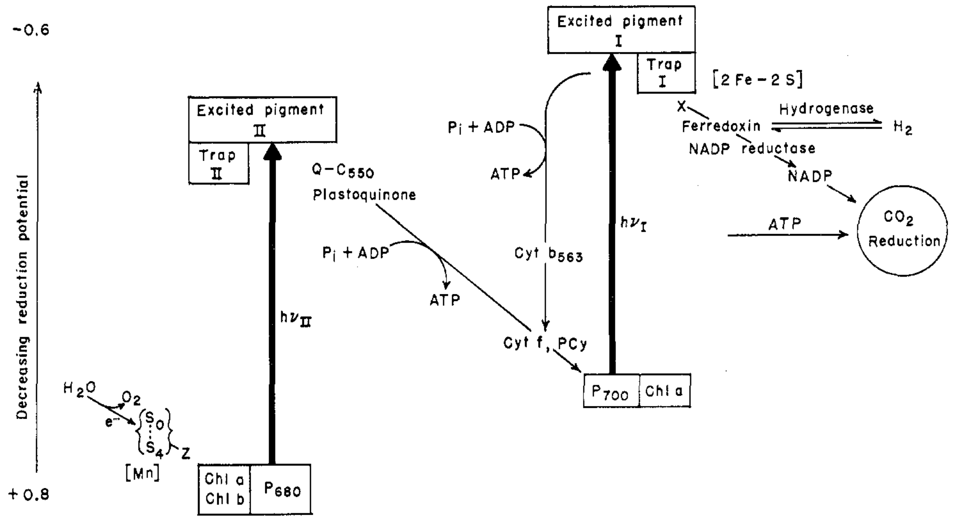

Figure 1. Photosynthetic electron transfer scheme.

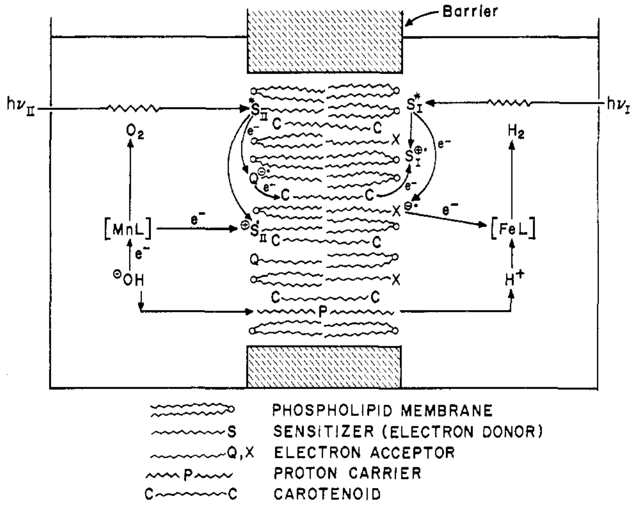

Figure 2. Photochemical cell modeled on photosynthetic membrane.

branes.[9] It represents a bilipid membrane into which two different sensitizing centers (two different dyestuffs) have been inserted in some fashion, one for the first quantum and the other for the second, PS I and PS II. On that bilipid membrane the two different sensitizers and also two different electron donors and acceptors are placed. The quinone, for example, would be an electron acceptor and the manganese complex system could be the electron donor. We would then have to transfer the electron from one side to the other side through a conduction system so that it could be released to make hydrogen or reduced carbon dioxide. Work recently reported[10] has indicated that this system might be able to reduce CO_2 as well as make hydrogen. When the CO_2 is absent, hydrogen is generated on one side of the membrane and oxygen on the other. Enough new information is now available to make me hope that it will be possible to design complexes which will also hold the CO_2 and in which the CO_2 reduction can occur as well. These complexes might be iron–sulfur compounds whose structure has already been elucidated.[11]

On the oxidation side of the membrane, on the other hand, the primary donor is probably a manganese compound of some type, but we do not yet know the environment of that manganese.[12,13] We have made many efforts to isolate that manganese compound, but these have resulted in its decomposition, and all that remains is the isolation of simple manganous ion. We must devise ways of exploring the nature of that manganese compound without destroying it, perhaps by leaving it intact in the plant environment. We are currently using photoelectron spectroscopy as a method for detecting the manganese and to try and define the nature of the ligands around it, i.e., the nature of its environment. Probably within a year or so, using the technique of photoelectron spectroscopy, we will be able to define the nature of the specific ligands for manganese and also the nature of the fields around it. There may also be other elements which could be important in this photoprocess, such as ruthenium,[14] which might generate the positive site, but in a different environment. The ruthenium monolayer experiment[15] failed of replication in several other laboratories in the world.[16,17]

Chemistry of Artificial Photosynthesis

The scheme shown in Figure 3 contains all the necessary elements of functionality to achieve the two photoprocesses required for quantum conversion. I wish to discuss the evolution of the sequence of events which has enabled us to conceptually and physically dissociate this system into accessible parts with the chemistry we know today. Eventually, of course, the complete system must be assembled, but with our present-day chemistry it seems better to resolve the entire system into simpler components and perform each of the reactions separately.

At the top of Figure 3 is the photoelectron membrane transport system with the two quanta PS II ($h\nu_{II}$) and

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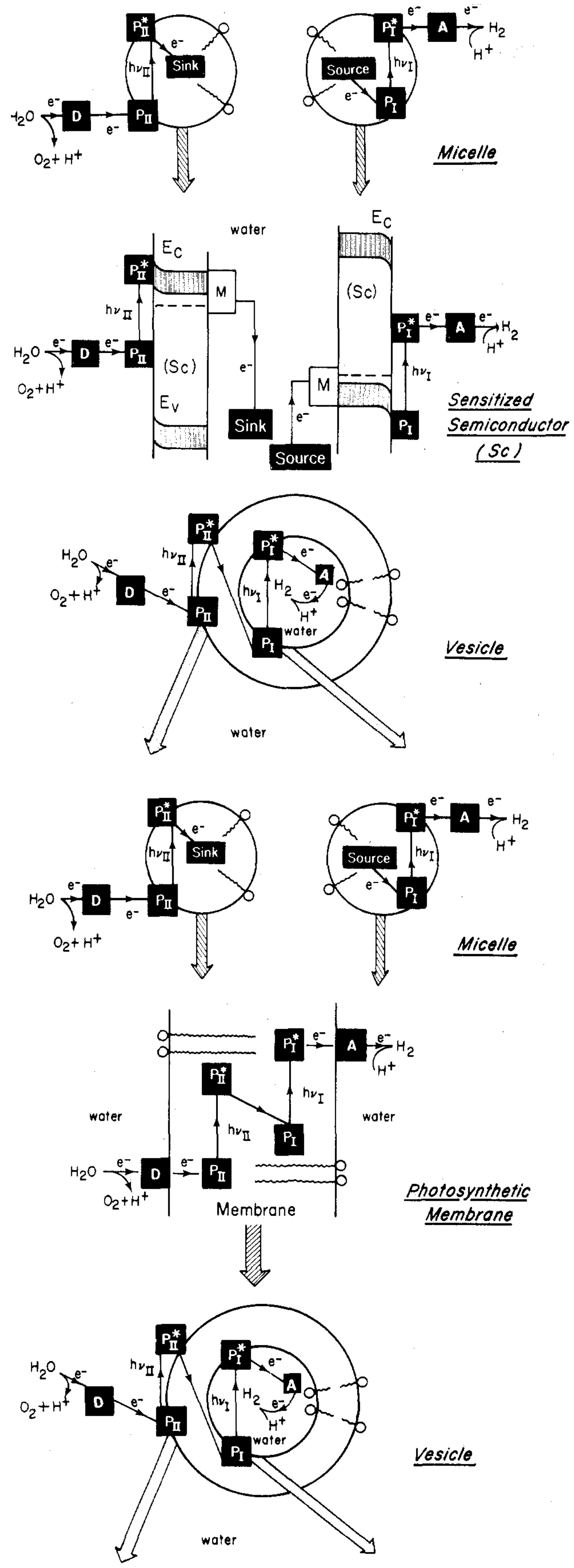

Figure 3. Photoelectron transfer scheme.

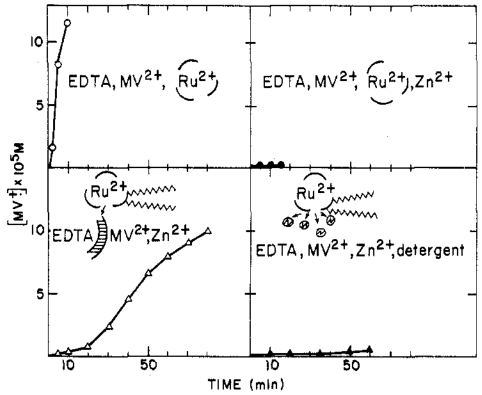

Figure 4. Photoinduced electron transfer across vesicle walls.

PS I ($h\nu_I$) representing the schematic membrane. As you can see, the electron must come from a donor (which is probably manganese) and eventually flow through the membrane to the acceptor (which is probably iron) on the other side to give hydrogen or eventually reduced carbon dioxide. We could try to make the membrane as a flat membrane on the surface of the water, or between two water layers, which would be very difficult.[3,18-23] We have, therefore, come to the simplification of rolling up the membrane into a sphere to produce what has been called a liposome or vesicle—vesicle when the membrane is artificial and liposome when it is constructed of the components of a natural membrane.[24]

You can see that the liposome, or vesicle, has two surfaces—one for PS I and one for PS II. Note that the focus is not on the cavity or local concentration but on the interface between the two phases. This phase boundary is crucial, not so much the size of the hole or the concentrations inside. The oil–water interface between the surfaces is the important factor.

Construction of Micelles.[25] We could attempt to put this system together all at once in a liposome or vesicle with one dyestuff and a hydrogen-generating system on the inside and another dyestuff and the oxygen-generating system on the outside.[26] In order to learn more about the actual mechanics of the system we are trying to take the liposome apart and produce the two surfaces separately, as shown in Figure 3. This is a simpler system than the liposome itself, with one interface on one micelle and the other surface on another micelle, quite separate from each other. We have

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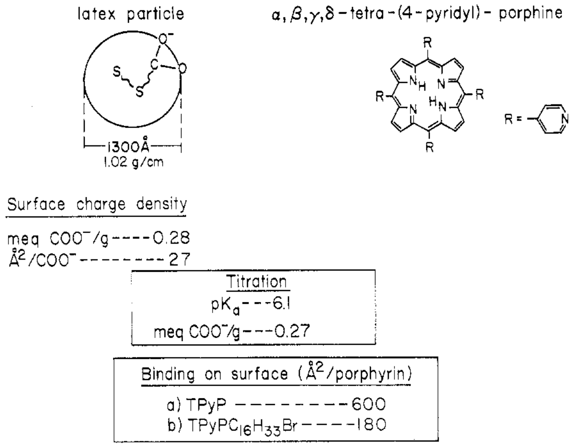

Figure 5. Physical properties of latex particle–porphine system.

also heard of the possibility of making reverse micelles for one or the other of these interfaces, but have not actually tried it ourselves in the laboratory.[27] Our work on micelles has been primarily on ordinary soap micelles in a water environment.[28-30] All our systems have the water environment on the outside and the oil environment on the inside. Now that we know it is possible to construct micelles in the opposite way, we might find it more convenient to insert either the electron sink or the source in the water medium and the sensitizer in the oil medium. This idea will open up new possibilities. Additionally, we are working with micelles and vesicles.[31] We have been able to demonstrate a photochemical electron transfer across a bilipid membrane up a potential gradient. What remains to be done is to introduce the proper oxygen-producing catalyst on the donor side of the membrane and the proper hydrogen-producing catalyst on the acceptor side (Figure 4).

Up until now we have been concerned with simplifying the natural liposome down to the level of two separate micelles to achieve each of the quantum acts separately. We now have the task of selecting a source for one micelle which eventually will be the sink on the other, and one sensitizer for the first quantum act together with a catalyst for the corresponding gas evolution. Another sensitizer, as well as a different source and a different sink, are required for the other micelle. Thus, we could perform the two separate surface acts in two separate surface systems, and eventually put them together. However, even that is complicated, and I would prefer to simplify the systems even further.

Micelles are in constant dynamic change, which is one of the difficulties of using them for this type of work. It is hard to change micellar size, to insert more (or less) porphyrin into the molecules. Therefore, we are trying another system, a cross-linked copolymer of styrene–butadiene–acrylic acid, and materials can be hung onto that particle since it is a stable latex. The latex particles are constructed as shown in Figure 5. The styrene latex particle is about 1300 Å in diameter, with a density of ~1 g/cm^3. Figure 5 also indicates the number of carboxyl groups on the surface, given as milliequivalents per gram, and translated into angstroms squared[32] per carboxyl group, and, finally, the binding of the dyestuff with and without the alkyl pyridinium tail. The binding of the surface of the latex particle corresponds to 600 Å^2 per porphyrin molecule, without any tail, that is, not too many porphyrin molecules are bound. However, when the molecule is modified by the addition of a C_{16} tail (the details of this reaction will be discussed later), a cation is created. The cation and the tail have increased the binding by a lttle over a factor of three. We do not yet know which of these (the cation or the molecular tail) is the effector of the increased binding. A related study on bare polystyrene particles without functional groups and, therefore, incapable of sustaining covalent linkage has been done by others.[33]

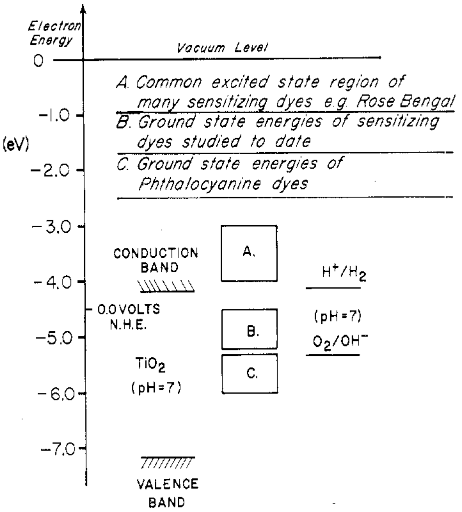

Figure 6. Electron energy diagram for hydrogen and oxygen production.

Dyestuff Selection.[34] Instead of trying to invent a sink and a source quite separate from each other and eventually bringing them together, we have tried to use a semiconductor crystal which has a valence band and a conduction band for the sink and the source.[35] We are also trying to adjust the sensitizer so that the excited state delivers electrons to the conduction band of the semiconductor.[36] If the conduction band is the sink and the valence band of the semiconductor can deliver the electrons to the hole left behind in the excited state of another sensitizer, we can then move from chemistry to physics and still retain the basic ideas of the photosynthetic electron-transfer system involving sequentially a phase boundary, a sensitizer, a sink, another phase boundary, a sensitizer, and a source. Eventually the two systems could be connected with a "wire".

Let me introduce one more piece of theoretical information to remind you of the problem of dyestuff selection. In one case, the excited dyestuff electron will be above the conduction band and in the other case the

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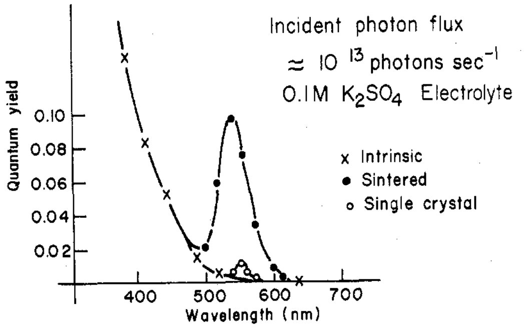

Figure 7. Rose Bengal sensitized ZnO sintered pellet.

valence band electron will be delivered to the vacancy in the excited state of the second dyestuff. The two dyestuffs must therefore be adjusted to match the valence and conduction bands of particular semiconductors. We have also arranged the system so that the potential, shown in Figure 6 with the valence band and conduction bands indicated for each of these steps, is adequate to perform the required chemistry. In addition, the potentials for hydrogen evolution and oxygen evolution are shown. We need dyestuffs in which the excited state is above the conduction band and the ground state is far enough down in potential so that we have a chance of generating molecular oxygen. The choice of dyestuffs is limited to fit the voltage requirement.

Construction of the Sensitized Semiconductor

What semiconductor and what dyestuffs can be used?[37] The first semiconductor we used was zinc oxide, a very common semiconductor and photoconductor; this material is used in photoreproduction systems of various kinds. Some of the results with the ZnO are shown in Figure 7.[38,39] Zinc oxide is not colored, and it absorbs intrinsically only in the ultraviolet region, below 5000 Å, which is not very useful for the visible light of sunshine. Therefore, the ZnO must be sensitized in some way with Rose Bengal. The quantum yield determined by the current through the cell is shown in Figure 7. If the conduction band of zinc oxide is connected through a wire to a platinum electrode on the other side of the cell, a complete circuit is created. Thus one can measure the number of electrons which the absorbed quanta induce to flow through the semiconductor and in the external circuit. The ZnO alone does not show conduction until illuminated in the ultraviolet region. For example, if a single crystal of zinc oxide is sensitized with Rose Bengal (which absorbs at about 5000 Å), it is possible to obtain a higher efficiency at 5500 Å. If, however, instead of a single crystal of zinc oxide a sintered powder (a powder with many faces) is used, that material is then sensitized with Rose Bengal by dipping it in a solution and immediately removing it; the dyestuff becomes adsorbed on the surfaces.

We have now created much surface area, thus raising the efficiency of the quantum conversion in this case by a factor of 5. This increased efficiency is due to the multiple reflections which the light performs before it escapes from the solid surfaces. In other words, there are many surfaces instead of a single surface, and the light gets into the aggregate and does not escape from the surface until it has five times as many opportunities to strike a zinc oxide surface. This system has an overall quantum efficiency of about 10%.

Titanium oxide, another semiconductor with a bigger band gap, has also been used for the identical purpose.[40,41] The titanium oxide does not cease absorbing until the wavelength rises beyond 3800 Å. When the TiO_2 is illuminated below 3800 Å oxygen appears on one side at the TiO_2 surface and the electrons collected by the TiO_2 flow through a wire to the platinum electrode, generating hydrogen at that side. The quantum must be of higher energy than the band gap, i.e., shorter than ~3200 Å, to get very efficient quantum conversion because the band gap is so wide.

We have tried to perform this experiment by sensitizing ZnO with two different dyes. We have so far been able to sensitize the ZnO in the visible range to generate a current (but not to generate gases) by using phthalocyanine, one of the very earliest porphyrin analogues which was found to be useful in studies of this type. The phthalocyanine has the stability necessary to achieve significant energy conversion without loss. The compound is made on the multicrystalline material.[39]

We have yet to construct a semiconductor on the platinum side for the other half of the system, thus making use of the entire solar spectrum. That semiconductor will probably be cadmium sulfide,[41,42] molybdenum sulfide,[37] or some other type of positive semiconductor rather than a negative semiconductor. So far such a semiconductor, which will withstand the acid medium which is required, has not been made, and efforts must be made to synthesize or sensitize and protect a positive semiconductor which will be stable in an acid environment and generate molecular hydrogen without decomposition; perhaps another iron–sulfur based material might even be able to do this.[43]

Photoelectron Transfer across a Phase Boundary

The kind of sensitized semiconductor system which we have so far been able to construct is on the solid-to-liquid phase boundary which accepts the electron from the excited sensitizer. In order to have a photoelectron transfer reaction "live" long enough to perform any chemistry, the electron must be transferred across a phase boundary. (This physical principle has not yet been firmly established.) The electron transfer across the phase boundary seems to me to be *the* essential feature contained in the natural photosynthetic membrane, a phase boundary over which the *excited* electron can move but back across which the ground-state electron cannot.[44] The excited electron is captured on the opposite side of the phase boundary from which it is excited, and cannot return.[45]

This seems to be the principle by which the living organism has succeeded in obtaining very high quantum

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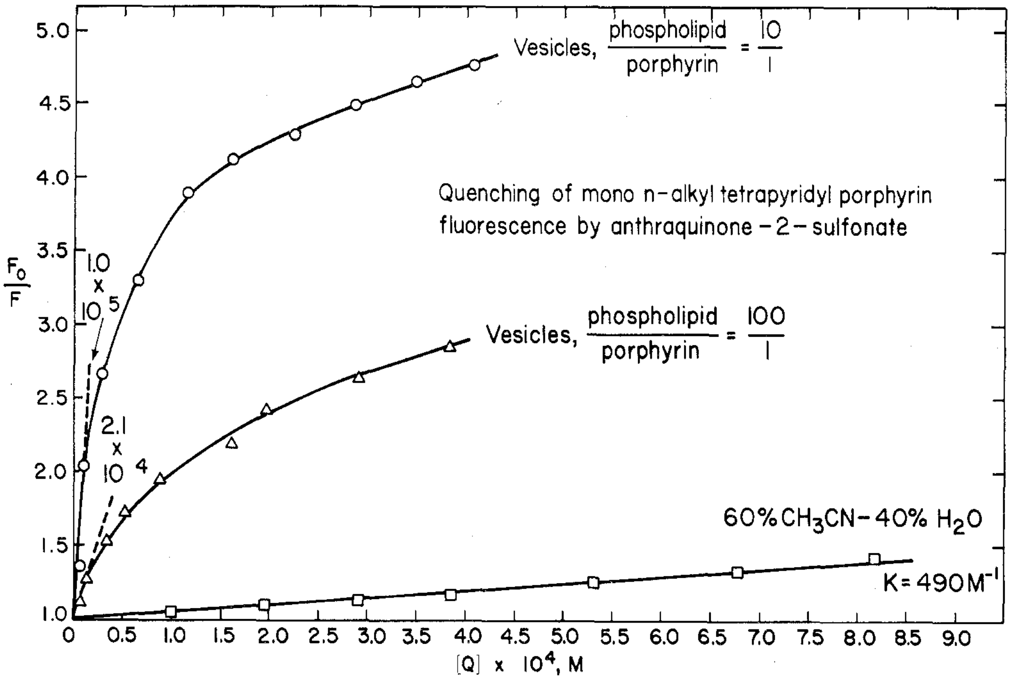

Figure 8. Homogeneous and heterogeneous quenching.

efficiencies for photoelectron transfer reactions, using such chemicals as chlorophyll.[46] Even though we have worked with chlorophyll for over 30 years, it is only in the last 2 or 3 years that we have thoroughly realized that chlorophyll is a surfactant dyestuff. With this realization, we have been able to create surfactant dyestuffs with the porphyrin head right at the interface between the oil and water in the micelles.[47]

Pursuing that idea further and trying to establish it in a more definitive way, we have studied photoelectron transfer across the phase boundary of micelles, in this case, photoelectron transfer from an excited porphyrin to a quinone.[48] The porphyrin is on (or in) the oil micelle and the quinone is in the water layer. Some of the results, using the quenching of the fluorescence of the porphyrin (*n*-alkyltetrapyridylporphyrin, a surfactant), are shown in Figure 8.[49] This diagram shows the results of measuring fluorescence efficiency instead of measuring electron transfer directly. The excited state of the porphyrin is far below the excited state of the quinone, so that quenching cannot be an energy transfer; it must be an electron transfer. In effect we are measuring the electron transfer from the excited porphyrin to the ground-state quinone. The two materials we are using are quinone-2-sulfonate in the water (which has some lipophilic character to bring it close to the interface) and an *n*-alkylporphyrin (C_{16}) with one tail on the molecule. Notice in Figure 8 that the efficiency of the quenching of the porphyrin by the quinone in a homogeneous solution is very low. However, if the porphyrin is placed in a phospholipid (phosphatidylcholine) vesicle and the quenching by anthraquinone is measured, a quenching constant of 2.1×10^4 is achieved, which is 20000 times the value of 500 in the homogeneous solution. If the porphyrin concentration in the lipid is increased, the quenching constant rises even higher, to 1×10^5. This effect seems to point out that the electron transfer between the excited porphyrin and the ground-state quinone acceptor is very efficient at the phase boundary but not in the homogeneous media.

Conclusion

I believe we can look forward to the creation of an artificial system for photosynthesis[10,49] which will mimic the way in which the green plant takes two 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 also repeated and extended somewhat the experiments[44] demonstrating directly the photoinduced electron transfer from a porphyrin in a micelle to a quinone in aqueous solution by directly measuring the photoreduction of the quinone, with relatively good efficiency.

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 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 here been discussed thus accomplish both of the necessary requirements for a useful solar energy device, namely (i) the 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 when in the service of mankind.

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