LBL-10115 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

To be published in Nature

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AN ARTIFICIAL PHOTOSYNTHETIC SYSTEM

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November 1979

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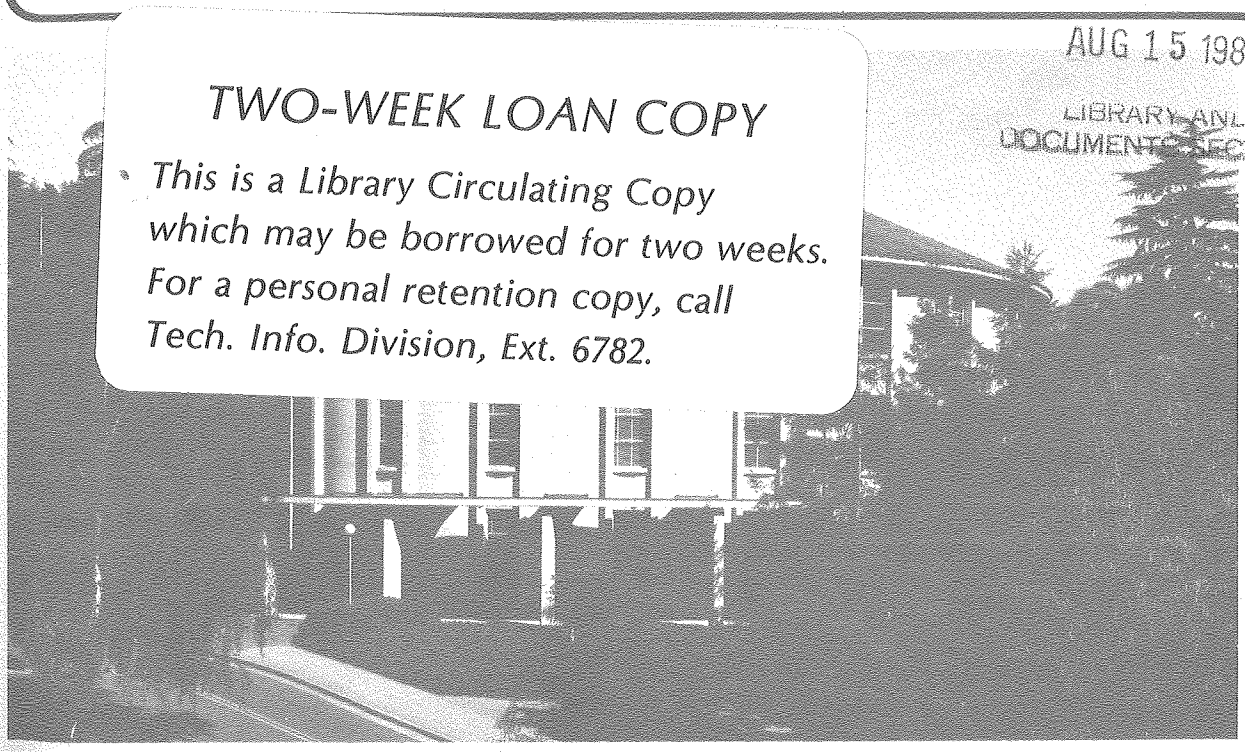

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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PHOTOINDUCED TRANSFER OF OXYGEN FROM WATER: AN ARTIFICIAL PHOTOSYNTHETIC SYSTEM

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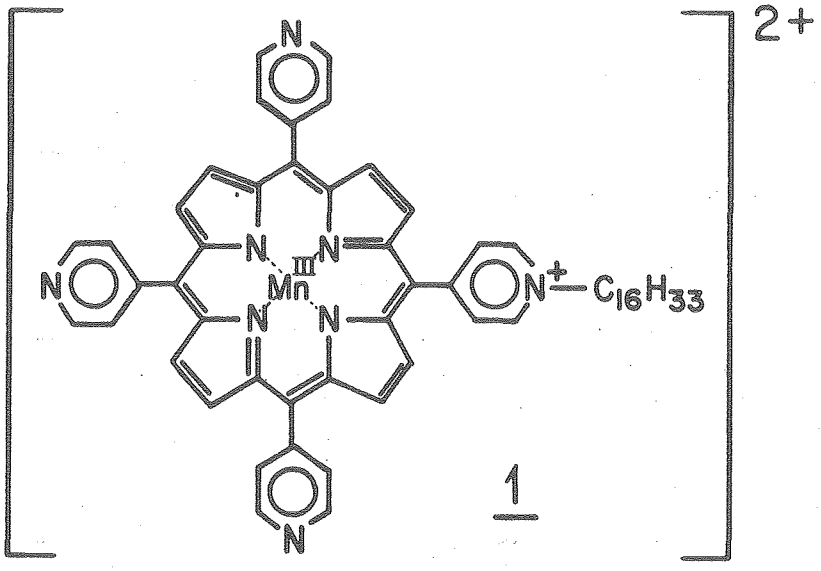
PHOTOINDUCED TRANSFER OF OXYGEN FROM WATER:

AN ARTIFICIAL PHOTOSYNTHETIC SYSTEM

The photoinduced splitting of water into hydrogen and oxygen has evoked great interest in recent years as a means for energy storage and fuel production.[1-4] Photoinduced reduction of water to hydrogen, using visible light, has been described using heterogeneous[5-8] or homogeneous[9] catalysts. However, the complementary part involving the oxidation of water to oxygen is required in order to create a cyclic artificial "photosynthetic" fuel system. The major difficulty associated with the photooxidation of water involves the requirement for a four electron transfer to produce oxygen. A stepwise one-electron oxidation of water is unfavorable due to the implied formation of active hydroxyl radicals. Very recently, it has been reported that RuO_2 can serve as a heterogeneous charge storage catalyst for oxygen production.[10,11] On the basis of our limited knowledge about natural photosynthesis, in which manganese ions play an important role in oxygen evolution,[4] synthetic manganese complexes, and in particular dimeric complexes, have been proposed as potential catalysts for oxygen production.[12] So far, efforts directed toward this goal have been unsuccessful.[13-15] Consequently, using a manganese complex, we attempted to perform a photoinduced oxidation of water whereby the active oxygen is transferred to a trapping substrate. In such a way, the requirement for a dimerization process to evolve molecular oxygen[42] is avoided. We wish to report a photoinduced redox cycle sensitized by a manganese porphyrin, 5-(4'-hexadecylpyridinium)-10,15,20-tri(4'-pyridyl)-porphinatomanganese(III) (1) (abbreviated to $Pn\text{-}Mn^{III}$)[16] in which the resultant reaction is the oxidation of water and trapping of the single oxygen atom by a substrate (triphenylphosphine).



XBL 796-4864

The investigated system consists of a homogeneous mixture containing methanol (2.75 ml), aqueous phosphate buffer (0.25 ml, pH 4.5, 0.36M), $Pn\text{-}Mn^{III}$ (9×10^{-6} M), methylviologen (MV^{2+}, 1.5×10^{-3} M), and triphenylphosphine (PPh_3, 3.25×10^{-2} M). Illumination of the solution, sealed in a cuvette under a nitrogen atmosphere, with a 900-W xenon arc lamp filtered through a cupric sulfate solution (330 nm < λ < 560 nm) results in the formation of methylviologen radical cation ($MV^{+\cdot}$) as well as changes in the absorption pattern of the porphyrin. The new Mn-porphyrin spectrum, λ_{max} = 435 nm ($\varepsilon = 1.7 \times 10^5$); 570 nm ($\varepsilon = 1.5 \times 10^4$); 615 nm ($\varepsilon = 9 \times 10^3$), is consistent with the formation of $Pn\text{-}Mn^{II}$. Chemical reduction of $Pn\text{-}Mn^{III}$ with $NaBH_4$ results in similar

spectral changes, and the assignment is further supported by published spectra of other meso-substituted manganese(II) porphyrins.[17,18] Further illumination of the mixture results in a continuous reduction of MV^{2+} to its radical cation ($MV^{+\cdot}$). The production of $MV^{+\cdot}$ is monitored spectrometrically[19] and the rate of production is displayed in Fig. 1a. Excluding triphenylphosphine from the system results in a considerable decrease in the rate of Pn-Mn^{III}-to-Pn-Mn^{II} conversion as well as in the rate of $MV^{+\cdot}$ production (Fig. 1b). Thus, triphenylphosphine plays a central role in the photosensitized reduction of MV^{2+}. Comparison of the sensitizer concentration (9×10^{-6}M) with the amount of $MV^{+\cdot}$ produced (1.4×10^{-4}M) indicates a mechanism in which the sensitizer is recycled. Introduction of air into the cuvette reoxidizes $MV^{+\cdot}$ to MV^{2+} and Pn-Mn^{II} to Pn-Mn^{III}. The visible absorption spectrum of the aerated sample reveals no change in the initial concentration of Pn-Mn^{III}. Thus, the sensitizer is preserved quantitatively in the redox cycle. On the basis of the rate of MV^{2+} reduction an approximate quantum yield of MV^{2+} reduction of 0.01 is calculated.

The formation of $MV^{+\cdot}$ together with Pn-Mn^{II} implies that triphenylphosphine is oxidized in a redox cycle. Since neither Pn-Mn^{III} nor Pn-Mn^{II} oxidizes PPh_3, while Mn^{IV}-porphyrins do oxidize PPh_3 (vide infra), and because of the high oxidation potential of Mn^{IV}-porphyrins[20] we propose the mechanism outlined in Scheme 1 as a possible pathway for the photochemical redox cycle. In this cycle, MV^{2+} is involved in two photochemical steps. Initially, photoexcited Pn-Mn^{III} reduces MV^{2+}, producing Pn-Mn^{IV}. The oxidizing agent thus formed oxidizes water and the active oxygen so produced as Pn-Mn-Oxide is transferred to PPh_3 to produce Pn-Mn^{II} and triphenylphosphine oxide. Recently reported oxygen transfer reactions to triphenylphosphine using organometallic oxo-complexes [21-23] support the intermediary formation of a manganese oxide. It should be noted that the proposed use of Mn-Porphyrins in oxygen production[12] is based

on a pathway similar to the one described in Scheme 1, except that the intermediary Pn-Mn-oxide is expected todimerize to a binuclear peroxide. In the present case, triphenylphosphine provides an alterante pathway by scavenging the proposed Pn-Mn-oxide through an oxygen transfer reaction. The following evidence supports the proposed redox cycle:

(a) The luminescence of $Pn\text{-}Mn^{III}$ in alcohol glass at $77^{o}K$ is quenched by MV^{2+}, thus implying an oxidative quenching of the sensitizer whereby the intermediary $Pn\text{-}Mn^{IV}$ is formed. Consequently, we find that the rate of reduction of $Pn\text{-}Mn^{III}$ to $Pn\text{-}Mn^{II}$, monitored spectroscopically, depends on MV^{2+} concentration (Figure 2).

(b) The appearance of triphenylphosphine oxide shows that an oxygen transfer to the trap has been accomplished. To accumulate the oxidation product, an alternative route for the subseqnet reoxidation of $MV^{+\cdot}$ is required.

The reduction potential for the $MV^{2+}/MV^{+\cdot}$ couple (-0.44 V)[19] is adequate for reduction of water at pH 4.5. Indeed, $MV^{+\cdot}$ reduces water to hydrogen in the presence of Pt or PtO_2 as catalysts.[5,7] Hence, a mixture containing 10 ml of methanol, 1 ml of phosphate buffer (0.03 M) (pH 4.5), MV^{2+} (1.6×10^{-3} M), triphenylphosphine (94.3 mg, 3.3×10^{-2} M), and $Pn\text{-}Mn^{III}$ (1×10^{-5} M) was illuminated while being stirred in a sealed flask under nitrogen in the presence of 2.2 mg of PtO_2 (Adams catalyst). No formation of $MV^{+\cdot}$ was observed, although the porphyrin was reduced to $Pn\text{-}Mn^{II}$, suggesting that MV^{2+} was geing recycled. After two hours of illumination, 32 mg of triphenylphosphine oxide (32% yield) were isolated. The high turnover number of about 1000 on Pn-Mn reveals that a photoinduced cycle whereby an oxygen transfer from water to the trapping substrate has been accomplished.

Finally, in an independent experiment, we were able to show that a Mn^{IV}-porphyrin is indeed capable of oxidizing PPh_3 in a two-electron oxidation process. In this experiment, Mn^{III}-TPP-acetate dissolved in benzene was oxidized to Mn^{IV}-TPP by $Na_2S_2O_8$ and KOH solubilized by the aid of 18-Crown-6 ether. Addition of PPh_3 to the Mn^{IV}-TPP solution resulted in a quantitative reduction to Mn^{II}-TPP.

The major importance of our proposed cycle is that coordinated water is oxidized photochemically. As this reaction can be coupled to hydrogen generation, the system may be considered as an artificial photosynthetic unit. The possibility for oxygen transfer to substrates other than triphenylphosphine is of considerable interest. Indeed, we find that substituting an olefin, e.g. cyclohexene, for the triphenylphosphine results in similar behavior, i.e. enhanced rates of reduction of Pn-Mn^{III} and MV^{2+} compared to the system without added oxygen acceptor. Other oxygen traps which function similarly on these rates are iodobenzene and phthalic acid. We believe that such oxygen transfer processes might be important in developing fuel sources (hydrogen) coupled to the production of useful oxygenated products. A further possibility rests on the utilization of the oxygenated products as a precursor for a subsequent catalytic evolution of oxygen. The possibility of initiating photosensitized oxidation of organic substrates using manganese porphyrins as well as the mechanism elucidation are now being explored. Furthermore, the results encourage continued search for binuclear manganese complexes as catalysts for oxygen production.

Acknowledgement

This work was supported by the Division of Basic Energy Sciences of the United States Department of Energy under Contract W-7405-Eng-48. Itamar Willner wishes to thank the Weizmann Institute of Science for a Chaim Weizmann

Postdoctoral Fellowship.

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Figure Captions

Figure 1: Methylviologen radical production as a function of cumulative illumination time: (a) with PPh_3, 3.25×10^{-2}M, (b) without PPh_3. Initial concentrations: $[MV^{2+}] = 1.5 \times 10^{-3}$M; $[Pn\text{-}Mn^{III}] = 9 \times 10^{-6}$M.

Figure 2: Mn^{III}-porphyrin photoreduction: dependence on methylbiologen concentration. ○, $[MV^{2+}] = 9.0 \times 10^{-4}$M; △, $[MV^{2+}] = 4.8 \times 10^{-4}$M; □, $[MV^{2+}] = 2.4 \times 10^{-4}$M. Initial concentrations of Mn^{III}-porphyrin (0.7×10^{-5}M) and PPh_3 (7.5×10^{-3} M) were the same in all three runs. In this experiment light intensity was attenuated with a neutral density filter to 18% of that used in data of Figure 1.

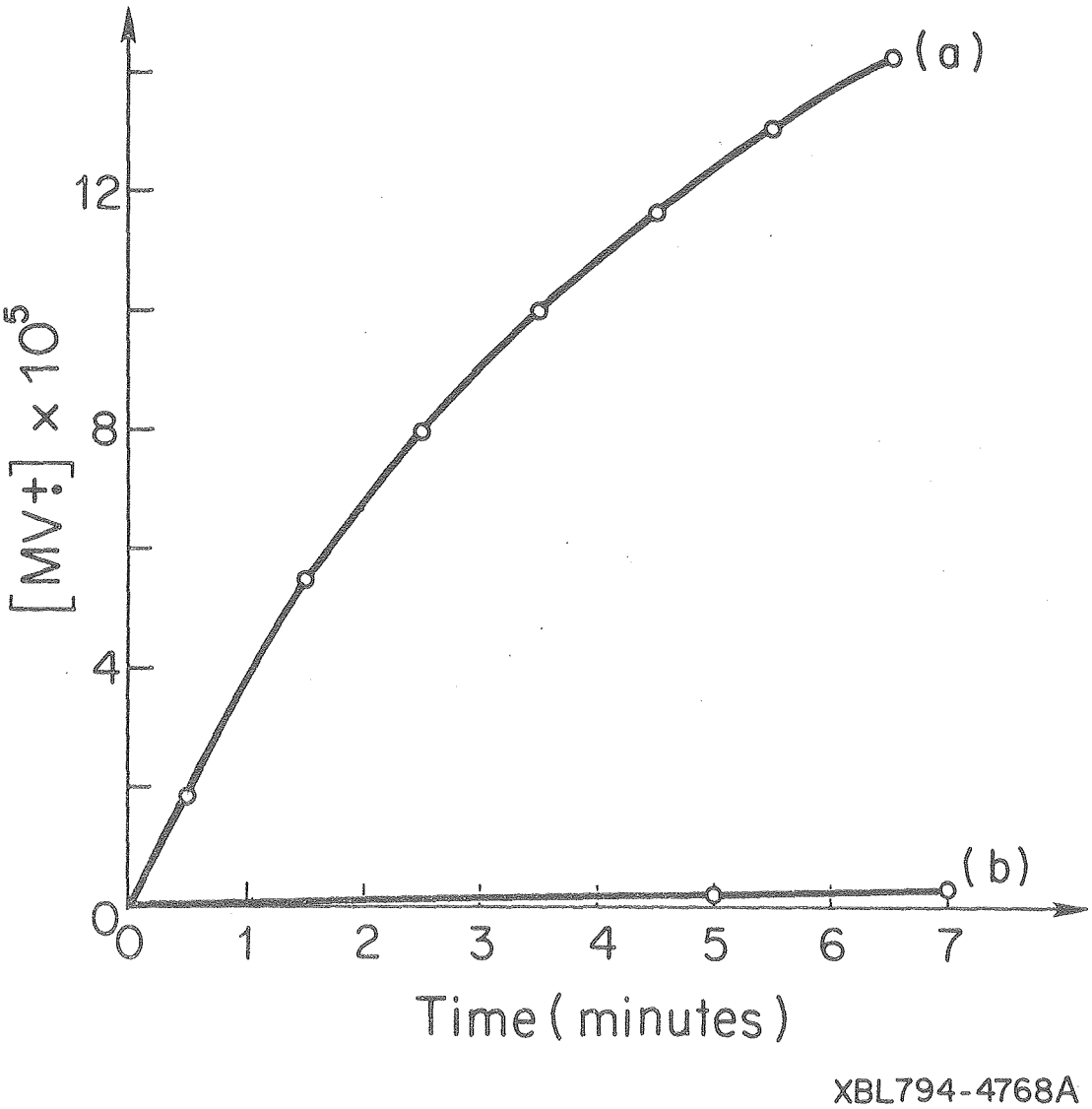

Figure 1 Willner et al.

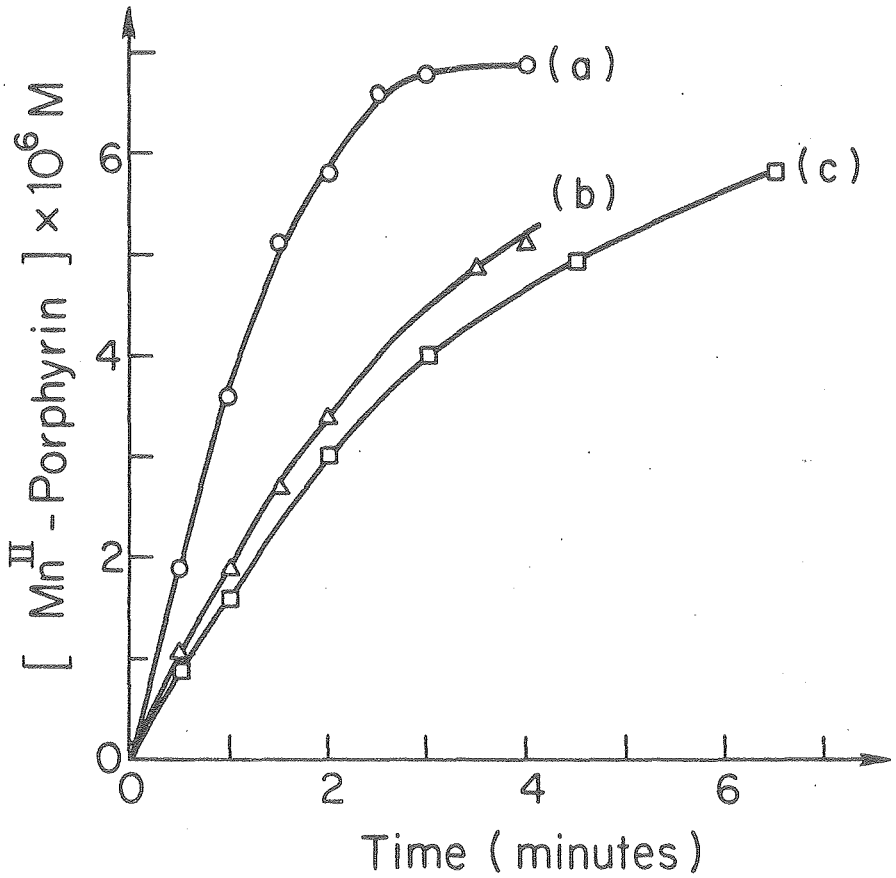

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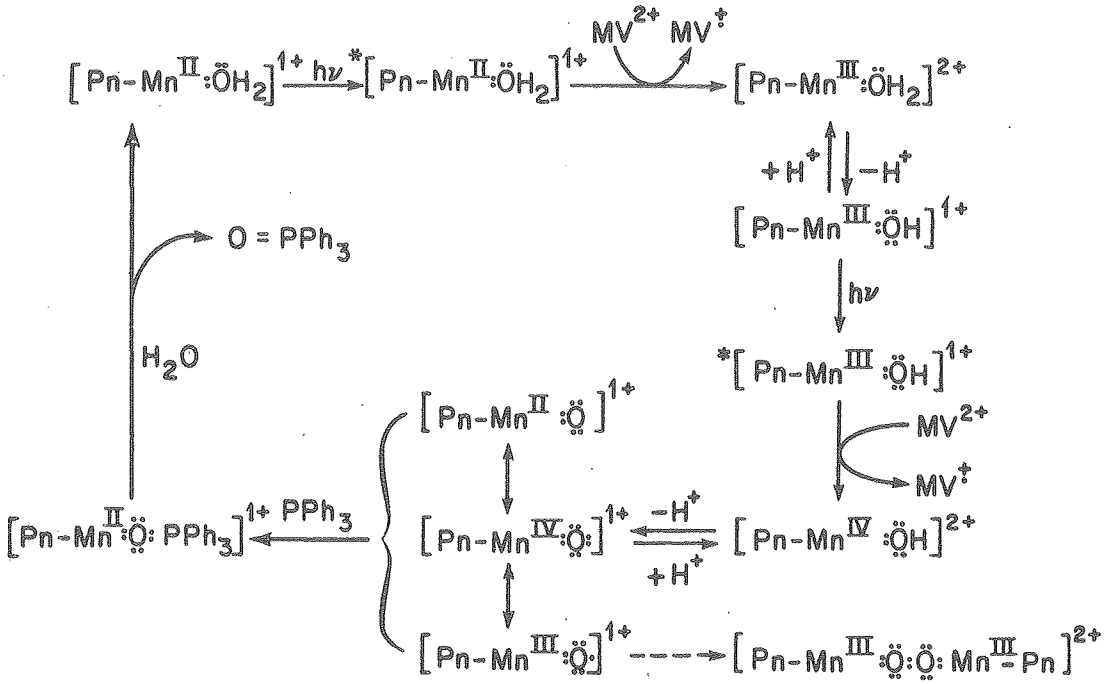
Figure 2 Willner et al.



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Scheme 1 Willner et al.