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QUANTUM CAPTURE AND REDOX STORAGE

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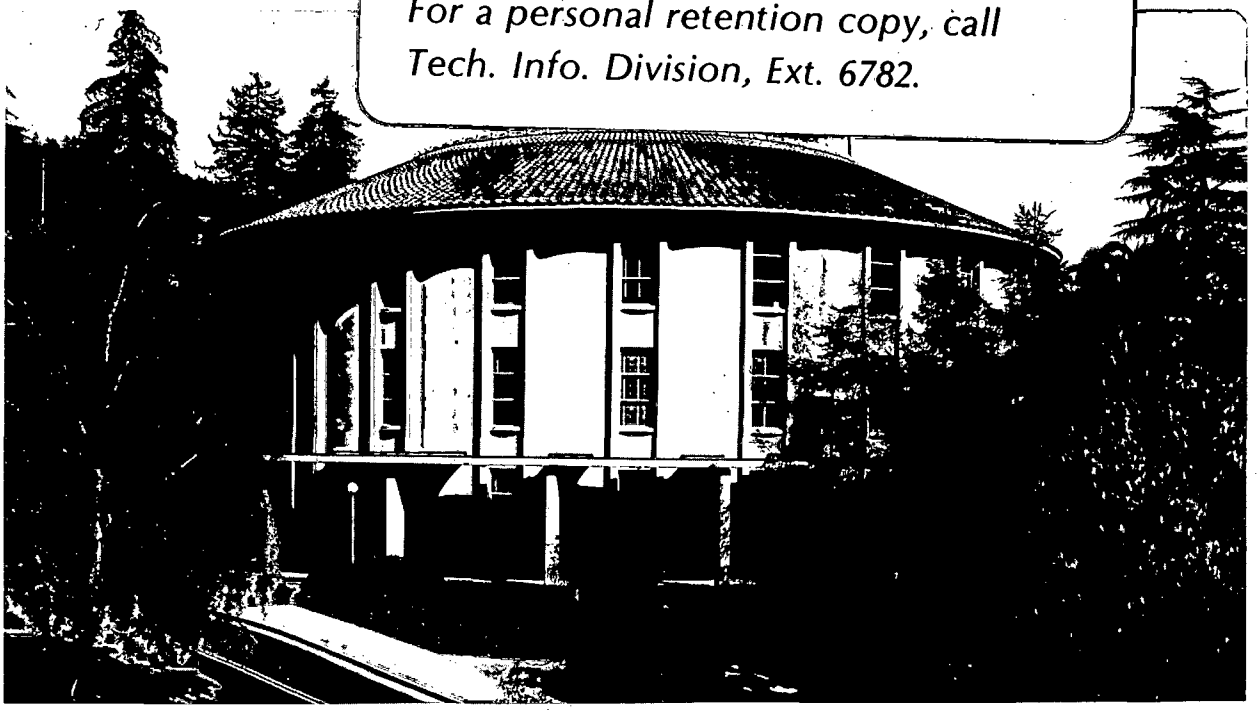

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QUANTUM CAPTURE AND REDOX STORAGE

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ABSTRACT

Over many years multiple investigations of the mechanism of the primary quantum conversion steps in natural photosynthesis have exposed the participation of some kind of manganese complex in the oxidation of water to molecular oxygen and the participation of a number of iron hemes in the electron transport chain between the two photosystems. It is almost certain that the participation of an iron-sulfur protein on the reduction side of the photosynthetic electron transfer scheme plays a role in the formation of reduced pyridine nucleotide through ferredoxin and in the evolution of hydrogen in plants deprived of CO_2 but having the hydrogenase present. The physical arrangement of the components is important as well, and the participation of at least one phase boundary (and probably two) in the same transport chain is likely. We have used this information to try to construct a synthetic chloroplast that would accomplish quantum conversion into stored energy in the form of intermediate oxidant and intermediate reductant. These could then be converted, respectively, into a useful oxidation product, or molecular oxygen, on the one hand, and molecular hydrogen, or a more useful reduction product, on the other.

INTRODUCTION

Artificial photosynthesis is a process that mimics the principles of green plant photosynthesis with a totally synthetic device (chemical system) that will capture the quanta from the sun and store them as stable chemicals (1-3). The primary problem of catching, storing and converting visible light into stable chemical form involves devising a system in which the short-lived energy of a sensitizer can be stored in some stable chemical form, usually by a redox reaction in which an electron is transferred from one point to another point nearby. If energy is to be stored after the electron is transferred, the system must be in a higher energy stage than it was before, that is, the immediate products of the electron transfer reaction will have a great tendency to back-react. Therefore, two problems must be solved: (1) We must convert the excitation of the sensitizer (chlorophyll in the green plant) in a very short time to a pair of redox molecules neighboring to each other, which must be capable of back-reacting to give energy. (2) We must prevent that back-reaction from occurring, while the two objects are close to each other, until we can move and store them in far greater stability. The green plant has evolved over several billion years and accomplishes these steps with a high degree of efficiency. Our problem is to generalize from what we know of green plant quantum conversion to some physical-chemical principles and to construct an entirely synthetic device that will be successful in splitting the water molecule to yield reductant and oxidant, e.g., hydrogen and oxygen.

The natural material of the green plant in which these reactions occur in the chloroplast is a series of very thin membranes (about 40 Å

this) containing molecules of various types. The membrane is unsymmetrical, suggesting that what takes place in the membrane is a result of two different quantum acts, one on either side of the membrane.

PHOTOSENSITIZED ELECTRON TRANSFER ACROSS BILAYER MEMBRANES

Photoelectron transfer in nature, as represented in Figure 1, shows that two quanta are absorbed in succession, and the quantum at 680 nm removes an electron from the water molecule through a manganese complex and raises that electron to a higher energy level,which is high enough to generate molecular hydrogen. The green plant, however, uses two quanta because the charge does not go directly from the first acceptor to NADPH, but rather goes through a series of downhill electron transfers with the generation of some ATP, the general energy currency of all living organisms. A second quantum then raises that electron again, whence it passes through a sequence of electron transferring agents such as iron-sulfur proteins, eventually reducing NADP to NADPH. The combination of NADPH formed here plus the ATP formed in the first quantum act together reduce carbon dioxide to sugars. With this two-quantum process and the asymmetrical membrane structure as a model, it seems altogether reasonable that an early step in a synthetic quantum conversion process should be the transfer of an electron across a membrane.

It has been possible to construct a synthetic membrane with sensitizers on both sides and to demonstrate the passage of an electron from one side of the membrane to the other side (4,5). The membrane consists of interfaces between phases, a water phase, an oil phase and another water phase (6). Sensitizers have been placed on either side of the membrane at the interface between the water and oil phases. We have

suggested as a basic physical principle that the electron must pass through the membrane. Before that happens, however, we must use the principles of photoelectron transfer across a phase boundary to stabilize the first reaction product of the quantum conversion act. The step would be the transfer of an electron from the donor to the acceptor at the phase boundary, i.e., separating the two phase boundary membranes into two separate parts. The transmission of an electron from the water phase, through the insulating membrane barrier to the other water phase, was demonstrated in vesicles using both synthetic and natural surfactant lipids (phospholipids). The synthetic lipids could be either dipolar or monopolar.

When we examined the natural system in the green plant we realized that chlorophyll, the sensitizer molecule, is actually a surfactant dyestuff. The chlorophyll has a hydrophylic head with a hydrophobic tail which is characteristic of surfactant structure. It was necessary to devise surfactant sensitizers more stable than the chlorophyll of the green plant. As one sensitizer molecule, we have used zinc porphyrin, which is more versatile and is capable of having a variety of substituent groups with both positive and negative charges, which can change the solubility function. The zinc porphyrin can also become a surfactant dyestuff by suitable adjustment of substituents. The synthetic electron acceptor, methylbiologen or heptulviologen, was modeled after propylviologen sulfonate, a neutral molecule, becoming a negative ion only after an electron is passed into it. When one electron is added to the heptylviologen, changing it from a dipositive to monopositive materila, it becomes a free radical with a blue color which is stable by itself but not stable to oxygen. It is thus possible to monitor the color and measure the number of electrons transferred across a vesicle wall. The surfactant dyestuff on both sides of the membrane with the electron acceptor (heptyl-

viologen) on the outside of the membrane is shown in Figure 2. There is a donor system on the other side of the membrane which is irreversible oxidized by Ru^{3+} to generate Ru^{2+} and oxidation products. An alternative donor [$Ru(bipy)_3^{2+}$] has an oxidation potential [as $Ru(bipy)_3^{3+}$] high enough to produce oxygen from water, if there is a surface, such as ruthenium oxide (7), which can accmulate four positive charges. It is possible to make hydrogen on the other side of the membrane by providing a platinum surface to give the two-electron collection which is needed (2).

It is therefore possible to perform a photochemical electron transfer from the inside to the outside of the membrane, producing a reduction product on one side of the membrane and an oxidation product on the other side, which cannot back-react because the membrane prevents it. This is the basic, funamdental structure of the photosynthetic membranes in the green plant chloroplasts.

A number of experiments (8) were performed to test this idea (Figure 3). A donor was placed on the inside of the membrane and an acceptor (methylviologen)on the outside. In the membrane (lower left), there is some surfactant acceptor present with a ruthenium surfactant sensitizer which produces a viologen radical on the outside; the reaction occurs rapidly at first and then gradually slows. The second experiment (upper) used methylviologen,without heptylviologen, and proceeded more slowly. In the third case (lower right) an electron carrier was added to the membrane which had little effect. This last experiment, however, did show that an electron carrier is not necessary to achieve electron transfer across a membrane.

The electron exchange between Ru^{2+} and Ru^{3+} across the membrane is an isoenergetic reaction, which is the reason electron tunneling occurs so readily. We have shown by kinetic arguments that this electron transport is the rate-limiting step in the overall reaction. If that is so,

then it should be possible to accelerate electron transfer by putting the proper potential across the membrane by selectively adding ions (such as potassium and sodium) on the inside and outside of the membrane with an ionophore in the membrane, a molecule which allows only passage of potassium ions(9). By varying the concentration of ions in the membrane system the potassium ion can be made to flow through the membrane down a concentration gradient while the sodium will be unable to come back. This generates a positive charge on the outside and a negative charge on the inside of the membrane, accelerating electron transfer from the inside to the outside. This experiment can also be reversed, in which case the electron transfer is slowed down. Thus, the potential construction across the membrane helps to substantiate our hypothesis with respect to the mechanism by which the electron transfer is occurring.

ENERGY TRANSFER ON MEMBRANE SURFACES

Recently (10) we have studied in greater detail the dynamics of the initial quenching reaction, using the convenient ferricyanide ion in the bulk phase as the quencher (accptor). A non-linear Stern-Volmer behavior indicated that a significant fraction of excited molecules was inaccessible to the quencher (Figure 4). Treatment of the data by a modified Stern-Volmer plot showed that only 66% of the luminescent sensitizer molecules were accessible to the quencher (11). Presumably these were the sensitizers on the outside. When ferricyanide quencher was placed both inside and outside the vesicle, all the luminescent molecules were available for quenching and normal Stern-Volmer behavior was observed (Figure 5). From the fraction of quenchable luminescence and the known thickess of

the lipid bilayer and the assumption that the head groups of the sensitizer lie at the surfaces, the outer diameter of the vesicles could be computed to be about 350 Å.

We found that over a wide range of sensitizer concentration in the lipid the percent of quenchable luminescence remained constant at 66%, indicating that there was no energy exchange between sensitizers across the membrane during the excitation lifetime even when the number of transmembrane neighbors was greatly increased. On the other hand, increase in surface sensitizer concentration did result in larger quenching rate constants, suggesting that exciton coupling may be taking place among sensitizers on the same side of the membrane. By this mechanism, the effective surface area over which a particular excitation can interact with quencher is increased, and, therefore, in a diffusion-controlled quenching reaction, the quenching rate itself is increased.

Implications of this added excitation migration process in the overall dynamics of photosensitized electron transport are still being explored. However, our major conclusion is unchanged, namely, that the mechanism of electron transport through the vesicle wall is by charge exchange between surfactant $Ru(bipy)_3^{3+}$ and $Ru(bipy)_3^{2+}$ on opposite sides.

A method entirely independent of fluorescence was then used to check on our vesicle size determination. The vesicles were prepared in a buffer containing ^{14}C-labelled sucrose, which does not penetrate the bilayer. After gel filtraton to remove the outside sucrose, the observed radioactivity of the vesicle suspension gave a measure of the total internal volume. Then from the total amount of lipid present and the known membrane thickness the average vesicle diameter could be computed to be about 500 Å, in fair agreement with the value obtained from the fraction

of sensitizer that is quenchable. The two values could be made consistent by assuming either that the sensitizer head groups protrude from the lipid surfaces into the aqueous phases by about 15 Å or that the surface density of sensitizer on the inside is somewhat smaller than out the outside, perhaps because of the higher degree or curvature.

PHOTOSENSITIZED ELECTRON TRANSFER IN WATER-IN-OIL EMULSIONS

It is also possible to transfer an electron across a single phase boundary in an emulsion (12) (Figure 6). The photosensitizer used is zinc tetraphenylporphyrin sulfonate, a negatively charged material with four sulfonic acid groups, which is water soluble and will remain in a water droplet. The acceptor, methylviologen, is also water soluble. The donor,thiophenol, is in the interphase region. When this particular system is illuminated, the zinc becomes excited, the excited state transfers an electron to the methylviologen which produces the blue color, the zinc porphyrin becomes oxidized and the oxidized zinc returns to the reduced form through the polar thiol group which concentrates at the water-toluene interface. When thiol is oxidized from sulfhydryl to disulfide, it moves away from the interface and is now oil soluble. Thus the separation of the oxidized product (disulfide) from the reduced product (viologen radical) is achieved by forming them in two separate phases.

The inner surface of the water droplet is surrounded by positively charged surfactants which affect the efficiency of this reaction. The positive charge attracts negatively charged zinc sensitizer but repels the positively charged electron acceptor. It is possible to use a neutral electron acceptor such as PVS, and to raise the quantum yield substantially.

PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN SiO_2 COLLOIDS

It occurred to us that it might be possible to use a surface potential to achieve separation, without having the charge go across the membrane boundary. It is possible to arrange the system in such a way that the surface potential of the interface will be the controlling factor in the efficiency of the electron transfer (13-15) if the right particles are used with the correct charge distribution and proper structure of donors/acceptors/sensitizers. We chose silica particles which are highly negatively charged to test this hypothesis, performing the experiments at pH 9 to be sure that the positive sensitizer is closely attached electrostatically to the negatively charged surface. The neutral electron acceptor, PVS, can approach either a positive or negative surface. When the sensitizer (Ru^{2+}) is illuminated and excited it can pass its electron to the neutral acceptor, creating a PVS^- radical which changes the charge on the ruthenium sensizer from +2 to +3. The Ru^{3+} is held even more tightly to the negatively charged surface, and the electron acceptor, now negatively charged, is ejected from the field around the negative particles. Thus, the back-reaction of the two materials, which should energetically go back downhill, is prevented (Figure 7). It is possible to regenerate the sensitizer by using a neutral donor. This reaction, using either ruthenium or zinc as sensitizer, is shown (Figure 8) as a function of the light absorbed. The experimental data for the ruthenium (Figure 8a) and for the zinc tetramethylpyridinium porphyrin (Figure 8b) indicate that addition of silica particles prevents the back-reaction. A confirmation of this information was found through flash photolysis experiments which follow the first milliseconds of the reaction. The flash photolysis data show the amount of reduced methylviologen, and there is no question that the silica allows the reduction of the PVS while the

negative surface prevents the reduced viologen from back-reacting with the oxidized ruthenium. The retardation of back-reaction can be modified by reducing the negative potential on the silica particles either by adding some salt or decreating the pH; both of these changes increase the speed of the back-reaction.

We would like to move those electrons even further away from the silica particles by using another electron carrier. We have used PVS as a shuttle to reduce ferri- to ferrocyanide. The ferricyanide has three negative charges and ferrocyanide has four, and neither can approach closely the highly negative charged SiO_2 particles. It would be difficult to reduce directly ferri- to ferrocyanide because of the high potential energy of the negatively charged ferricyanide in the field of the silica particles. Therefore, the neutral PVS can be used as a shuttle because it can appraoch the silica particle. PVS is converted from a neutral to a negative molecule, is ejected from the negative field of the particle and reaches the ferricyanide and reduces it to ferrocyanide. The shuttle can then go back and accept another electron (Figures 6 and 9). The same shuttle function occurs in the chloroplasts where the electron transfer chain pulls the electron further away from the initial sensitized membrane surface.

As mentioned earlier, we can control the negative potential on the silica surface by adding salt to the environment, which reduces the negative surface potential, controlling what can approach the surface. Other surfaces, such as that of sodium laurylsulfonate micelles (Figure 10) have surface potentials much lower than that of silica. The quantum yield, therefore, can be controlled by the negative charge of the particle upon which the reaction is occurring. Thus, PVS could be used as

a shuttle between two different negatively charged particles, one of the negative particles generating hydrogen and the other generating oxygen (Figure 11).

DEVICE FOR PHOTODECOMPOSITION OF WATER

We have outlined two different methods for generating or building a device to separate water into its constituent parts using only synthetic materials for this purpose. We have also indicated how such a device can be constructed. We have already used vesicles which are spontaneously formed ... microspheres composed of phospholipids or synthetic lipids. These vesicles are 40 Å thick and the particle itself is 500 Å in diameter. It may also be possible to use synthetic membranes, which were developed for artificial kidneys or desalinization membranes, and spun in the form of hollow fibers (16). The hollow fibers are the sites for the sensitizers and the medium through which the electrons can move. Our experiments used a hollow fiber originally synthesized for a desalinization membrane. We stained the fiber with oil-soluble porphyrin by swelling the fiber with an organic solvent (dioxane). The sensitizer (zinc tetraphenylporphyrin), when dissolved in the dioxane, penetrates the swollen fibers; the solvent is then washed out with water, leaving behind in the fiber the water-insoluble sensitizer. Therefore, it has been possible to create a stained fiber with a wall thickness of about 80 microns, containing a dyestuff which resists water. A substantial amount of sensitizer-dyestuff material is required in order to have one dyestuff molecule every 40 Å of fiber body. When an electron is removed from the outside of this hollow fiber, the hole may jump 40 Å each time to reach the other side.

The hollow fibers are mounted so the inside and outside can be reached separately (Figure 12). In this prototype for the system, the inside of the hollow fibers is connected to the inside of the upper plastic tubes, and the outside is connected to the water layer which is accessible to the side-arms of the U-tubes.

With the hollow fiber (membrane) device for photoelectrochemically transferring electrons from one side to the other, it will be possible to place the catalyst for hydrogen production on one side and the catalyst for oxygen production on the other. The reactions have all been performed separately but not yet together in a single device.

DEVELOPMENT OF CATALYSTS FOR ARTIFICIAL PHOTOSYNTHETIC SYSTEMS

Until recently, we have not used our knowledge of the natural catalysts used by the green plants for the generation of hydrogen from water and generation of oxygen as a byproduct. We have used the phase boundary idea, the surfactant sensitizer idea, the photoelectron transfer idea and the charge migration idea, but not what we know about the function of the natural catalysts that produce the final products in the plant.

The natural catalyst for molecular hydrogen in plants turns out to be an iron-sulfur cluster of four iron atoms and four sulfur atoms hanging in a protein by mercaptide groups of the cysteine residues of the polypeptide. It is possible to construct a synthetic iron-sulfur cluster that is the catalyst for hydrogen production and this has been done electrochemically but not yet photochemically (17). However, we have recently used synthetic iron-sulfur clusters to determine their photoelectron accepting capability. If one of the synthetic iron-sulfur clusters, tetra[alkylmercapto-μ_4-sulfido-iron] (aryl) is placed in the water solution with the ruthenium or zinc sensitizer, it quenches the fluorescence of the sensitizer either by energy transfer or

by accepting an electron from the excited sensitizer. We propose that the latter mechanism is the correct one (18). We have thus indicated a hydrogen generating system which does not require platinum as a catalyst by using the iron-sulfur clusters.

Not as much is known, however, about the oxygen generating catalyst. Manganese is indicated, and experiments over many years have sought to determine the state of that manganese. At one time, we felt it was a binuclear manganese compound, but more recent experiments indicate that the manganese must also be in a cluster, containing at least two manganese (perhaps four, in actuality) because it is necessary to move four electrons from the water to make molecular oxygen.

With the idea that the oxygen generating catalyst contains two manganese atoms, we synthesized the type of molecule(s) which would have the required characteristics. Our first efforts involved manganese atoms on a rigid bridge-type connection; this turned out to be unsucccessful (19,20). We then turned our attention to constructing a flexible binuclear manganese compound in which the manganese atoms could change the distance between each other. This can be explained as follows: Two manganese porphyrin molecules hooked together by a flexible chain could be in solution; two water molecules could enter, changing the distance between the manganese atoms in the porphyrin molecules, closing the hook so to speak. Then the electrons would be removed via the manganese atoms and the two oxygen atoms could be brought together to make oxygen (21).

We have synthesized a mononuclear surfactant manganese compound (22), and inserted it into a thin membrane together with a zinc porphyrin. By photoexciting the zinc compound it was possible to eject an electron from the zinc to an aqueous viologen acceptor (23). The oxidized zinc in the membrane then extracts an electron from the nearby manganese,

also in the membrane, indicating that it is possible to oxidize the manganese catalyst by sensitized oxidation This is similar to the process used to reduce the iron-sulfur clusters (catalysts) on the hydrogen evolution side. The experimental basis for this observation is shown in Figure 13. The data indicate that the back-reaction between the reduced acceptor (viologen in the water) and photo-oxidized catalyst in the membrane is inhibited. This inhbition occurs by (1) organizing the manganese compound and the photosensitizer (zinc porphyrin) on one side of a membrane interface (Figure 14), while the acceptor resides in the aqueous phase; (2) making the membrane interface negatively charged; and (3) using a zwitterionic acceptor, propylviologen sulfonate, whose reduction product is then repelled from the membrane surface. These experiments suggest that the back-reaction between the oxidized zinc sensitizer and the reduced propylviologen sulfonate acceptor is retarded by the negatively charged membrane (Figure 14).

CONCLUSION

We can look forward to the creation of an artificial system for photosynthesis, using the principles of synthetic chloroplasts to mimic the way the green plant takes quanta to generate oxidizing power (oxygen) on one side of the membrane and reducing power (hydrogen) on the other. We have used analogues of most of the components of the natural photosynthetic system to achieve the synthetic chloroplasts: (1) The phase boundary concept, (2) the charge distribution idea, (3) electron transfer across the membrane via isoenergetic electron exchange (electron carriers), and (4) the use of two catalysts, one for the hydrogen evolution and the other for the oxygen evolution side. We have achieved, outside the green

plant, all of the parts of the natural system; it now remains to put them together into one device.

In our efforts to devise means for the photolysis of water using the light and creating hydrogen as a fuel, we have found that oxygen is generated as a byproduct. In actuality, molecular oxygen, because it is not a fuel, is not the material which is the most useful. It should be possible to use the elctron transfer step sometime before molecular oxygen is formed to generate an intermediate oxidant such as a peroxide which is a more useful chemical reactant.

Therefore, it now appears that it will be possible to capture the energy of the sun for energy use (to make molecular hydrogen) and also for chemical use in the form of intermediate oxidants which are used in many chemical processes. The systems described accomplish both of the necessary requirements for a useful solar energy device: (1) The capture of the quantum and its conversion to some other energy form and (2) 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.

(This manuscript represents a summary of the plenary lecture in the Symposium in Honor of H. E. Gunning. V. Physical Photochemistry, at the meeting of the Canadian Institute of Chemistry, Toronto, Canada, May 31, 1982.)

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FIGURE CAPTIONS

Figure 1 Photosynthetic electron transfer scheme

Figure 2 Scheme for photosensitized electron transfer across a lipid vesicle wall

Figure 3 Cofactors in photoelectron transfer reactions across a membrane

Figure 4 Luminescence quenching with quencher outside of vesicles only

Figure 5 Luminescence quenching with quencher inside and outside of vesicles

Figure 6 Electron transfer across interface of water-oil emulsion leading to separation of redox products. Zinc tetraphenylporphyrin sulfonate is photosensitizer. Quantum yields using two acceptors, methylviologen (MV^{2+}) on the left and propylviologen sulfonate (PVS^{o}) on the right are compared.

Figure 7 Schematic function of SiO_2 particles in separating multicharged photoproducts

Figure 8 Propylviologen radical, $PVS^{\cdot -}$, formation as a function of light absorbed, monitored by the increase of absorbance at λ = 602 nm.

Figure 9 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 time of PVS^{o} addition. (c) homogeneous system; (d) NaLS micellar system.

Figure 10 Quantum yield for propylviologen, $PVS^{\cdot -}$, formation as a function of surface potential of negatively charged interfaces. (o) SiO_2 system; (●) NaLs micellar system

Figure 11 Utilization of SiO_2 colloids in the photodecomposition of water

Figure 12 Hollow fiber apparatus for photodecomposition of water

Figure 13 Difference spectra between system I and system II after illumination

Figure 14 Single unilamellar vesicle with diameter between 200 and 500 Å, prepared by sonication with indicated ratio between phospholipid and sensitizer of 86:3:1 with PVS added outside the vesicle

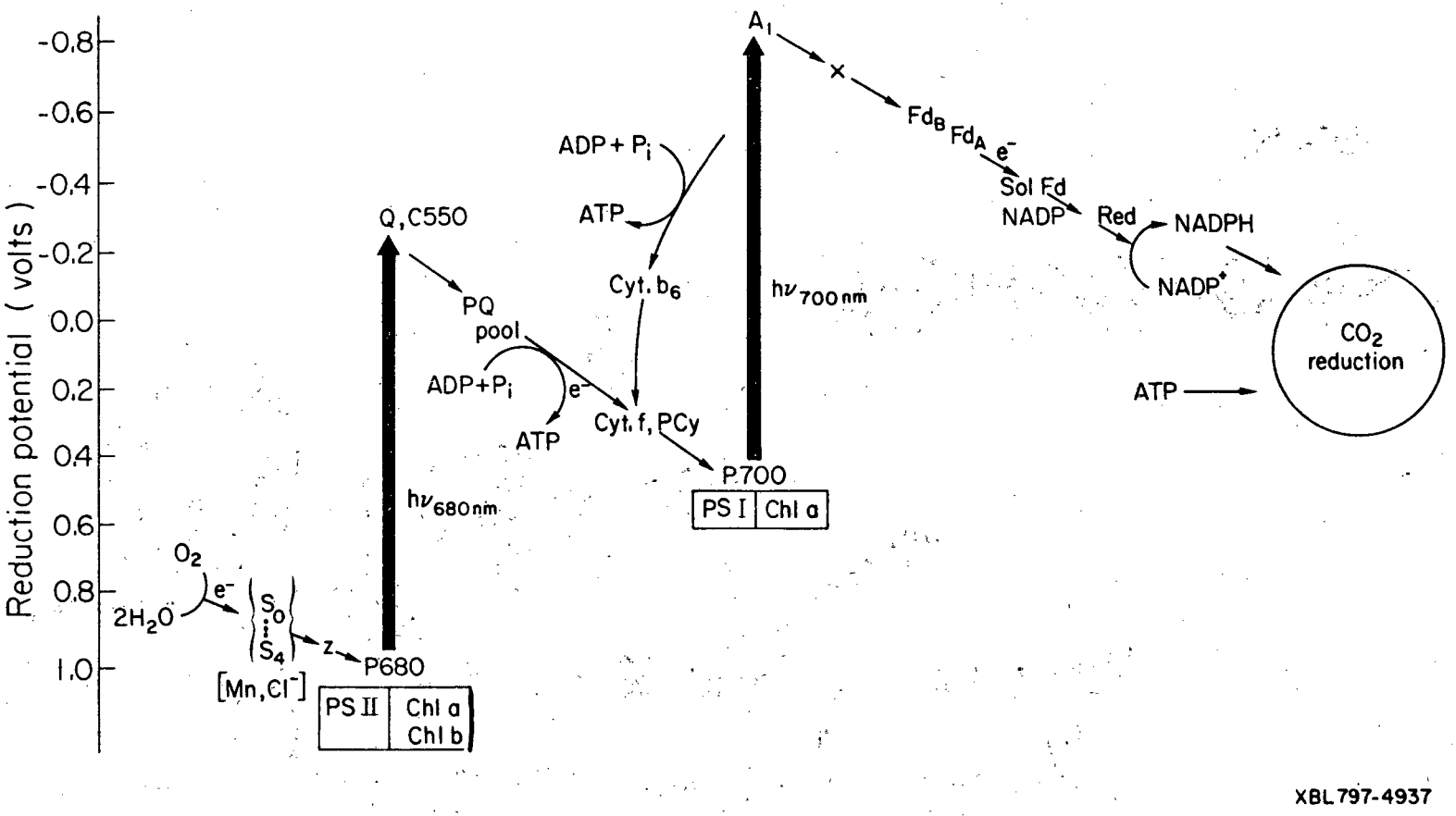

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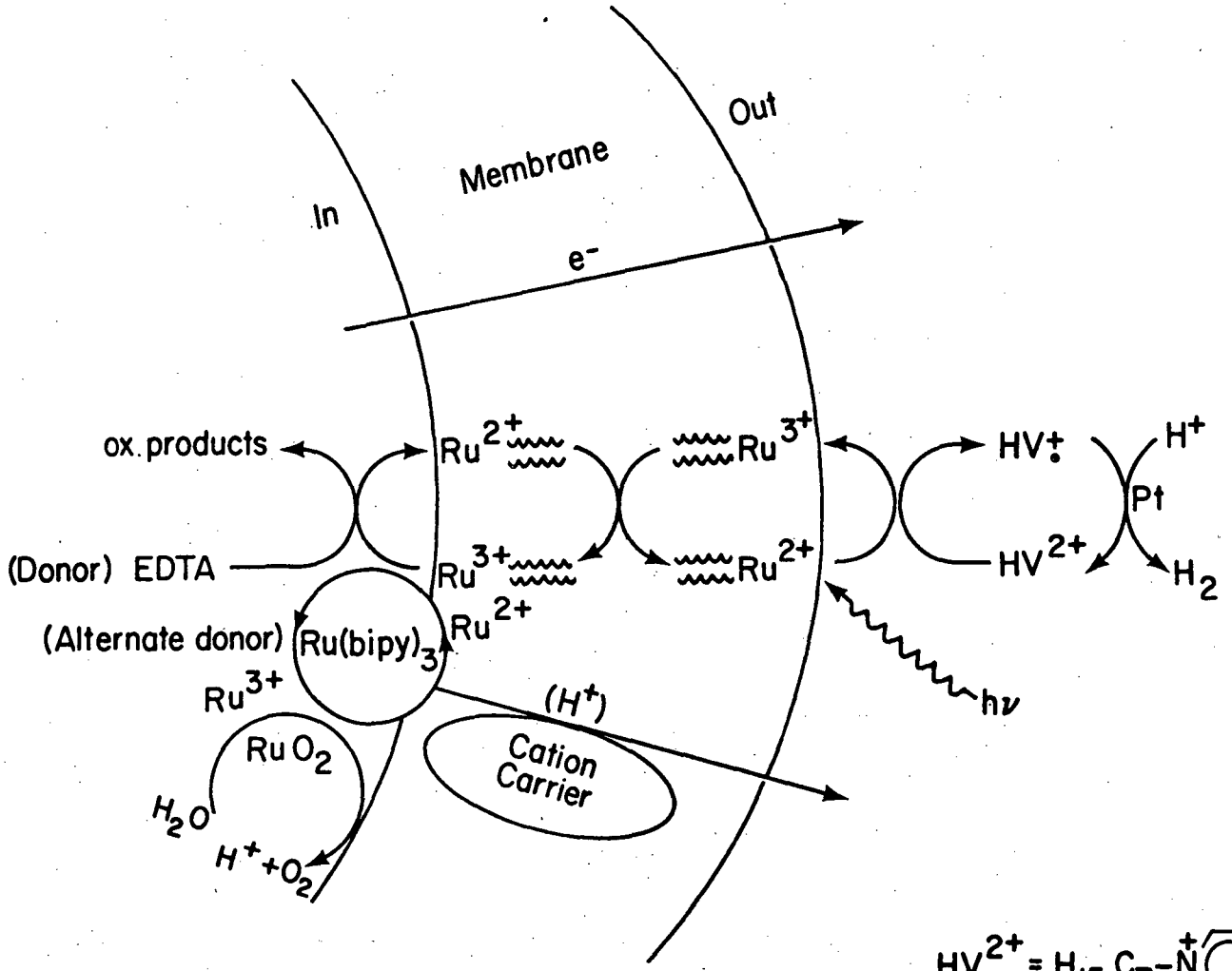
Figure 1



$HV^{2+} = H_{15}C_7-\overset{+}{N}$⟨⟩$-\overset{+}{N}-C_7H_{15}$

XBL 821-61

Calvin
Figure 2

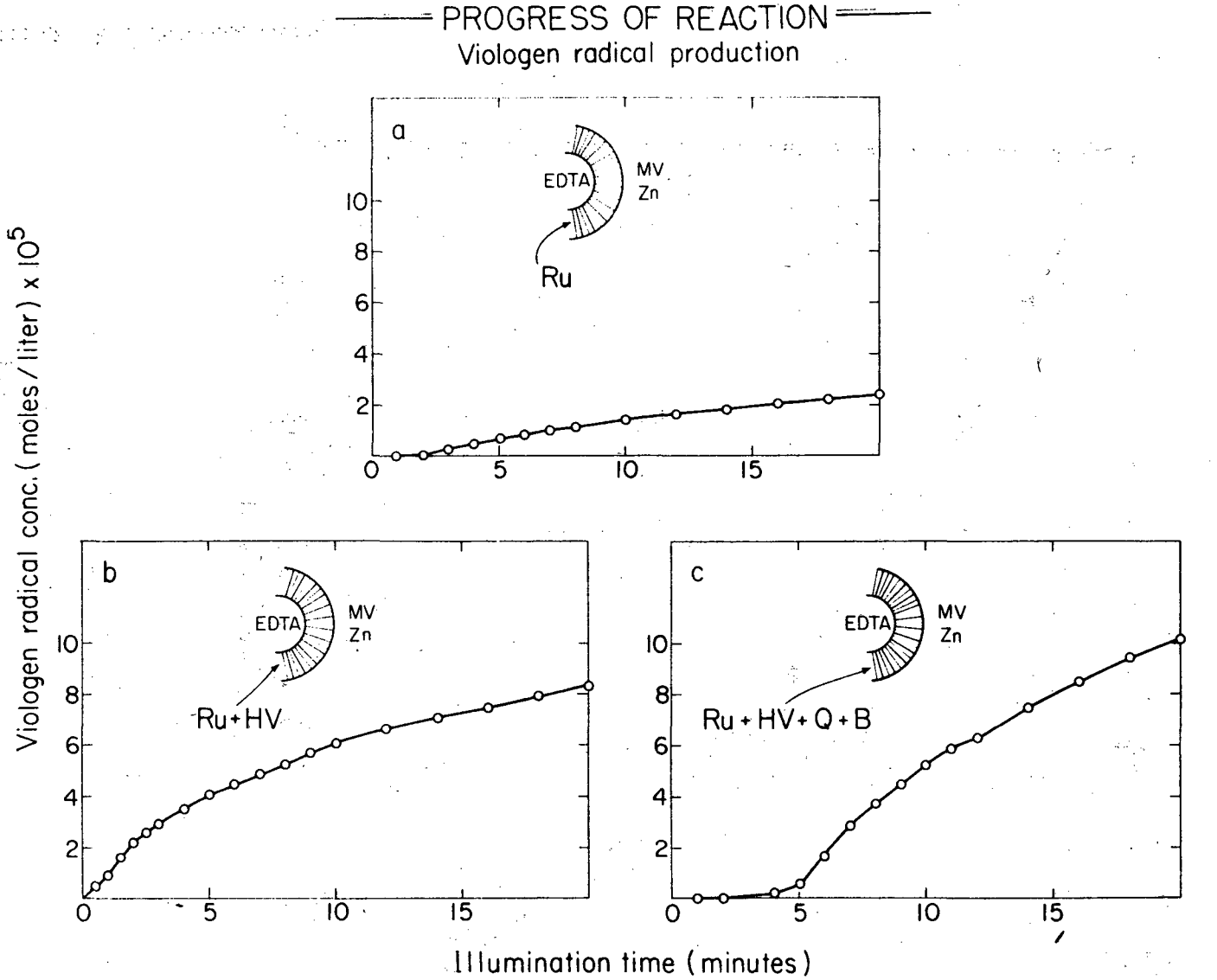


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Figure 3

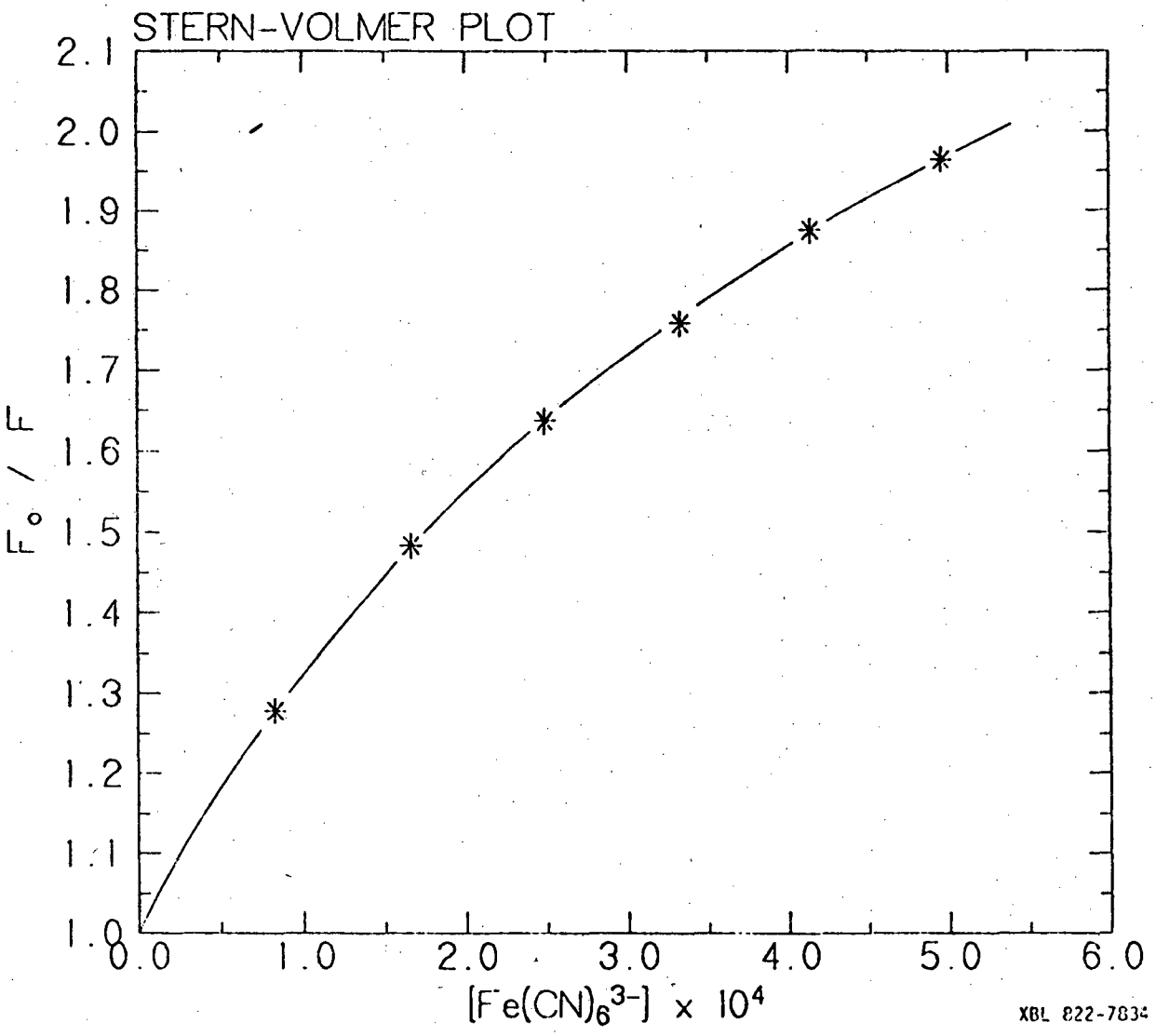

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Figure 4

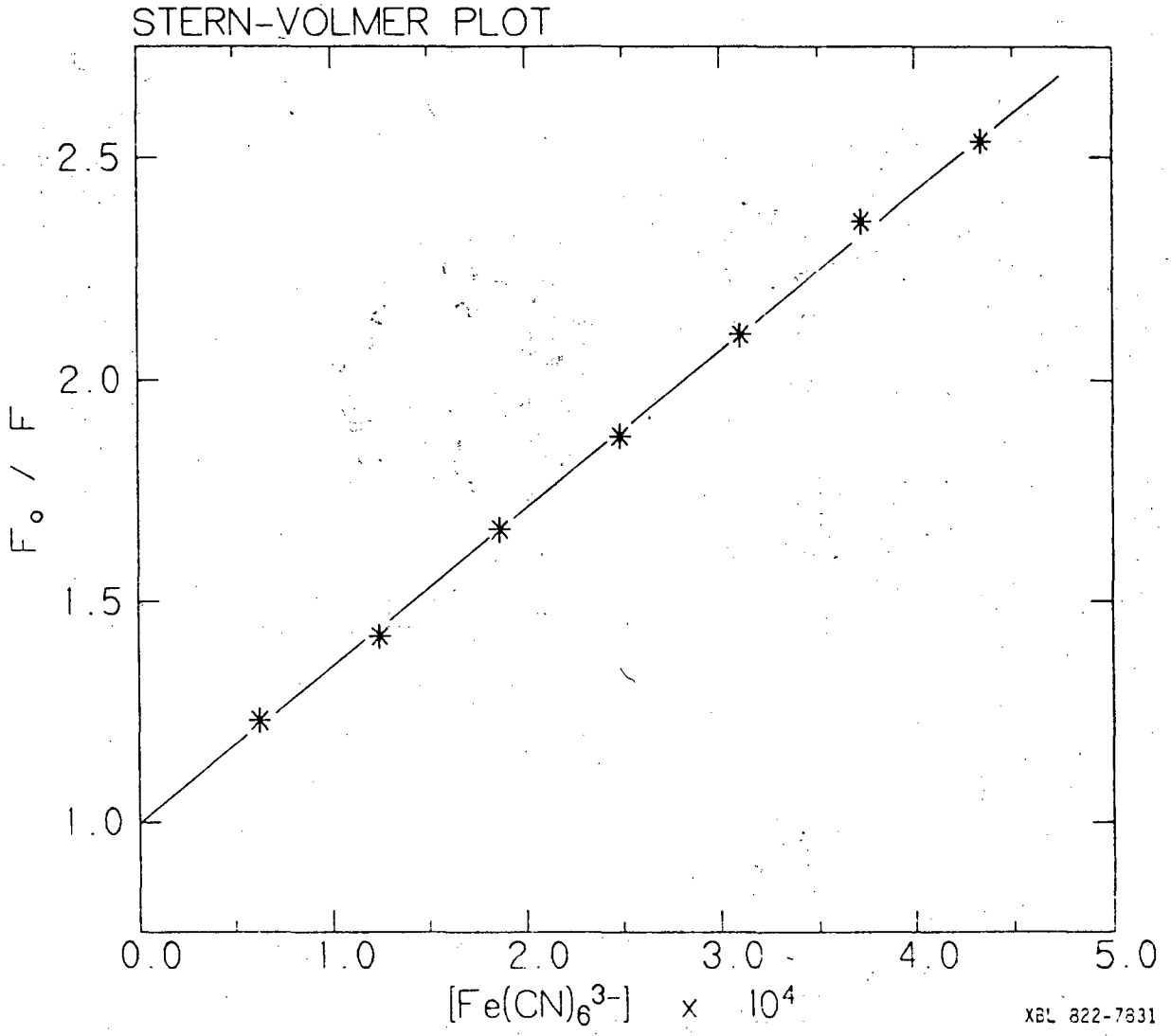

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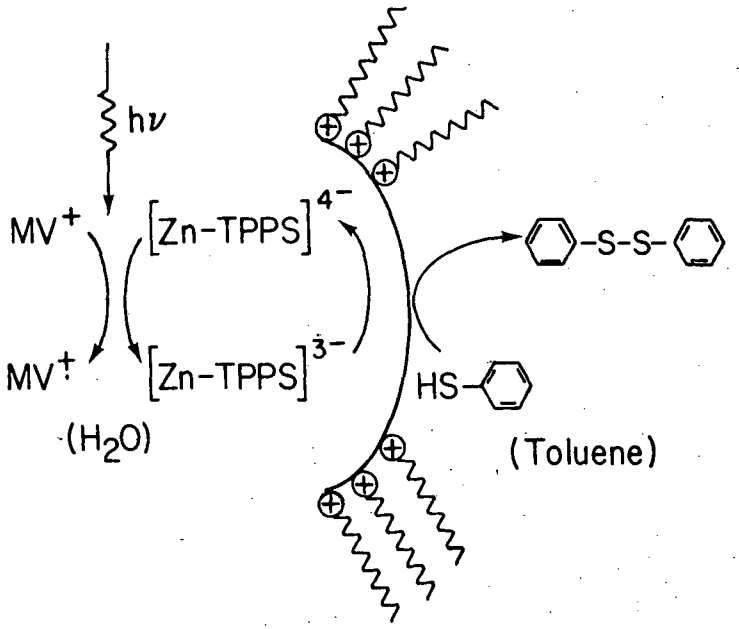
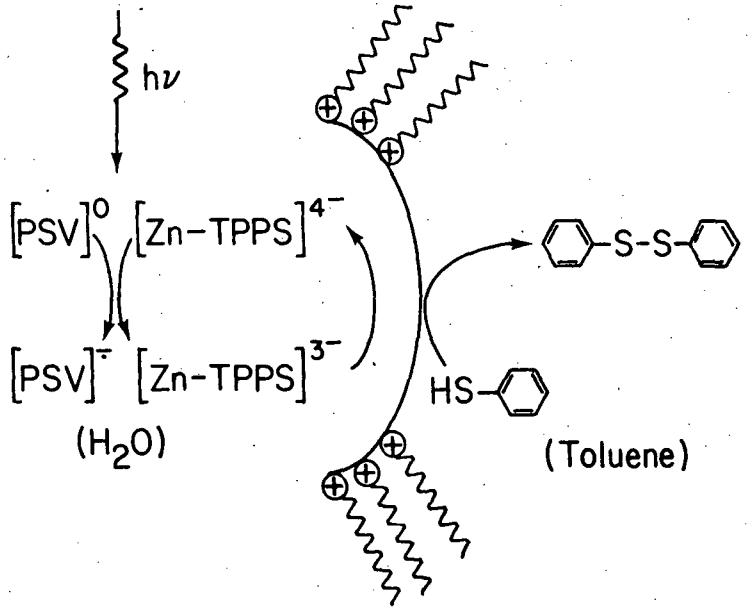
Figure 5





MV^{2+} = CH_3-N^+⟨⟩$-N^+-CH_3$

$\phi_{max.} = 0.0067$

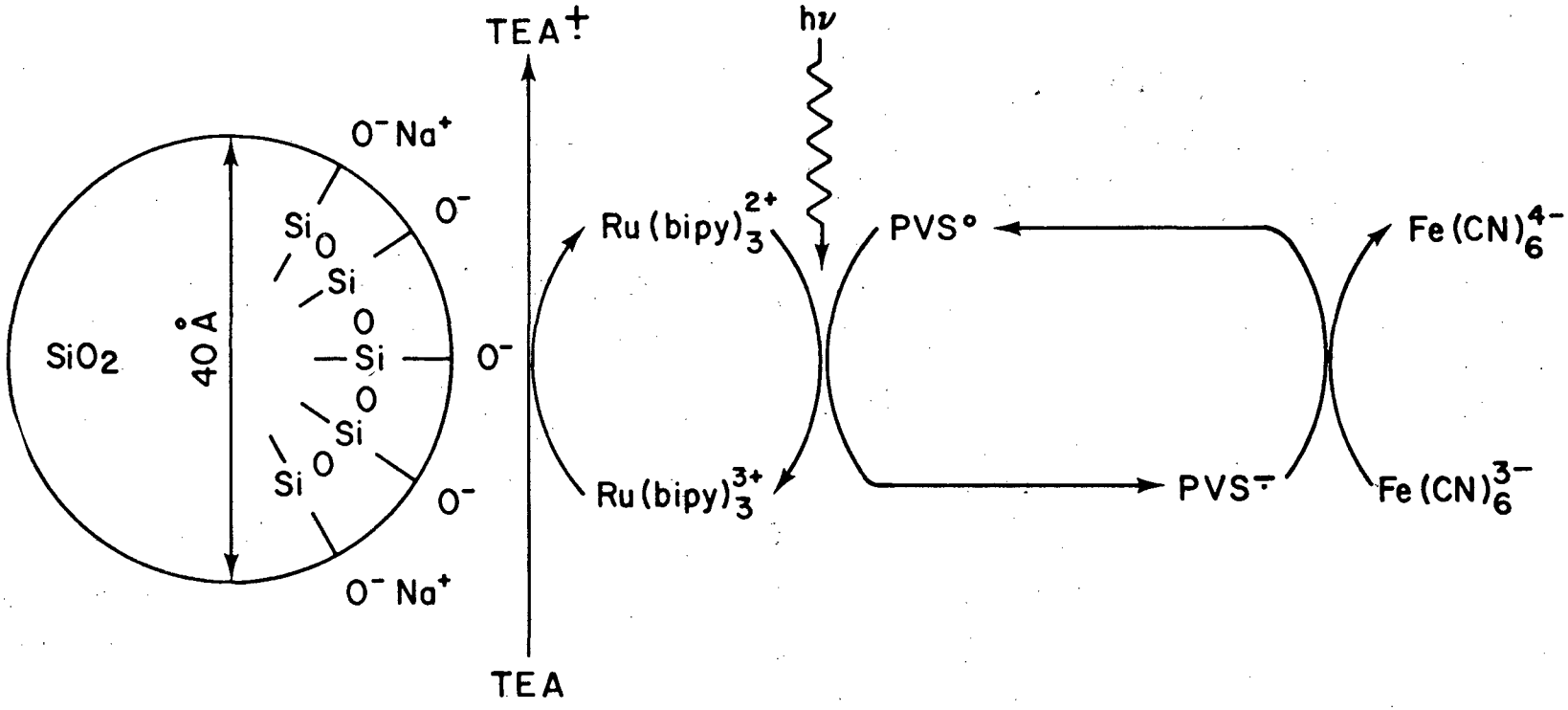
PVS = $-N^+$⟨⟩$-N^+-$ (SO_3^-, SO_3^-)

$\phi_{max.} = 0.03$

XBL 805-4193

Calvin

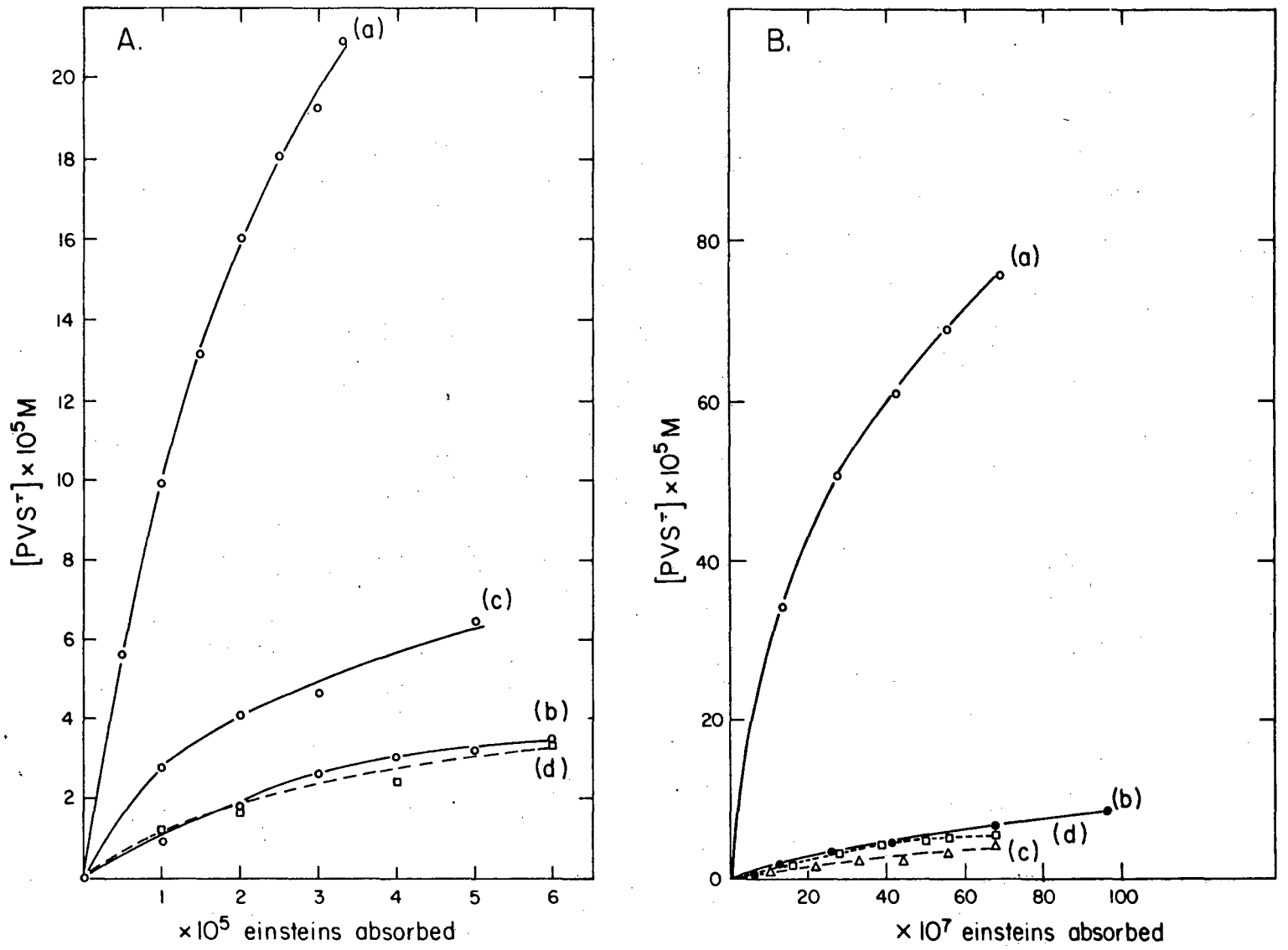
Figure 6



XBL 812-4456

Calvin

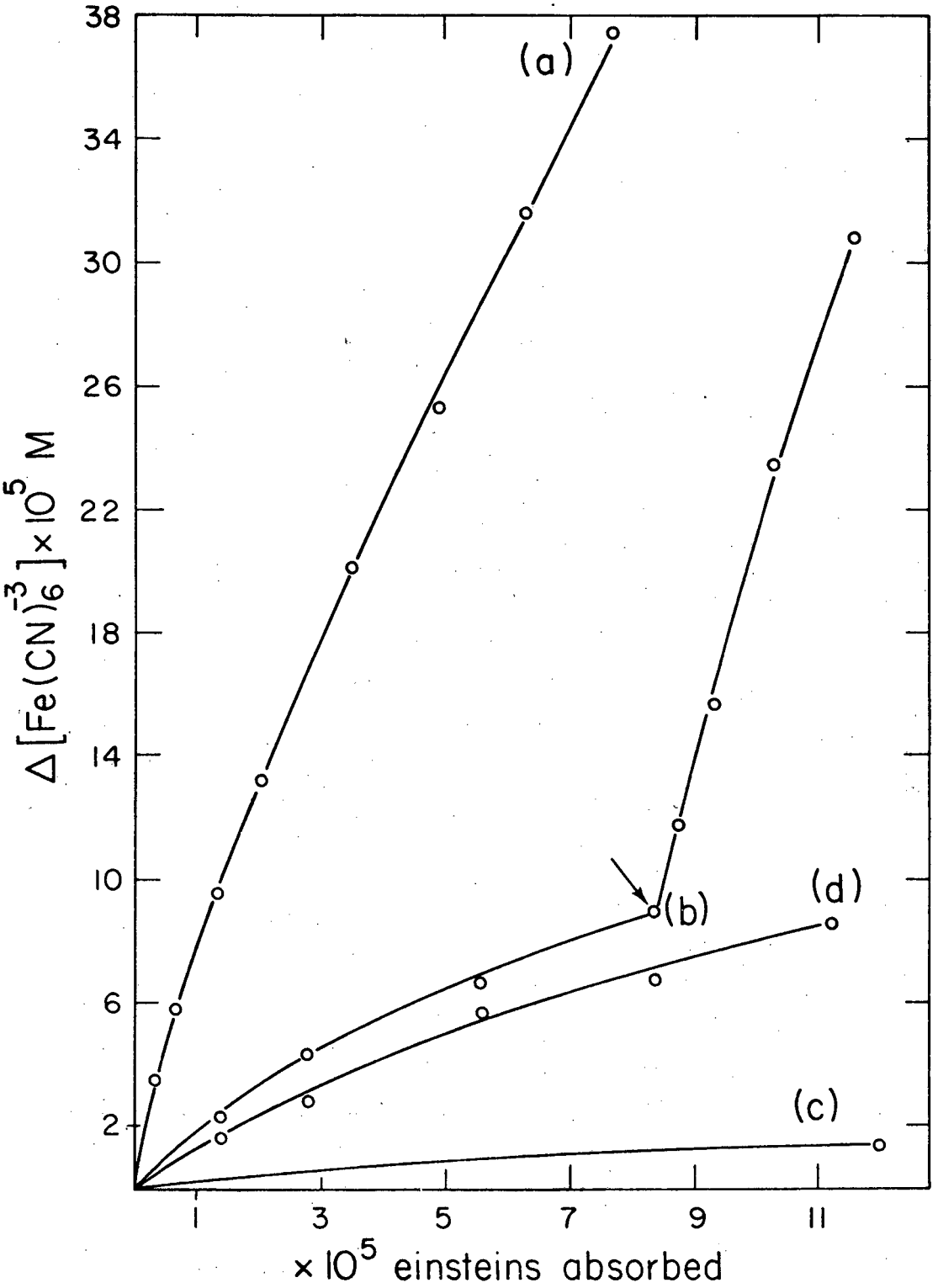
Figure 7



XBL 814-4529

Calvin

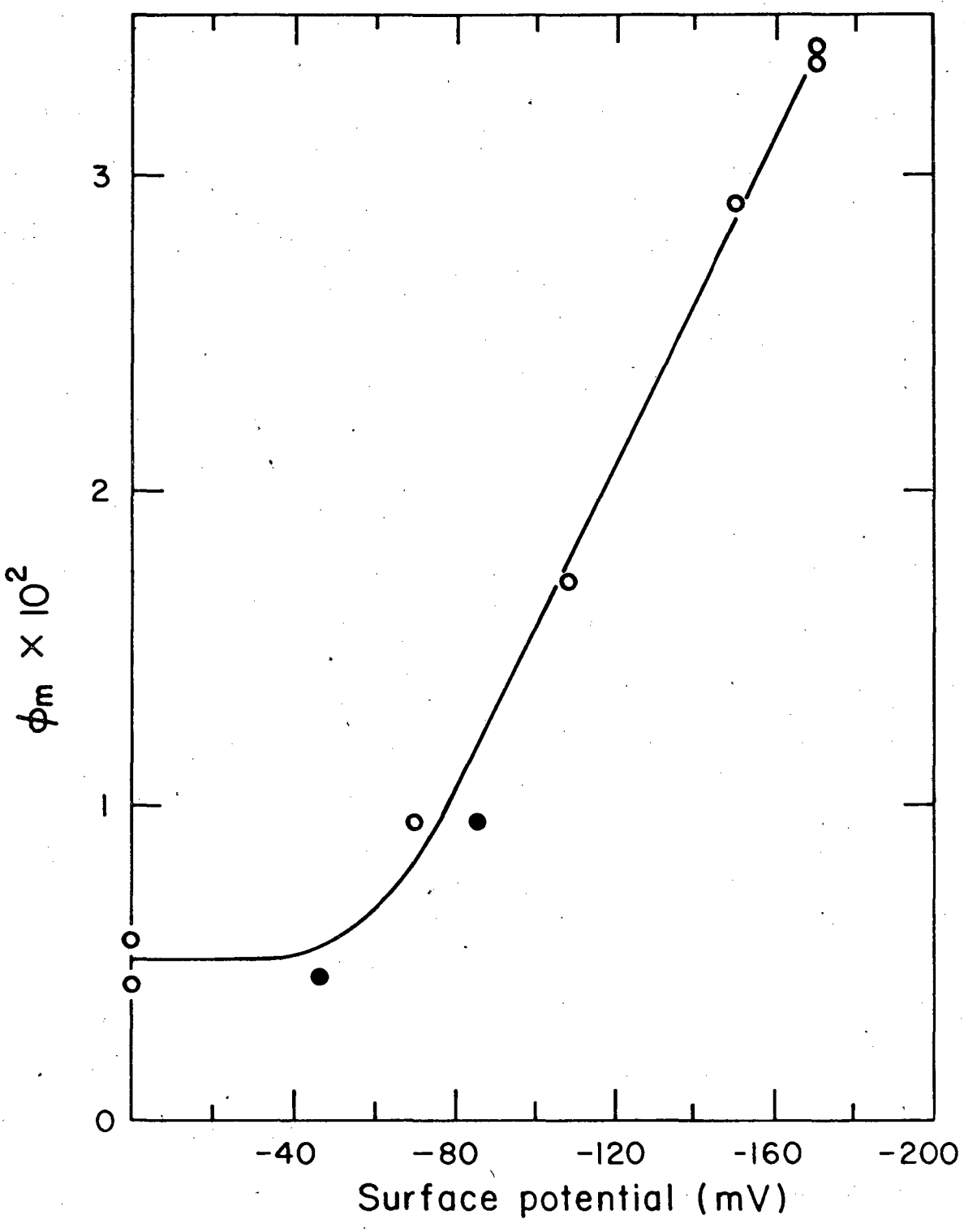
Figure 8



XBL 812-4455

Calvin

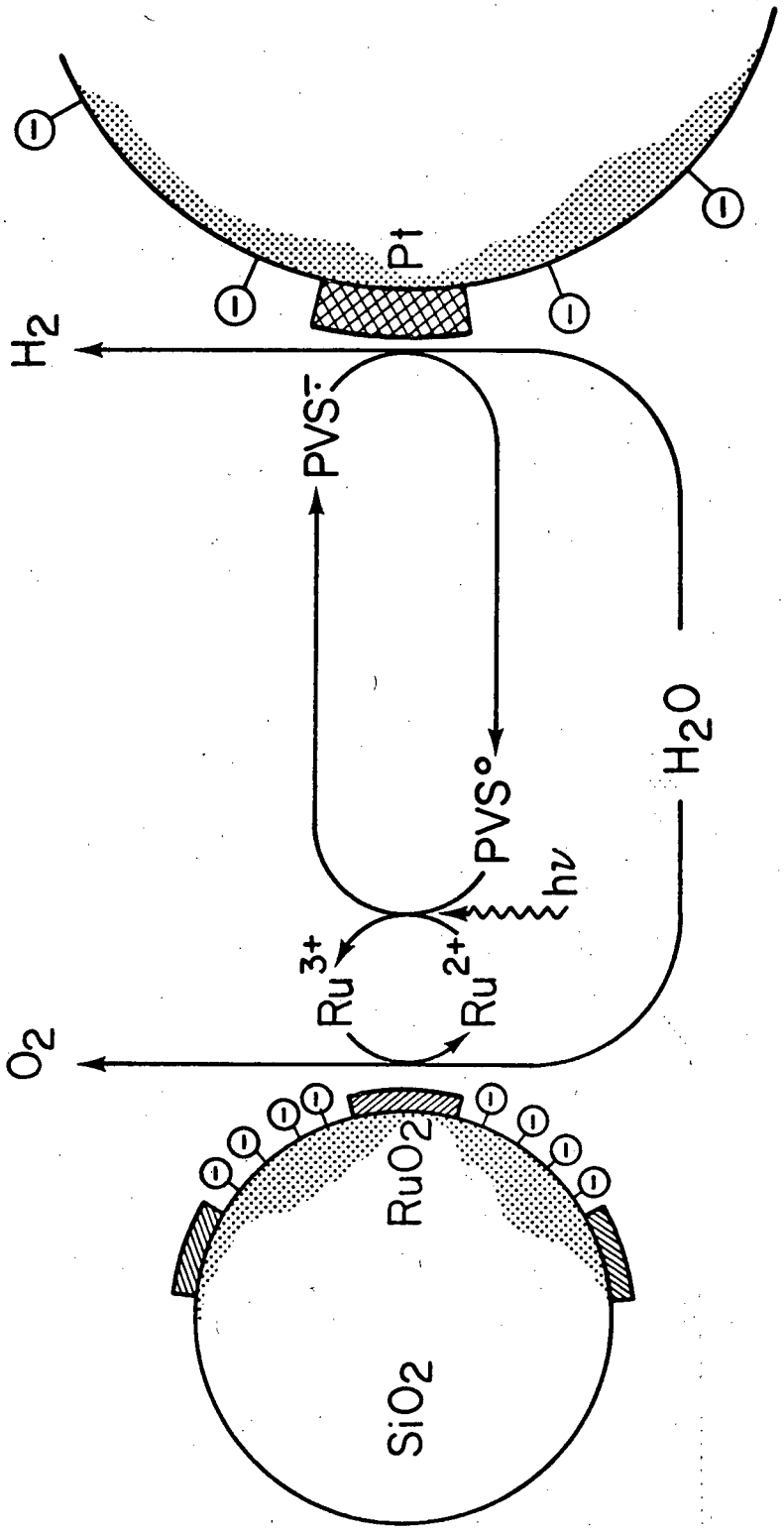
Figure 9



XBL 811-4425

Calvin

Figure 10



XBL 812-4486

Calvin

Figure 11

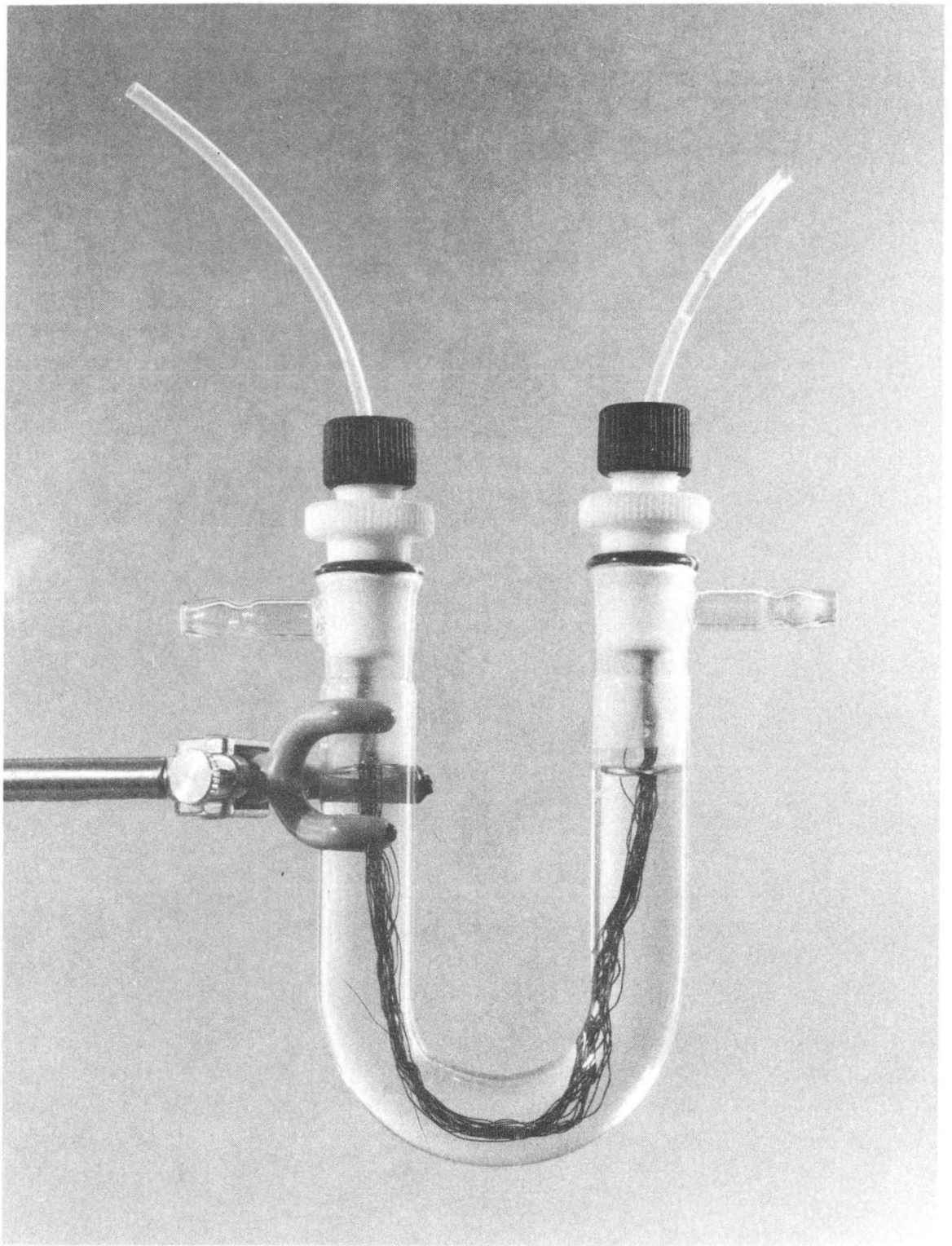


Figure 12

CBB 814-3554

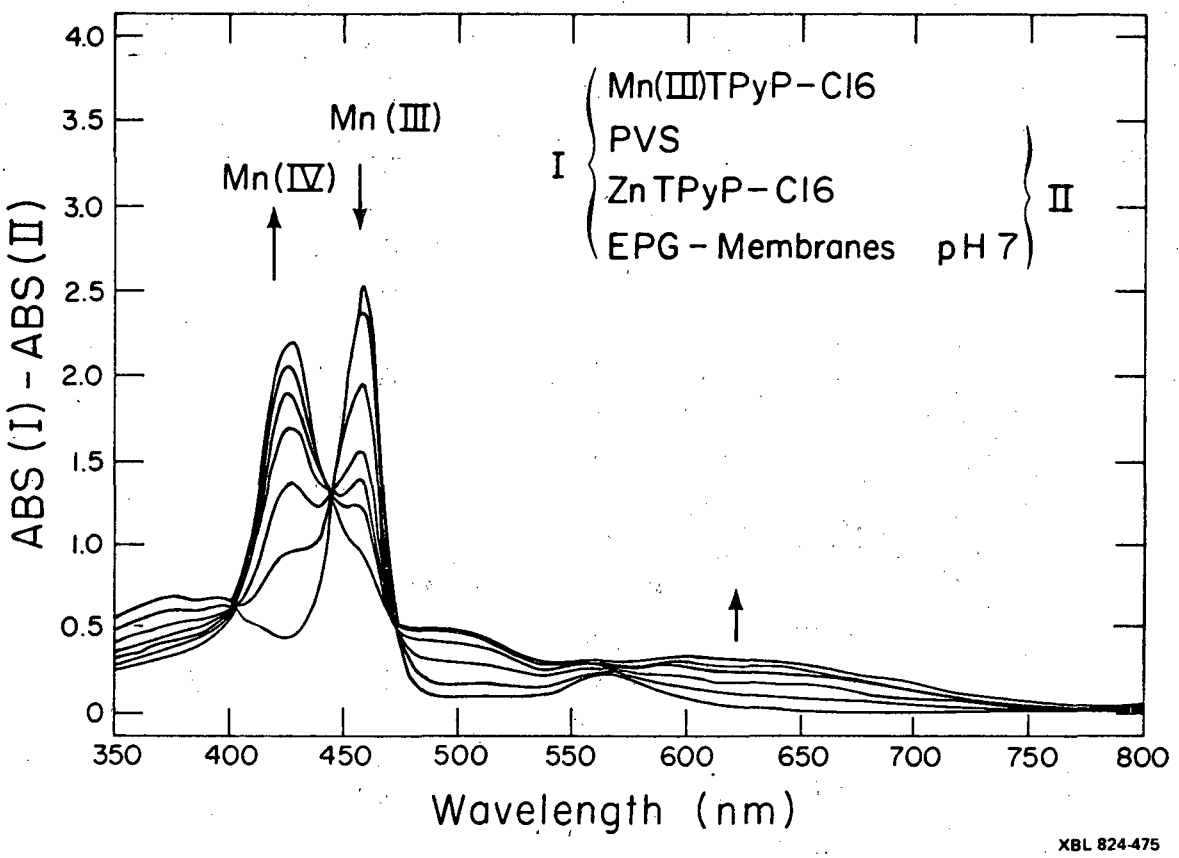
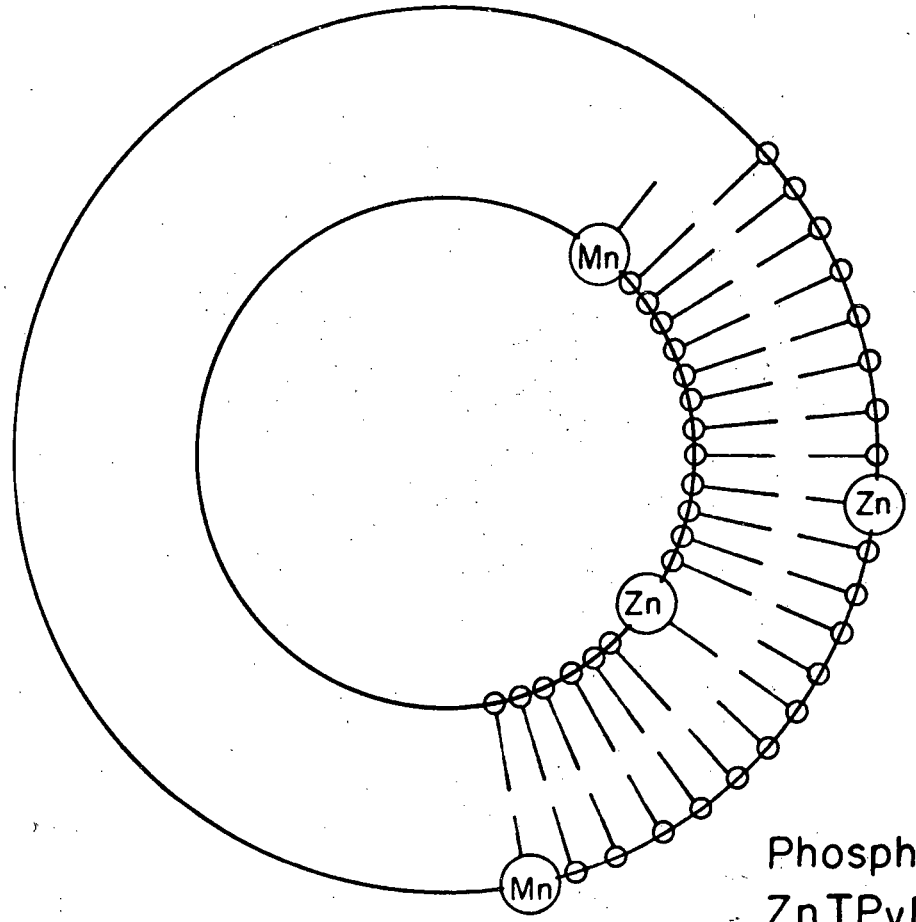

4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
ABS (I) - ABS (II)
Mn (III)
Mn(IV)
I
Mn(III)TPyP-C16
PVS
ZnTPyP-C16
EPG - Membranes pH 7
II
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)
XBL 824-475

Figure 13



Phospholipid : Mn TPyP-C16 :
Zn TPyP - C16 = 86:3:1

10^{-3} M PVS outside, pH 7

XBL 824-476

Calvin

Figure 14

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