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ARTIFICIAL PHOTOSYNTHESIS

Melvin Calvin

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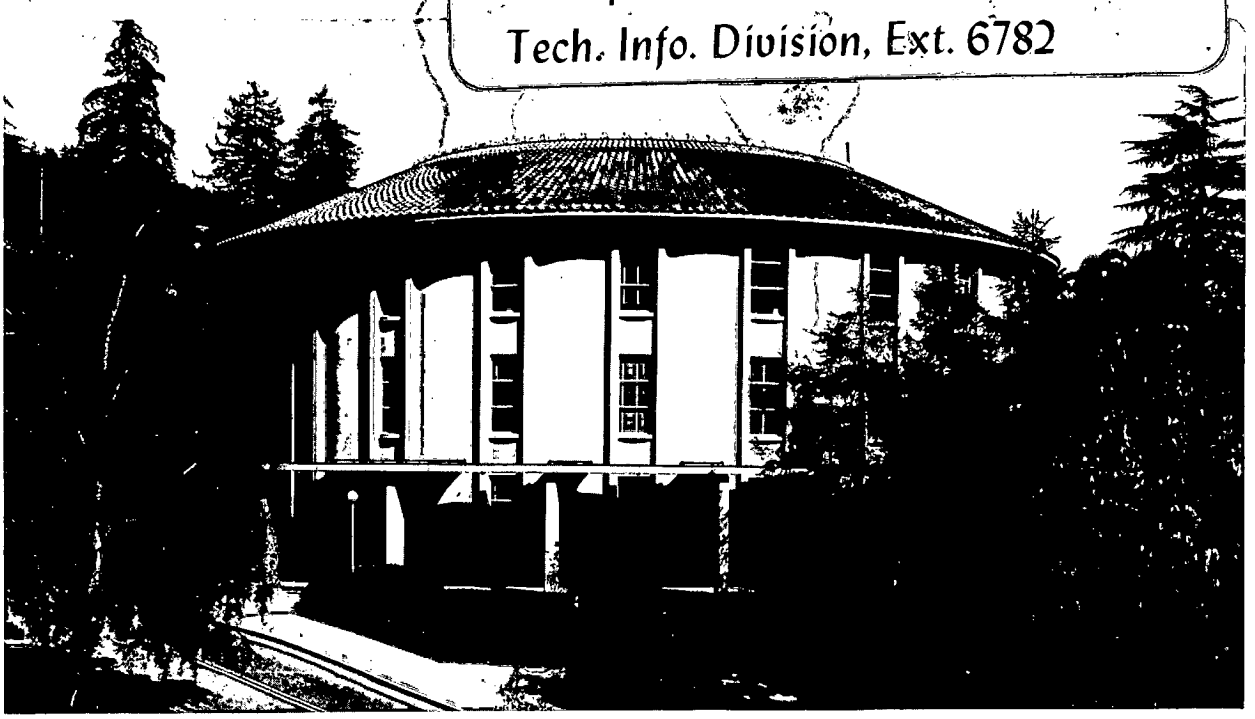

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ARTIFICIAL PHOTOSYNTHESIS

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Abstract

Knowledge of the mechanism of primary energy capture and conversion by green plant chloroplasts is used as a guide for the design of artificial systems for conversion and storage of solar energy. An essential fucntion to be imitated is the conversion of absorbed light energy by charge separation in an oxidation/reduction reaction, and prevention of back reaction between the oxidized electron donor and reduced electron acceptor. We have achieved this goal in two ways: One has been to phototransfer an electron across an insulating lipid layer between two separated acqueous phases, one containing the donor and the other the acceptor.A more recent method is to employ small particles, either lipid vesicles or silica particles, with a high negative surface/charge density. The sensitizer adheres to the particles and the negatively charged reduced acceptor is repelled into the continuous phase after electron tranfer. The separation of products thus achieved has led to great increase in quantum yield, as high as 30%. Ways are now being sought to use catalytic reactions to bring about the oxidation and reduction of water to hydrogen and oxygen.

INTRODUCTION

This discussion describes an effort to produce totally synthetically, not using the materials of biology but only the information, a system that might perform some of the quantum conversion process steps which are done so elegantly and efficiently in nature by the green plant chloroplast. At this point we hope to simulate only that part involved in the capture of the quantum and its conversion into longterm stable chemical form. The simplest stable chemical conversion that we know some of the green plants can perform and which is a limited target which hopefully can be achieved is the dissociation of water into its components molecules (molecular hydrogen and molecular oxygen) using the information we have gained over the years in the study of green plant photosynthesis.

We, as a western civilization, must find a way to fulfill our energy needs which does not depend on the accumulated ancient photosynthetic product which is bound to be exhaustible, i.e., petroleum and natural gas. Data is available which gives evidence that we are exhausting our supplies of liquid and gaseous energy in the form of petroleum and natural gas. Historical data about the rate of discovery of new oil and gas deposits in the United States from 1920-1980 shows short-term rises as well as drops, but overall the rate of discovery is falling as time goes on. Also, in the same data there is an indication that the energy cost of raising drilling and exploring for oil and gas is rising. These two lines will cross in about 2000 and then the energy cost of finding a barrel of oil, for example, will represent more than the energy contained in that barrel of oil. This means that it is unlikely that extensive exploration and drilling will continue as it will no longer be economic or energy producing.

Therefore, we must find a way to harvest the energy of the sun on an annual basis to replace our "capital account". It seemed to me that one of the best ways to do this would be to use plants themselves, but in the longer term future the best way will be to actually mimic the way in which the green plant is able to capture the energy of the quantum and convert that energy into stable chemical form. It will be necessary to understand the essential part(s) of the quantum conversion process in green plants and reconstruct that mechanism in a totally synthetic manner.

QUANTUM CONVERSION IN GREEN PLANTS

Green plant chloroplasts have laminated structures which contain two different types of particles (large and small) which perform the quantum conversion act in two successive steps. These steps are shown schematically in Figure 1, the first act being called Photosystem II and the second, Photosystem I. Photosystem I involves moving an electron from somewhere near the redox potential of water to an intermediate oxidation level in an acceptor system. The electron then passes down through an electron transfer system (plastoquinone, cytochrome f, plastocyanin, etc.), generating some ATP on the way. A second quantum is then absorbed, raising the electron from some intermediate level, to which is has fallen in generating that ATP, to a second higher level, higher than that of molecular hydrogen. We know this level because if carbon dioxide is withheld from some plants it is possible to have the plant use the reducing power that that electron represents to generate reduced protons and/eventually molecular hydrogen. Some plants have an enzyme (hydrogenase) which can use this reduced pyridine nucleotide, ferredoxin (or both), to generate molecular hydrogen. Such molecular hydrogen could be our annually harvested fuel from the sun, if the

details of this natural process could be imitated successfully in the laboratory in an efficient manner.

The fact that there are two quanta and that there are two sides to the green plant chloroplast membrane is suggestive, if not indicative, that the electron passes from one side of the membrane to the other, and the ability of the plant to perform the quantum conversion step resides in the peculiar arrangement of sensitizers, electron transferring agents and catalysts present in the natural material. The electron is moved from one side of a membrane to the other, across two phase boundaries--a water-to-membrane boundary and a membrane-to-water boundary on the other side. This appears to be the crucial point in the construction of the apparatus used by the chloroplast, i.e., the transfer of an electron across a membrane or, more simply, the transfer of an electron across a phase boundary from one phase to another. On either side of the phase boundary exist donor and acceptor molecules, and special kind of catalysts (such as the hydrogenase enzyme) to transfer the reducing power into molecular hydrogen. Alternatively, there will be a catalyst on the other side of the membrane to convert the "holes" that remain, having removed the electron, into molecular oxygen.

We believe that we have some knowledge of the nature of the hydrogenase-enzyme catalyst, an iron-sulfur complex (probably a 4Fe-4S complex in a protein), but on the opposite side of the membrane the catalyst for the generation of the molecular oxygen is really unknown, but it appears to be some form of manganese. The reason we believe manganese may be a catalyst for molecular oxygen formation is: if plants are grown carefully in the absence of manganese they lose their capability to generate oxygen; suitably

chosen plants can be reactivated by merely adding manganese ion and the plant immediately recovers its oxygen-generating capability. This is an old observation and has been repeated many times and there has been an extensive search for that manganese-bearing oxygen-generating catalyst. The hydrogen-generating system appears to be a multi iron-sulfur protein. Just looking at the chemistry involved and realizing that the generation of hydrogen is a two-electron process suggested that at least two iron atoms must be involved.

Having come to the conclusion that manganese did play a part in the oxygen-generating system, requiring four electrons, the question arose concerning the number of manganese atoms actually involved. Manganese normally has only three easily accessible oxidation states (2,3 and 4), and manganese in going from the +2 to the +4 state involves only two electrons. This would suggest that in order for oxygen to be generated, which requires four electrons (or holes) accumulated in the same center, the complex should have at least two manganese atoms in it. It turns out not to be so far off, experimentally.

Some years ago we synthesized a dinuclear manganese compound with the idea that it might be capable of generating oxygen if we could remove the four electrons from it. The compound we made is shown in FIGURE 2, as determined by a special spectroscopic method, EXAFS. I felt it might be possible to extract electrons from each of the manganese atoms, and if they could be raised to the +4 oxidation state of manganese, the two oxygen atoms would join, one oxygen molecule would come off, and each manganese atom would go back to the +2 oxidation state.

With the development of EXAFS (X-ray absorption fine structure) we used the dinuclear manganese compound which have been synthesized previously to calibrate the method for the manganese in

biological material. We felt we could examine the manganese in the chloroplast itself to see if it could be detected and learn something about its environment using the EXAFS method. You can see by the information in FIGURE 2 that the manganese is detectable, and it is possible to say that one of the manganese atoms in the calibration compound (the dinuclear manganese) is in the +3 state and the other manganese atom is in the +4 oxidation state. The absorption edge could be analyzed in terms of the manganese-manganese distance and the other atoms present, which is a complex computational process. This diagram indicates the manganese distance is approximately 2.5 Å, which is the distance measured by x-ray crystallography. Therefore, the absorption edge analysis gives us the correct information.

When an absorption edge analysis on biological material (chloroplasts) is done, a similar pattern is obtained. We cannot say, however, exactly how many manganese atoms are involved in the cluster separated by that distance. The information indicates that the manganese atoms are in clusters separated by only 2.5 Å, but the number in the cluster is not unequivocal. There are at least two manganese atoms, but perhaps more. Thus, we have some confirmation of the notion that the manganese catalyst consists of a multi-manganese atom molecule. It is a catalyst similar to the hydrogenase system which involves four iron atoms and four sulfur atoms. All we can really say at the moment about the oxygen-generating system of plants is that the catalyst contains at least two manganese atoms separated by about 2.5 - 3 Å.

MEMBRANE STUDIES

The photosynthetic membrane is shown in FIGURE 3, with the particles on both sides of the membranes and indicating how the electron(s) might transfer through the membrane. Manganese, in this diagram,

We excite the Ru^{2+} to the excited state, and the excited singlet state very quickly transforms to the excited triplet state which has a long life. The triplet state passes an electron on to the viologen and goes to Ru^{3+}. The viologen is reduced to the blue color of the monocation radical. The Ru^{3+} on the outside of the vesicle can then exchange an electron with the Ru^{2+} on the inside, an isoelectronic exchange, resulting in Ru^{3+} on the inside and Ru^{2+} on the outside. This is not a diffusion of the ruthenium through the membrane but a tunneling of the electron from the Ru^{2+} to the Ru^{3+}, giving a Ru^{2+} on the outside of the vesicle and Ru^{3+} on the inside. The Ru^{3+} can perform an oxidation (it's a very strong oxidant), and it takes an electron from EDTA, or some other water-soluble material. Tris-bipyridyl Ru^{2+}, without the tail, could be placed inside the vesicle. It would exchange with the Ru^{3+} in the membrane, returning it to Ru^{2+} in the membrane. The Ru^{3+} in the water could then oxidize the EDTA, or, alternatively, in the presence of a solid catalyst, such as RuO_2 or CoO, could oxidize water to molecular oxygen.

We are moving electrons from the inside of the vesicle to the outside, thus generating a potential across that membrane. We need something to carry balancing cations through the membrane, or the reaction will stop. We adjusted the potential across the membrane by mixing sodium and potassium in different ratios and constant total cation concentration on both sides and putting a potassium ion carrier in the membrane, in other words, adjusting the transmembrane potential, and generating a potential gradient across the membrane in either direction, depending on which side had the highest concentration of potassium, with the total cation concentration on both sides of the membrane being the same. We used valinomycin as a specific potassium carrier, with the results shown in FIGURE 7. When sodium ion is the only cation on both sides of the membrane the valinomycin has no effect. When there is no valinomycin

present the effect is not noticeable. The quantum yields can be increased by moving cations through, using other specific carriers such as gramicidin. This type of system is suitable for the vesicles and gives a great deal of theoretical information.

Think of the circles in Figure 5, shown there as a cross section of a liposome, as the cross section of a hollow fiber, a microphotograph of which, constructed of a suitable polymer (cellulose acetate, a salt-rejecting fiber) is shown in FIGURE 8. The question arises as to whether or not it is possible to get the dyestuff into the hollow fiber. At first it seemed it would be necessary to hang the dyestuff onto the polymer covalently, by some chemical process, but experiments were performed to swell the hollow fiber membrane and dissolve the dyestuff in it. The dyestuff, therefore, has actually penetrated throughout the membrane, and the question now arises as to whether or not it would be possible to transfer electrons through the thickness of the hollow fiber, a much greater distance than the transmembrane electron transfer distance of the vesicle.

We already know that electrons will hop from molecule to molecule in a solution of materials that can carry an odd electron easily, such as zinc porphyrin with one electron removed leaving a zinc porphyrin cation radical. A similar experiment has been done with a small amount of quinone dissolved in a liquid insulating medium, reducing it to a semiquinone. To that solution can be added a larger amount of quinone which lacks the extra electron which can thus provide the vacant orbital for an electron to hop from one molecule to another. If the electron spin resonance (ESR) of a solution of the semiquinone radical with no added quinone is examined, a five-line hyperfine structure of the quinone radical

results due to the aromatic four protons on the semiquinone. If extra quinone is added, the lines broaden out and eventually a broad band is created. As a result of electron hopping, the orientation of the proton spin with respect to the electron spin is lost, with concomitant loss of hyperfine structure. In the membrane, the quinone will be replaced with the zinc porphyrin, and when the zinc tetraphenylporphyrin is illuminated on the membrane with an acceptor molecule on one side, there will be an electron transfer to the acceptor molecule, leaving the zinc porphyrin cation radical. On the other side there will be a donor molecule, and the cation radical ion will wander by exchange until it comes to a zinc tetraphenylporphyrin on this donor side of the membrane. This results in a radical on the side which can be filled with electrons from the donor molecule. The above results indicate the possiblity of moving an electron from one side to the other through this rather thick membrane by having the concentration of the zinc tetraphenylporphyrin correct.

HOLLOW FIBER APPARATUS

The next approach was to construct an experimental apparatus, shown in FIGURE 9, which contains forty hollow fibers (of the type described above) in one bundle.* The insides of the fibers are connected to the small vertical plastic tubes and the outside of the fibers are connected to the horizontal sidearms. Illuminating this apparatus and measuring the electron transfer, either electrically or chemically, still remains to be done, although we have demonstrated that we can transfer an electron across a membrane by sensitizing the membrane. We are now in the process of constructing a laboratory device based upon that principle.

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* Carl E. Wamser; unpublished results from this laboratory.

CHARGE SEPARATION PROCESSES

The essential features of the process we are trying to imitate, which occurs naturally in the chloroplast (the natural photosynthetic apparatus) consists of a system on which light impinges, separating charges, actually generating plus or minus charges. By definition these two opposite charges are at a higher energy than the state at which they started. They should, therefore, recombine to the initial state, a downhill reaction. In order to prevent that, we try to take one charge off on one side of the membrane and the other charge off on the other. One method to achieve this purpose would be to have the charge separation occur in the presence of a large negatively charged particle to attract the positive charge and repel the negative charge. This type of experiment has been done, and its essential components are shown in FIGURE 10. Silica particles are used for the highly charged negative surfaces, the potential on those charges being controllable. Ruthenium tris-bipyridyl is used as sensitizer and propylviologensulfonate (PVS^{o}), which is neutral (having both a positive and negative charge on it) as acceptor. The excited ruthenium compound transfers the electron to the PVS^{o}, the PVS^{o} becomes a negative ion radical ($PVS^{\cdot -}$) and the ruthenium becomes Ru^{3+}. This reaction takes place in the presence of the huge negative surface potential, and the $PVS^{\cdot -}$ is expelled from the reaction sphere, with the ruthenium tris-bipyridyl being attracted to that negative potential. Thus, the positive charge and the negative charge which would back react if they had a chance are prevented from recombining by a negative charge, without the presence of a membrane. We are using the particles as a means of separation.

We are able to regenerate the ruthenium by reduction with a suitable donor. This eventually has to be the manganese catalyst and water, but in the meantime we are using triethanolamine as the electron donor (neutral

to reduce the Ru^{3+} to make the Ru^{2+}. In effect, the triethanolamine reduces PVS^{o} sensitized by ruthenium as shown in FIGURE 11, indicating the $PVS^{-\cdot}$ radical formation as a function of the light adsorbed. The two parts (A and B) show the behavior of two different sensitizers, ruthenium tris-bipyridyl (left, A) and zinc tetramethylporphyrin radical (right, B), together with various controls. This shows unequivocally that the micellar system (sodium lauryl sulfate, NaLS) is nowhere near as efficient as the silicon dioxide particles. Also (right side, B) the porphyrin ions could be either positive (pyridinium) or negative (sulfonates). The reaction on SiO_2 works only with a positive ion sensitizer, not with a negative ion sensitizer.

If our supposition is correct, the explanation of this data would be that the presence of the silica slows down the back reaction, i.e., the rate at which the negative charge car combine with the positive charge to give a neutral particle. Flash photolysis experiments proved the supposition to be correct, with the results shown in FIGURE 12, indicating the transient absorption changes of PVS^{o} under homogeneous conditions and in the presence of silica.

We would like to carry the electron further away from the hole, as in the natural photosynthetic membrane, and we are trying to construct synthetically that electron transfer chain with the right charges. An experimental system (FIGURE 13) has been devised which will reduce ferricyanide to ferrocyanide with ruthenium in the presence of silica. It is necessary to have a shuttle in between to carry the electron between the negative silicon dioxide and the negative ferricyanide, a vectorial electron transfer in one direction. The data from the system in Figure 13 are given in FIGURE 14, with four different systems, using PVS^{o}, ruthenium and ferricyanide. We are following the reduction of ferricyanide

rather than the reduction of PVS^{o}. Similar data is shown in FIGURE 15. giving the formation of reduced product as a function of light adsorbed and indicating the syngergism of the shuttle. The rate (Figure 15(a) is not the sum (calc. as d) of the two separate parts (Figure 15(b) and (c)) but the shuttle system allows the reaction to go much faster.

A plot of the quantum yield for propylviologen formation as a function of surface potential of negatively charged interfaces of the silica system and sodium lauryl sulfate (NaLS) micellar system is shown in FIGURE 16. The quantum yield is reduced upon addition of salt and correlation of surface potential with NaLS can be observed on the same curve.

CONCLUSION

It should be possible to construct a system of two different kinds of particles, one with a higher surface charge density than the other, so that the oxygen-generating system can be on one particle and the hydrogen-generating system on the other. The charges can then be separated and the two catalysts associated with the two different functions can also be separated with the shuttle between them. This idea is shown schematically in FIGURE 17, with ruthenium oxide on the highly negative surface to accumulate the four electrons necessary to generate oxygen from Ru^{3+}, and the PVS^{o} shuttle to the platinum (or something equivalent),on a less negative surface, to generate hydrogen. The two particles will be kept separate from each other, since both are negatively charged. This type of device, with hydrogen on one side of the vessel and oxygen on the other side, is nominally constructable, although we have not yet finalized it. Only the component parts have been actually constructed.

We are well on the way to generating a device that will photolyze water using visible sunlight. Remember that in the chloroplast ATP is made with the energy drop between the two absorbed quanta. Because in the synthetic system we are not trying to synthesize ATP, the reaction can be run with one quantum.

The sensitizers we have used in our synthetic studies are well defined, absorbing relatively narrow bands of the solar spectrum. Therefore, the efficiency of the reduction of propylviologen by the present system is 40% of the light adsorbed. It will be necessary to use more than one sensitizer, i.e., a system of sensitizers, to cover more of the solar spectrum. The catalytic steps are separate from the photochemical steps in which we use silica particles, for example, to separate the charges with the requirement for two catalysts. We have used PVS^{o} to generate hydrogen with platinum as catalyst and the Ru^{3+} to generate oxygen with ruthenium oxide as catalyst. Until now, we have focussed our attention on how to separate the charges efficiently, and this separation occurs at an efficiency of about 37% with the light absorbed by the ruthenium tris-bipyridyl sensitizer.

We have also been searching for a manganese catalyst to replace the ruthenium oxide in these reactions. The suggestion was made to use a single manganese compound, both as sensitizer and catalyst. However, instead of photo-oxidizing the manganese catalyst directly, we have sensitized the oxidation of the manganese catalyst with the zinc porphyrin. We have now a manganese compound which will undoubtedly generate oxygen. We have shown that the photosensitized oxidation of the manganese compound can indeed be accomplished. It is therefore entirely possible that the manganese compound will eventually be the oxidizing

system and the oxygen generating system that we will use in the construction of our synthetic devices.

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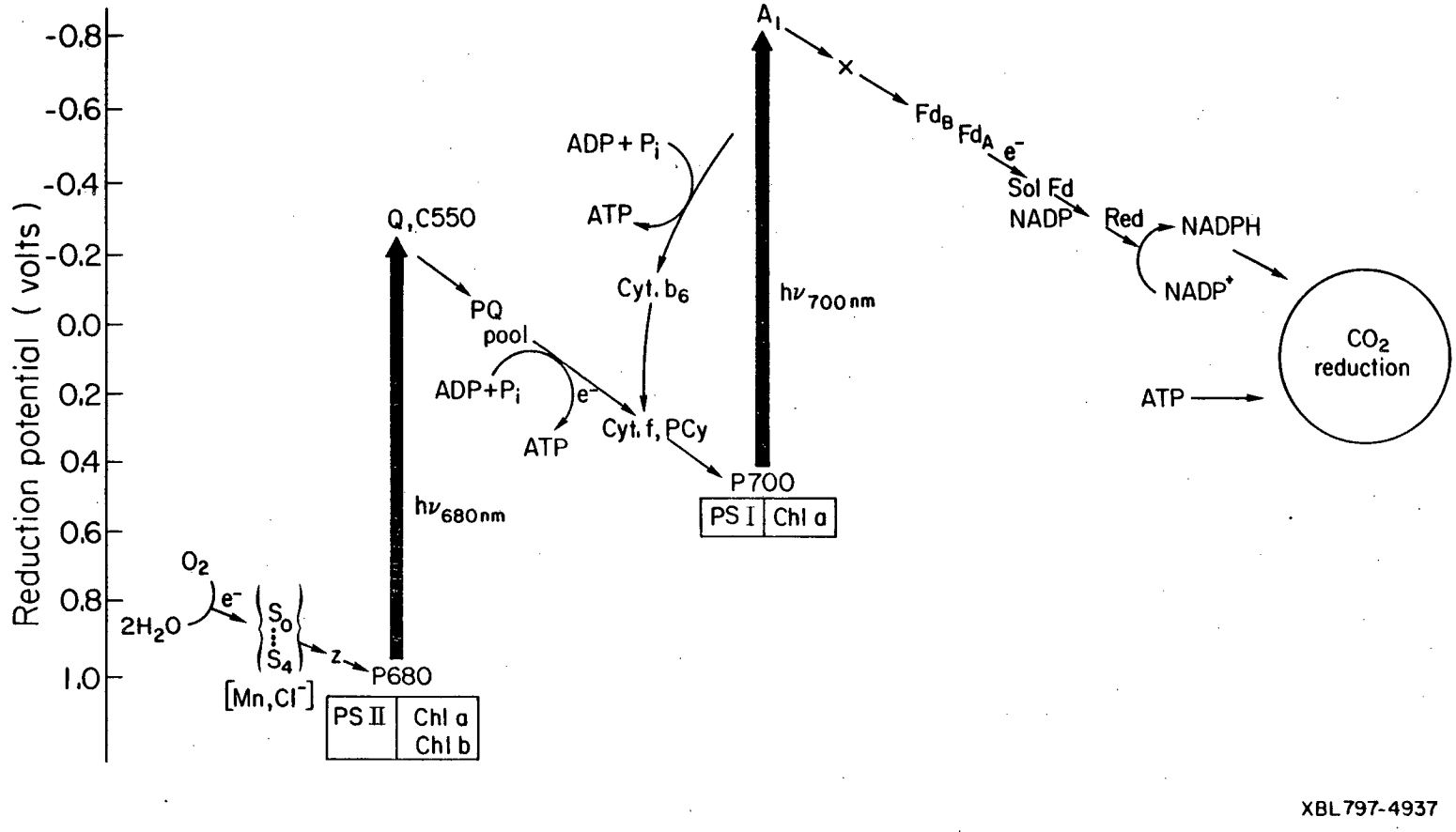

Figure 1. Photosynthetic electron transfer scheme

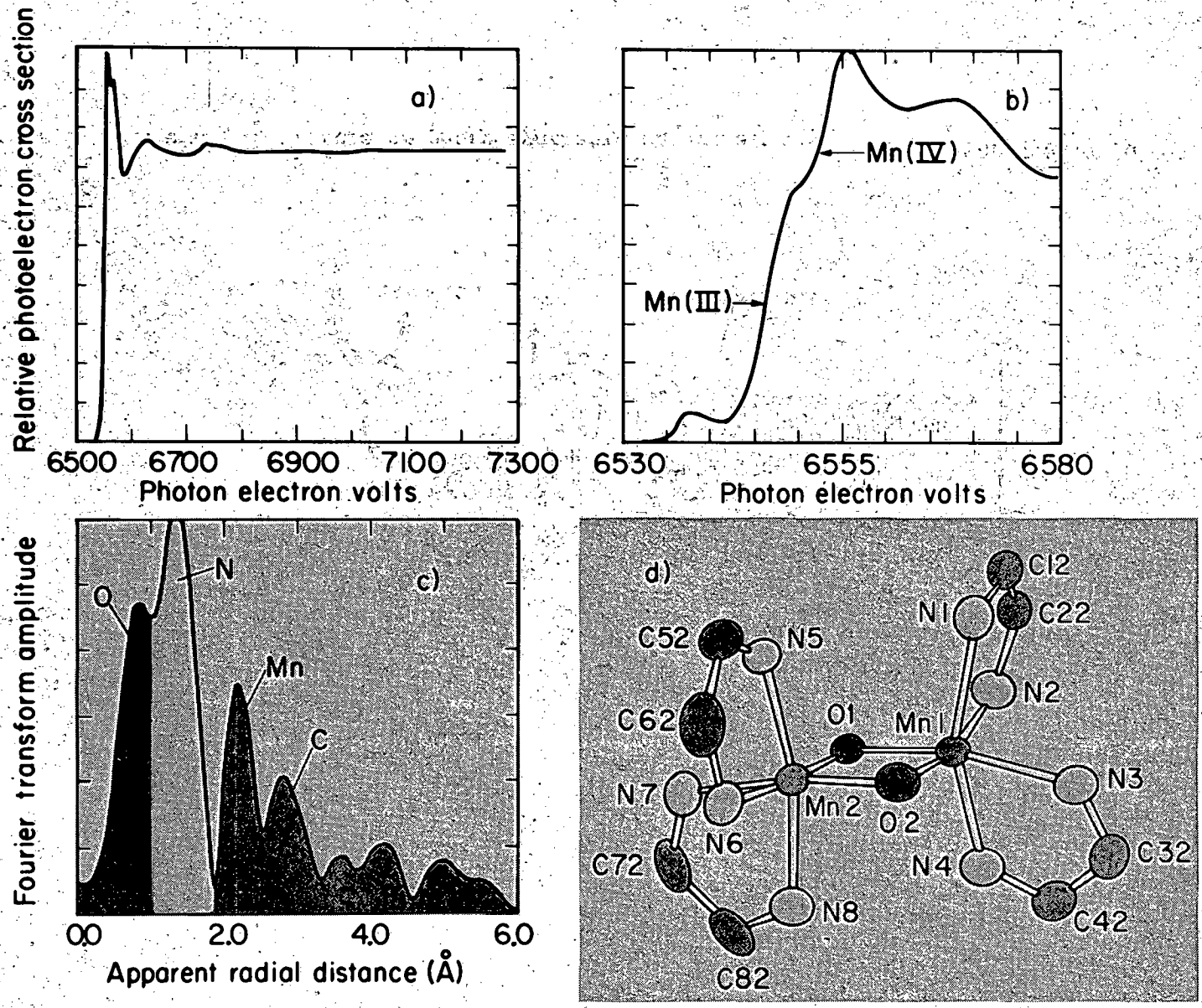

Figure 2. EXAFS of dimeric manganese compound.

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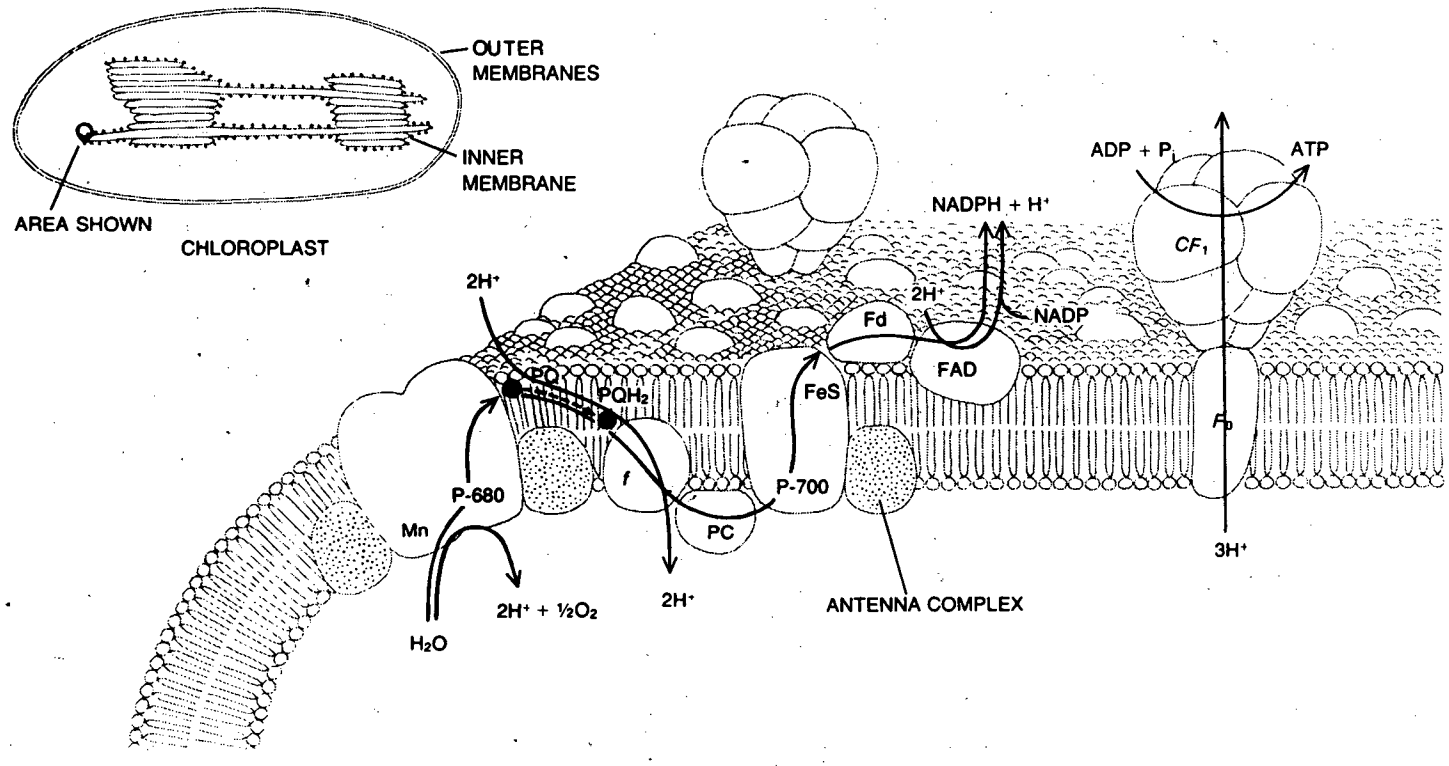

Figure 3. Schematic structure of photo-synthetic membrane.

BBC 798-10370

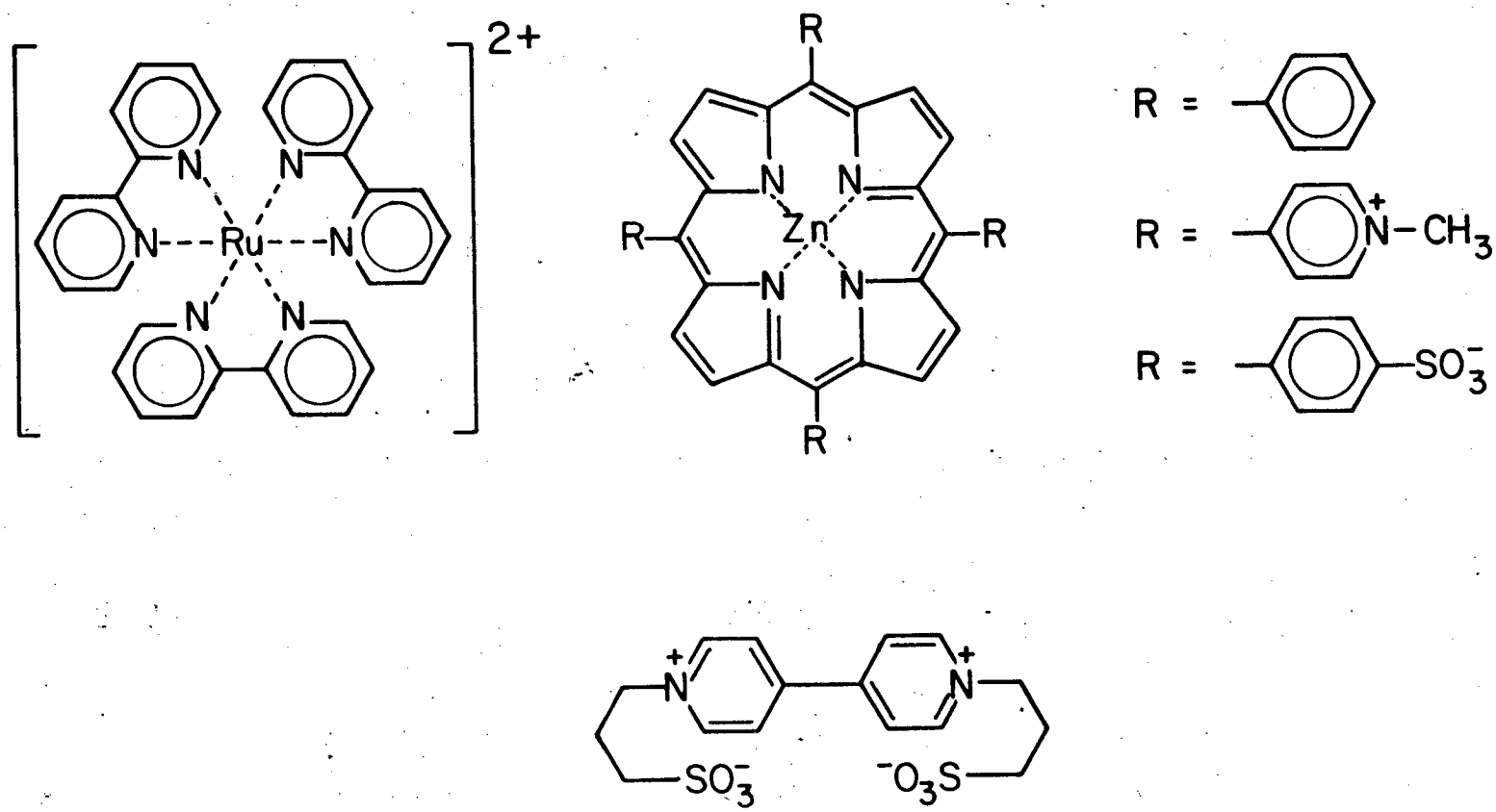

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Figure 4
Structures of donors/acceptors/
sensitizers

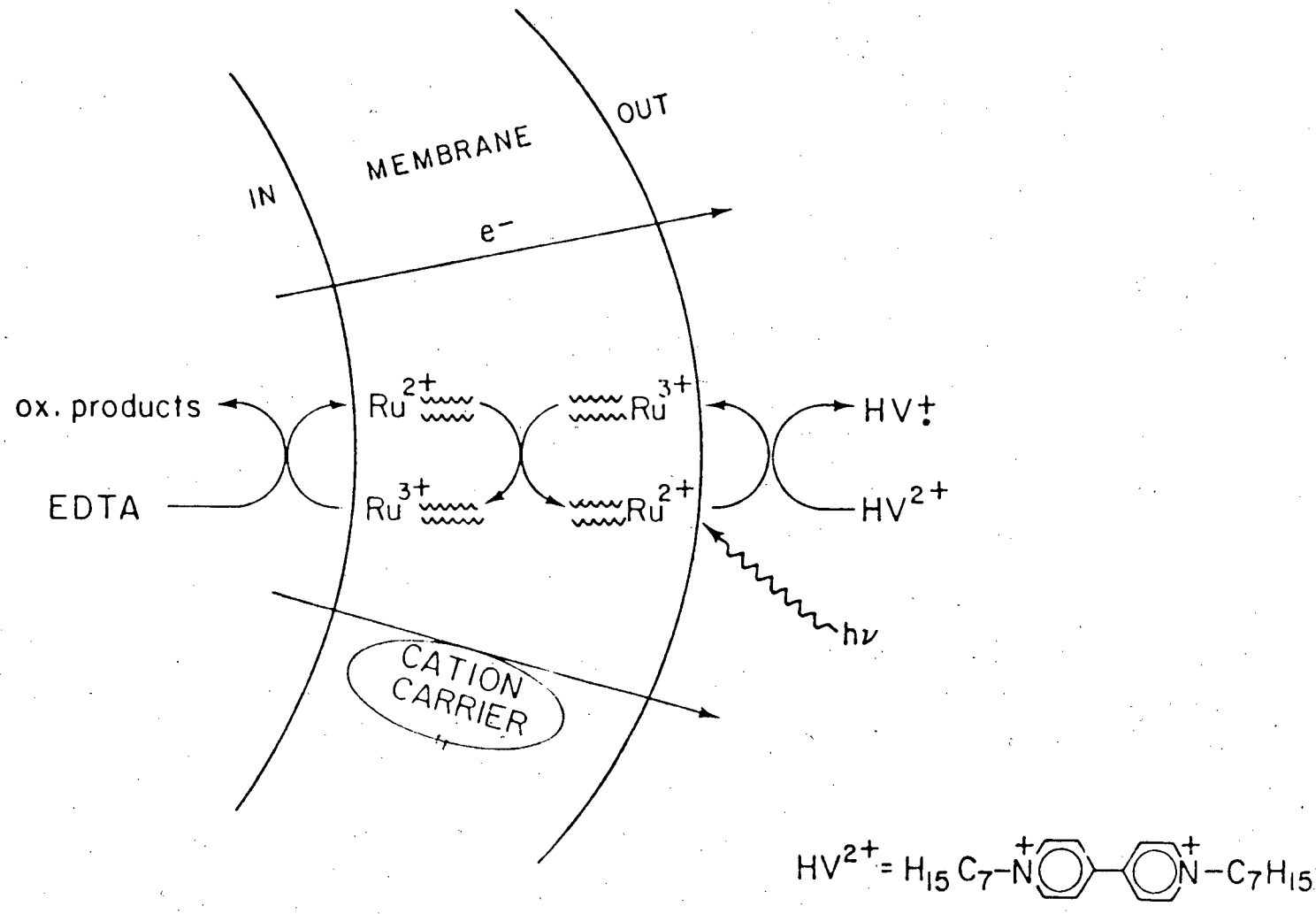

Figure 5. Scheme for photosensitized electron transfer across a lipid vesicle wall.

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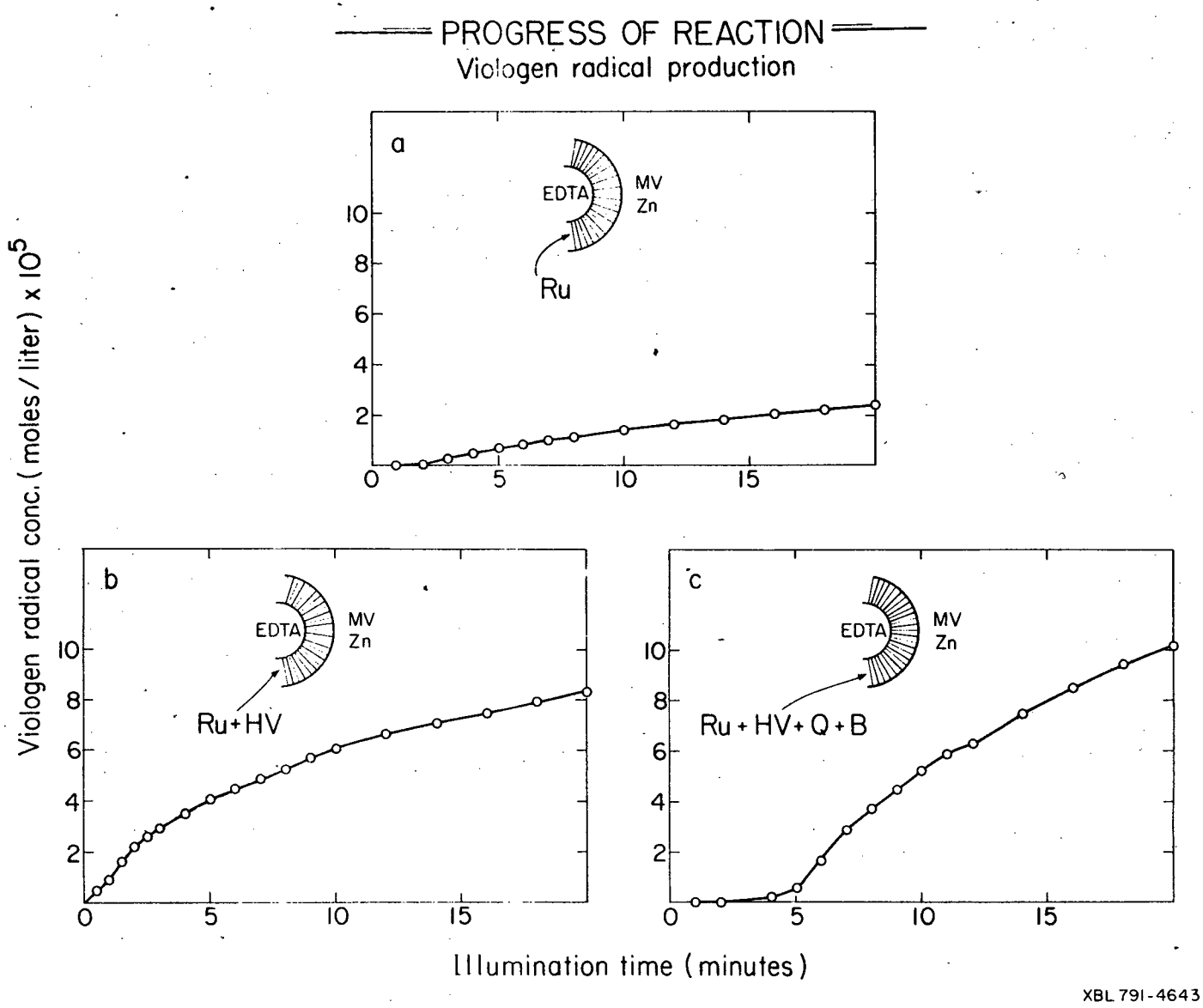

Figure 6
Cofactors in photoelectron transfer reaction across membrane

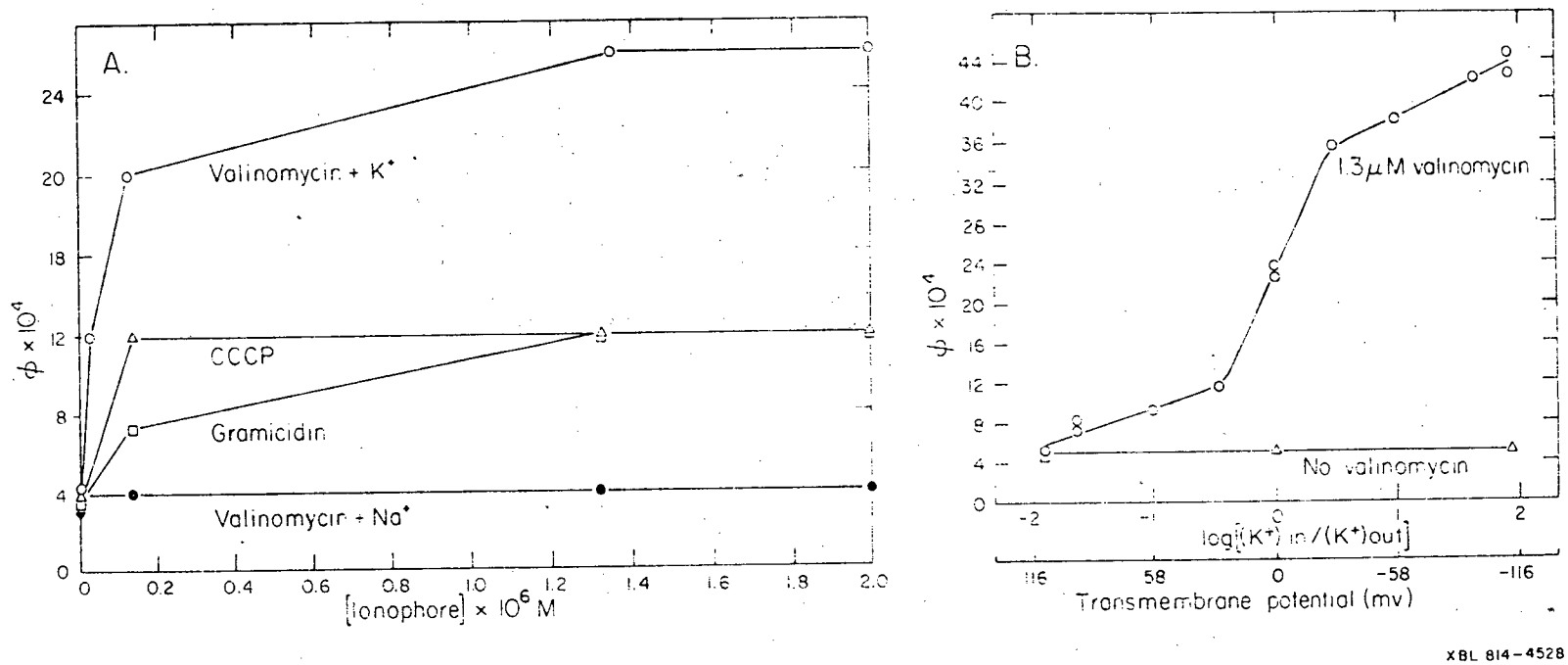

Figure 7. Effect of ionophores (A) and transmembrane potentials (B) on quantum yield of heptulviologen reduction in the vesicle system. Ø = quantum yield; CCCP (carbonyl cyanide m-chlorophenylhydrazone), H^+ carrier; valinomycin, K^+ carrier; gramicidin makes membrane permeable for several cations such as H^+, K^+, Na^+

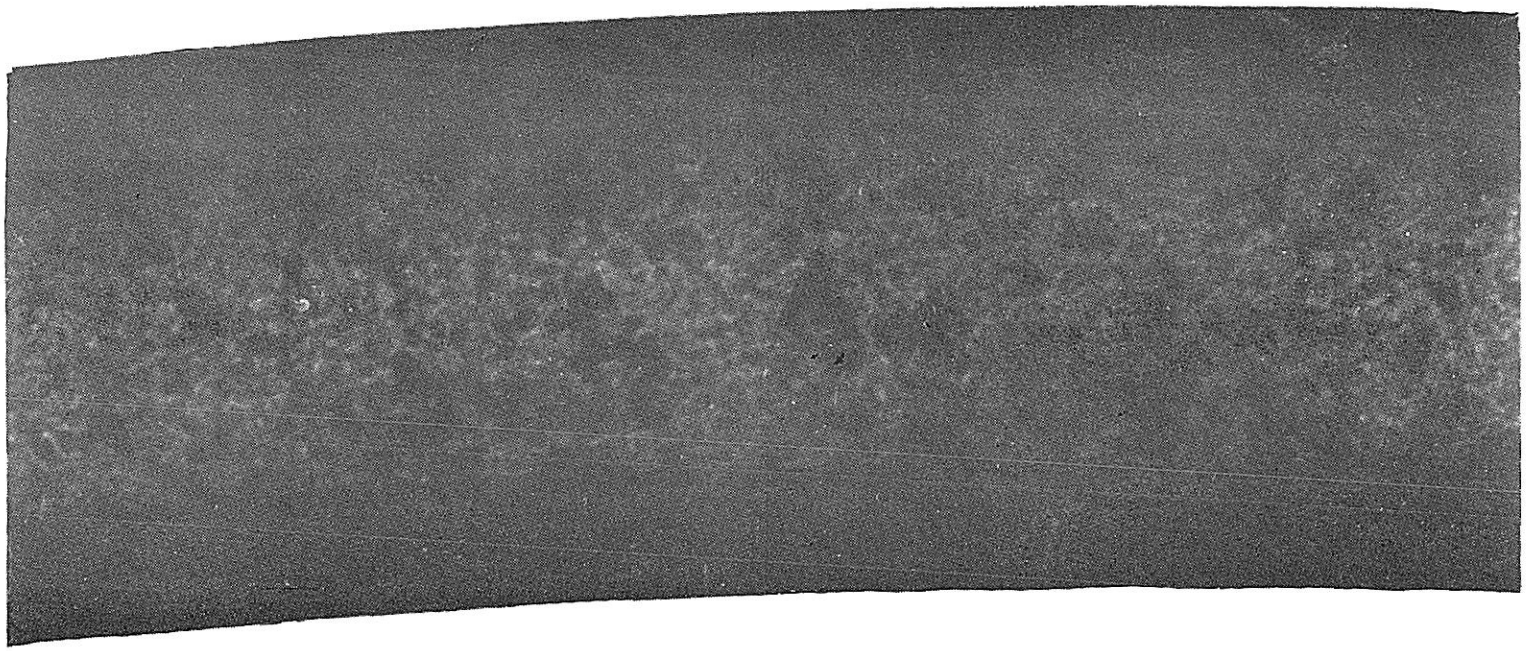

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Figure 8. - Treated hollow fiber from ZnTPP (acetone) - (50x)

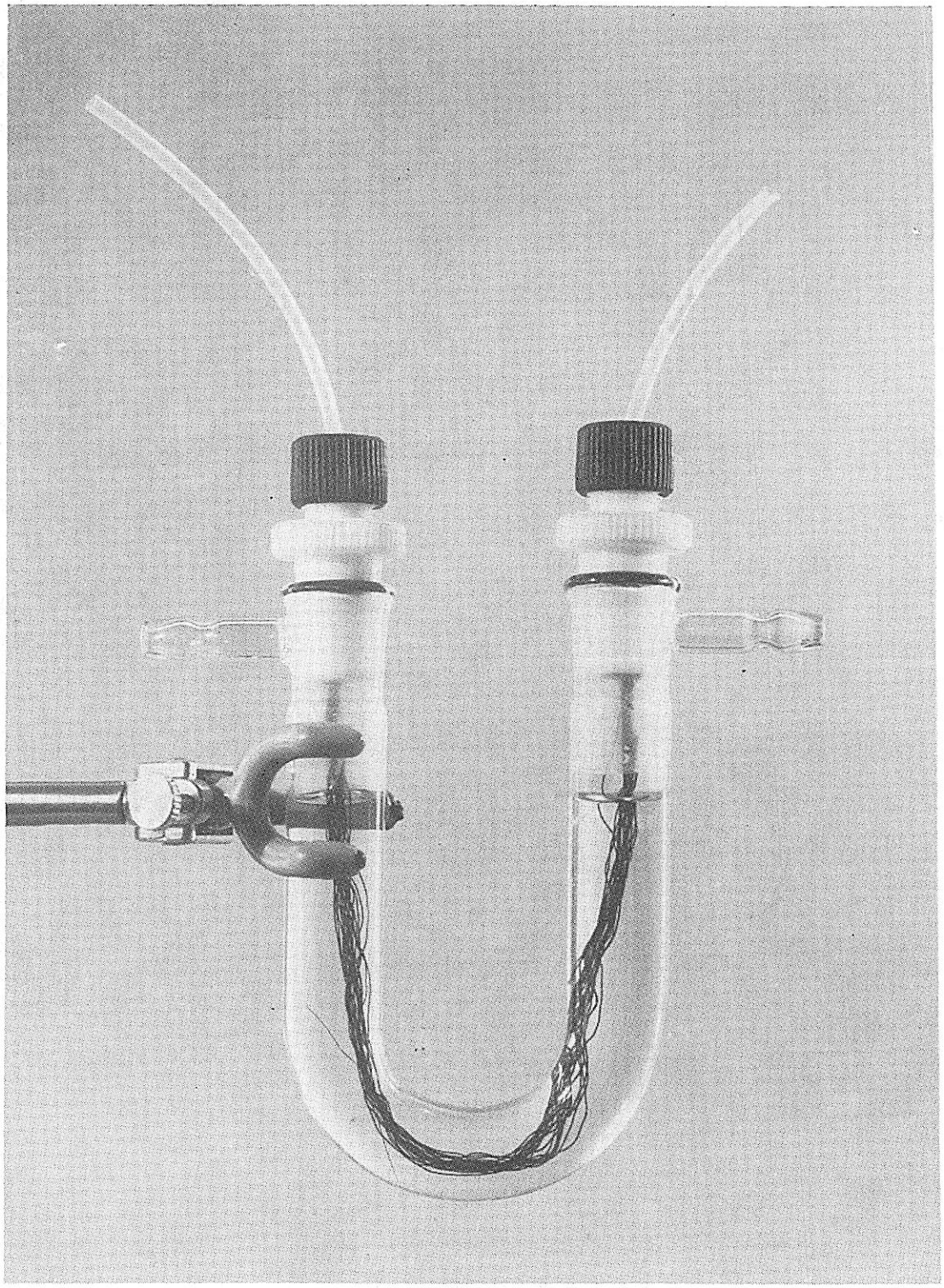

Figure 9. Hollow fiber apparatus for separation of hydrogen and oxygen.

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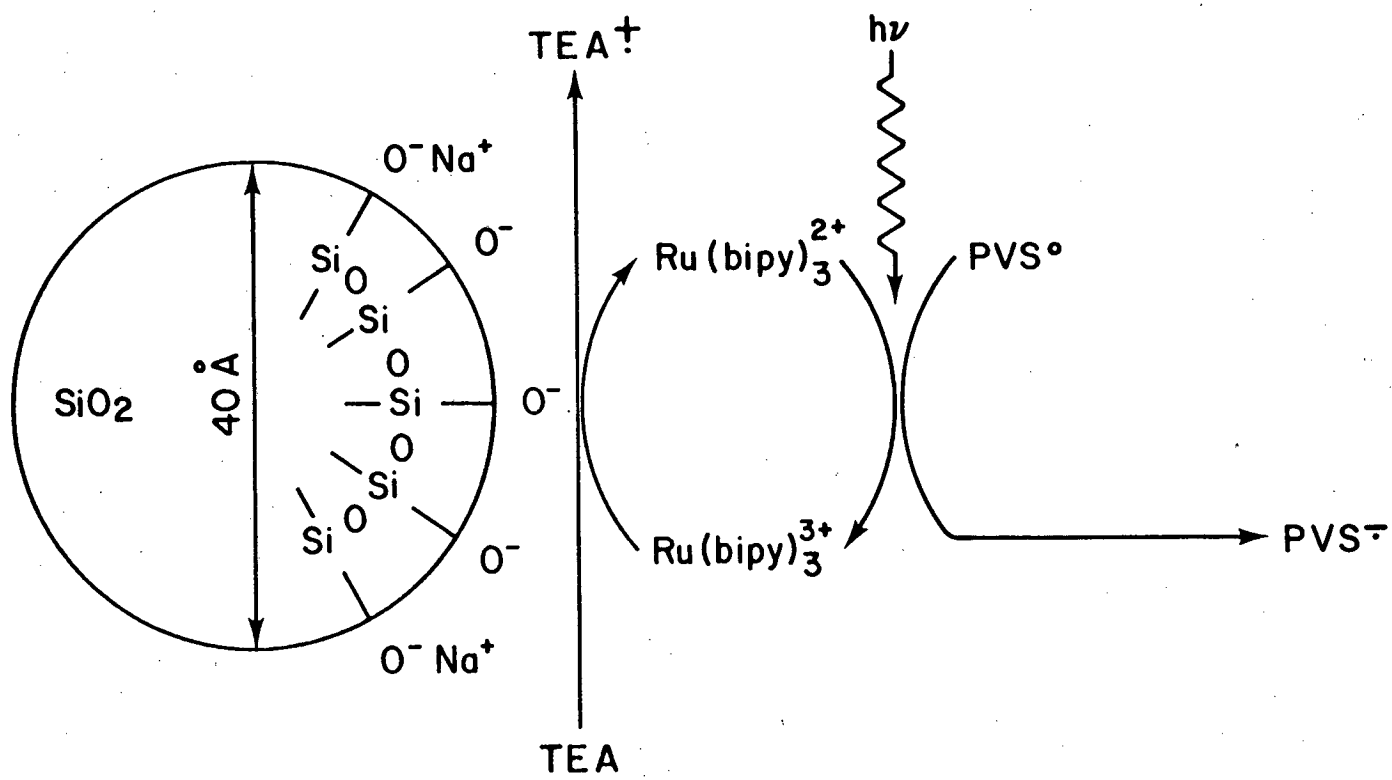
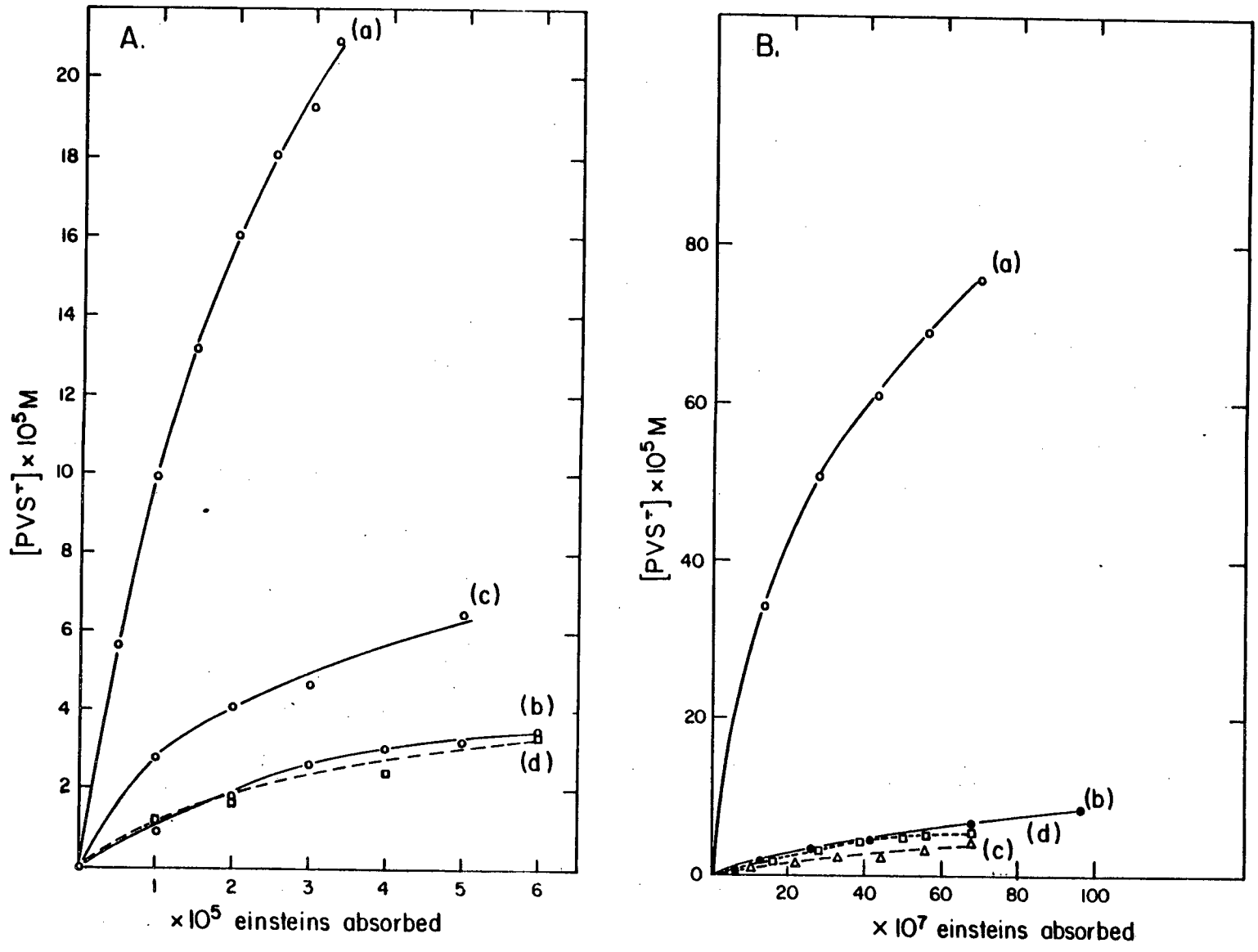


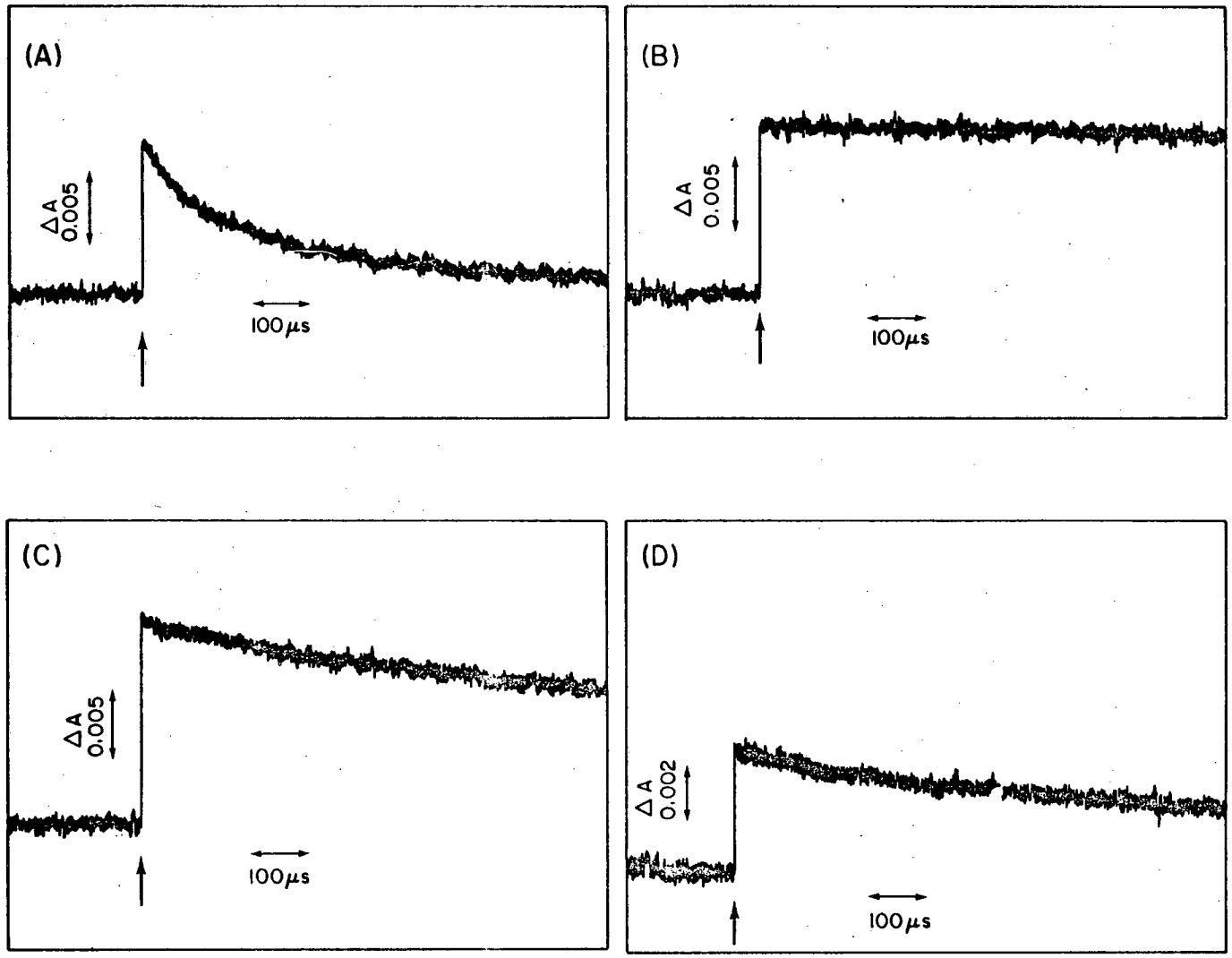
XBL 811-4426

Figure 10
Schematic function of silica dioxide particles in separating photoproducts



XBL 814-4529

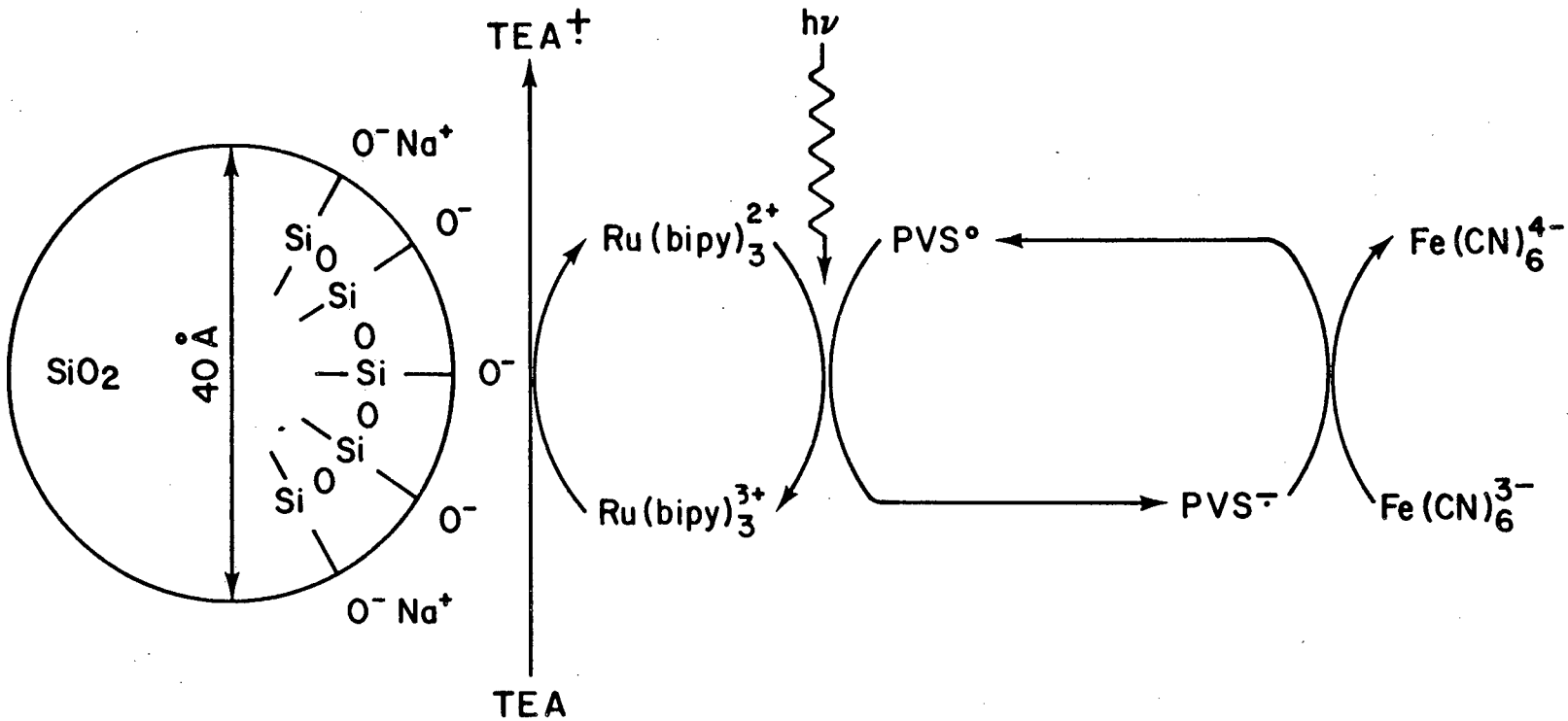
Figure 11. Propylviologen radical, $PVS^{\cdot-}$, formation as a function of light adsorbed, monitored by the increase of absorbance at ξ = 602 nm. (ξ = 12500 $M^{-1}cm^{-1}$). (A) $Ru(bipy)_3^{2+}$ as sensitizer; (a) SiO_2 system; (b) homogeneous system; (c) micellar system; (d) NaLS micellar system with 0.1 M NaCl. (B) Zn-$TMPyP^{4+}$ and Zn-$TPPS^{4-}$ as sensitizers; (a) SiO_2 system with Zn-TMPyP4+; (b) homogeneous system with ZnOTMPyP4+; (c) SiO_2 system with Zn-$TPPS^{4-}$; (d) homogeneous system with ZnOTPPS^{4-}.



XBL 814-4561A

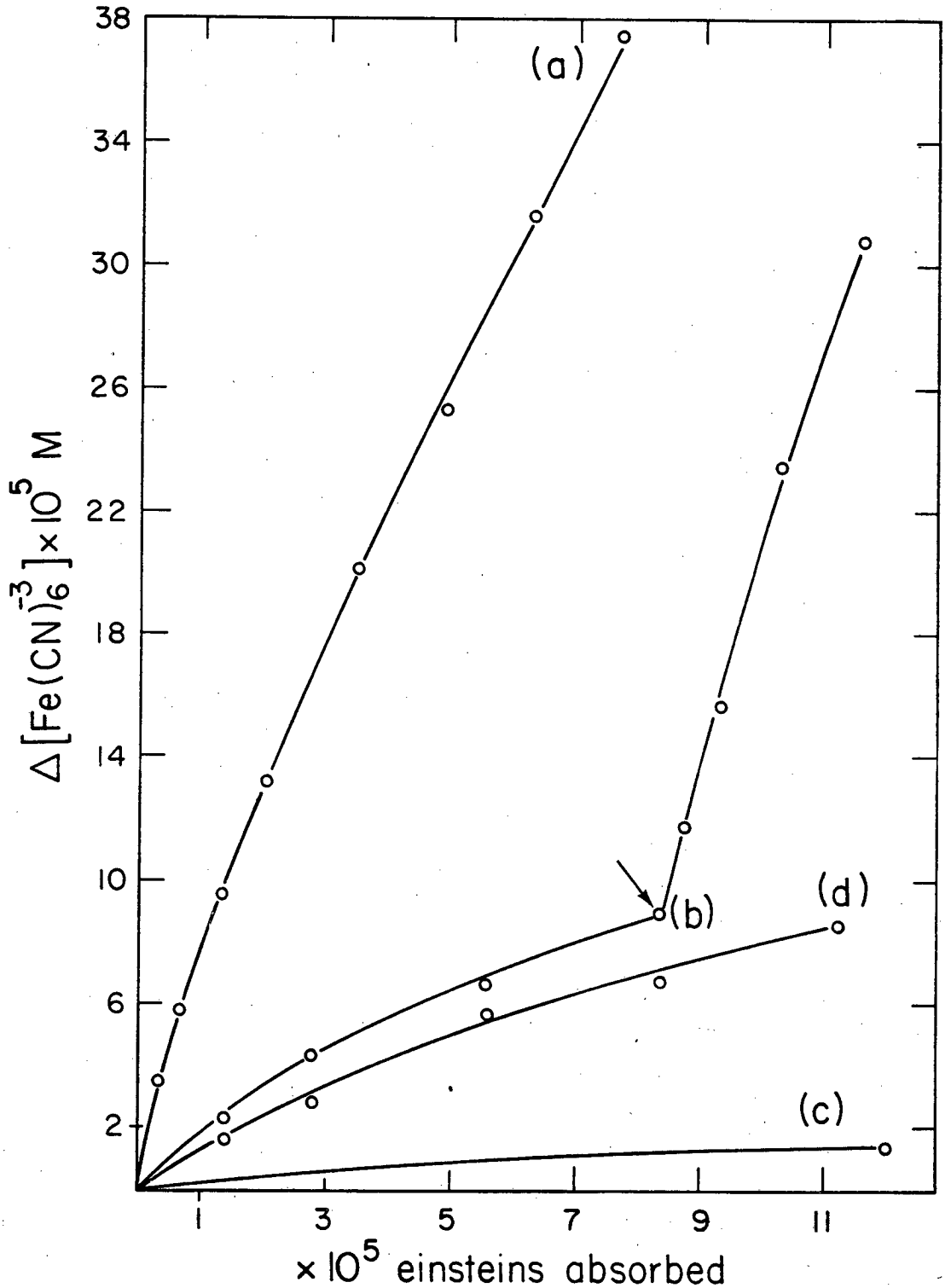
Figure 12. Transient absorption changes of $PVS^{\cdot-}$ followed at 602 nm. Arrow indicates the laser pulse. $[Ru(bipy)_3^{2+}] = 3.6 \times 10^{-5}$ M; $[PVSO] = 4 \times 10^{-3}$ M.

(A) In a homogeneous aqueous phase, pH = 9.8
(B) In a 0.2% SiO_2 colloid, pH = 9.8.
(C) In a 0.2% SiO_2 colloid, pH = 9.8 with added salt [NaCl] = 0.1 M.



XBL 812-4456

Figure 13
Schematic function of silica dioxide particles in separating charged photoproducts



XBL 812-4455

Figure 14. Reduction of $K_3Fe(CN)_6$ as a function of light adsorbed. (a) SiO_2 system including PVS^o; (b) SiO_2 system. Arrow indicates the time of PVS^o addition; (c) homogeneous system; (d) NaLS micellar system

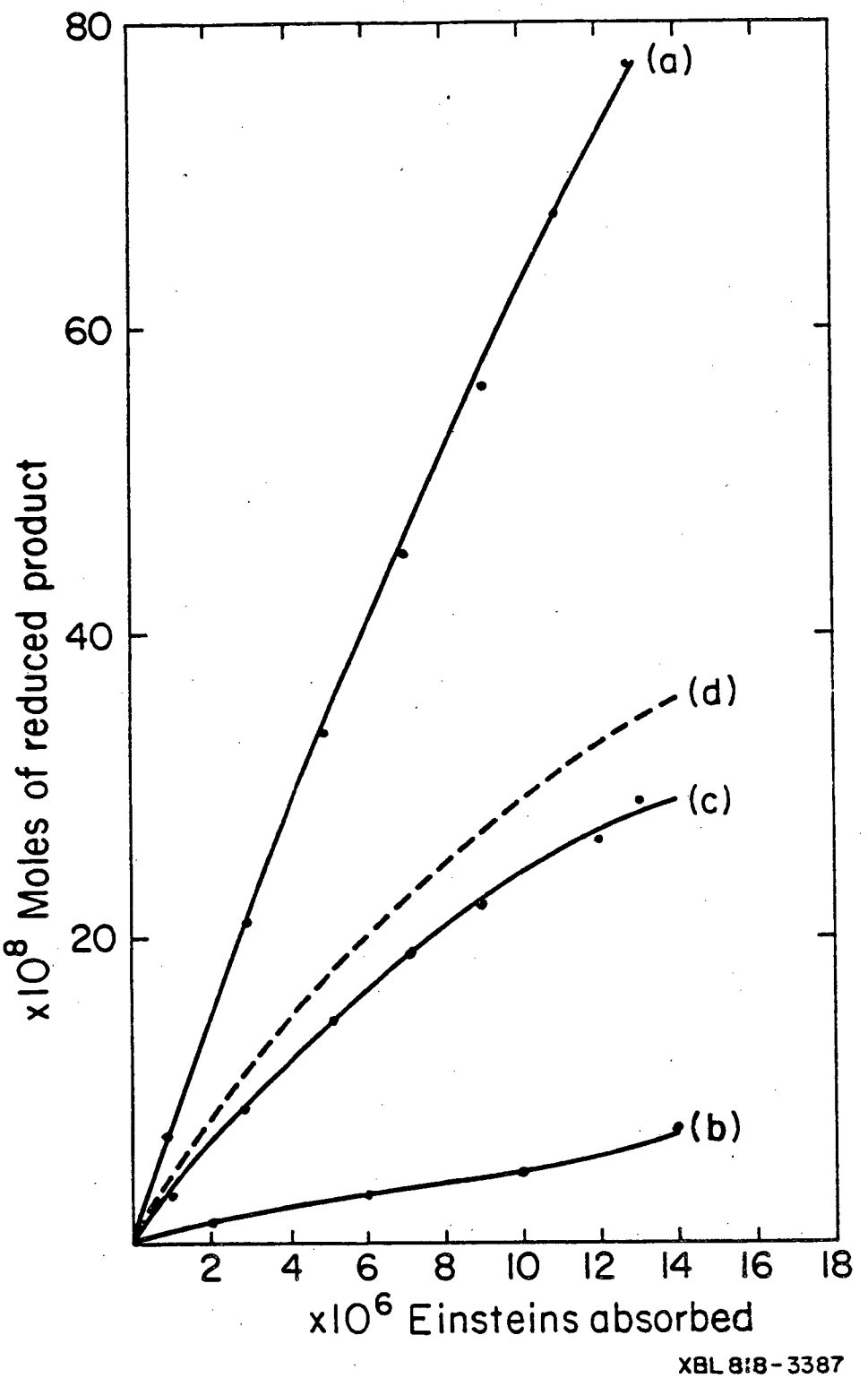


Figure 15.
Formation of reduced product as function of light adsorbed, showing synergism of shuttle.
SiO_2, 0.2%; pH 9.8; TEA, 10^{-3}; $Ru(bipy)_3$ 3×10^{-5}

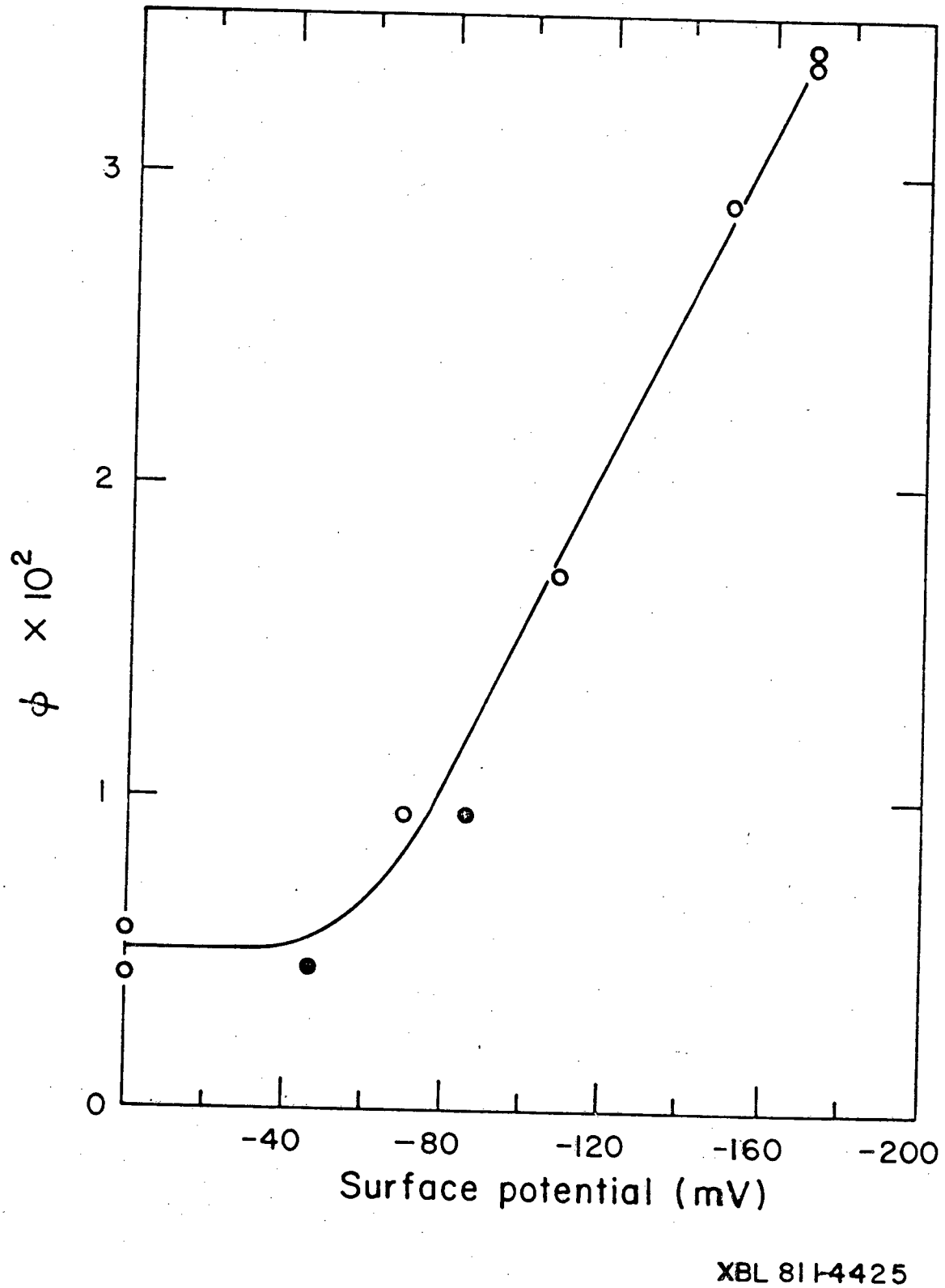
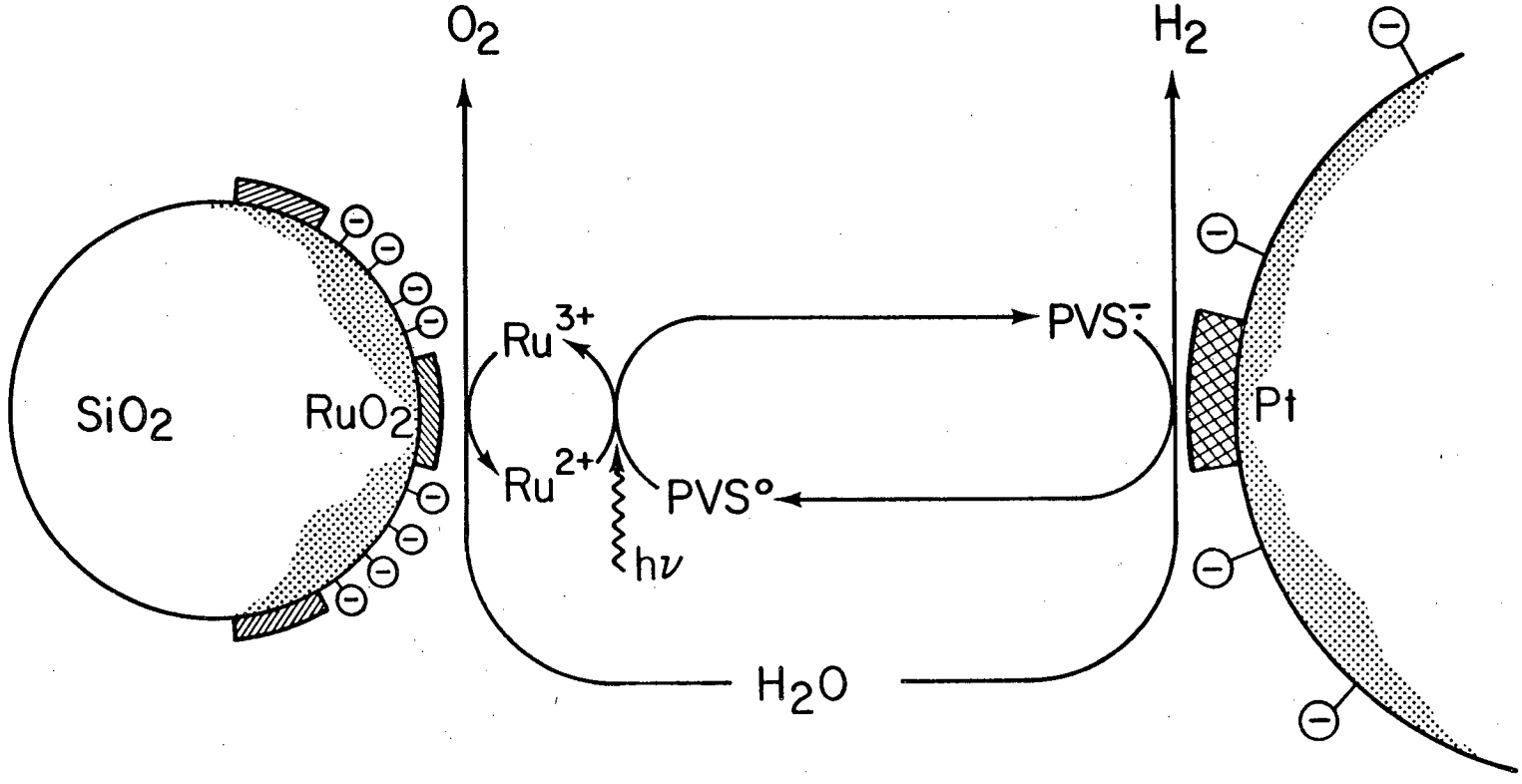


Figure 16. Quantum yield for propylviologen, $PVS^{\cdot-}$, formation as a function of the surface potential of negatively charged interfaces (o) SiO_2 system; (●) NaLS micellar system.



XBL 812-4486

Figure 17
Utilization of silica dioxide colloids in the photodecomposition of water

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