48. Light Induced Redox Reactions of Water Soluble Porphyrins, Sensitization of Hydrogen Generation from Water by Zincporphyrin Derivatives

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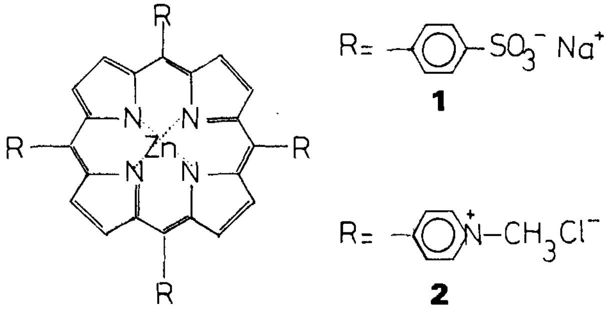
Summary

The photoredox behaviour of two water soluble derivatives of zincporphyrin, 5,10,15,20-tetra-*p*-sulfonatophenyl (**1**) and 5,10,15,20-tetra-p-*N*-methylpyridinio-chloride (**2**), was investigated using laser and continuous photolysis techniques. Photoexcitation produces triplet states whose lifetimes in aqueous solution exceeds 1 ms. These triplet states can be quenched reductively by donors such as EDTA and oxidatively by acceptors such as methylviologen (MV^{2+}). Electron transfer to MV^{2+} is greatly influenced by the charge of the porphyrin, rate constants being $1.4 \times 10^{10} M^{-1}s^{-1}$ and $2 \times 10^{6} M^{-1}s^{-1}$ for **1** and **2**, respectively. In the presence of colloidal Pt catalyst, the cationic porphyrin sensitizes photoreduction of water to hydrogen with remarkable efficiency.

Introduction. - The photochemical production of hydrogen from water is a primary target in research related to solar energy. So far, a variety of aqueous systems have been identified that generate hydrogen [1] and oxygen [2] under illumination and recently cyclic water cleavage in a combined catalytic device has been achieved [3]. The sensitizers employed almost exclusively in these studies are the ruthenium complex $Ru(bipy)_3^{2+}$ and the acridine derivative proflavin which both have an absorption maximum at around 450 nm. It is desirable to explore



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chromophores that make use of a larger part of the visible solar spectrum than these dyes. Water-soluble porphyrins offer a very attractive alternative. They are cheap and easy to synthesize, absorb far into the visible, the redox potentials of ground and excited state are appropriate to afford water decomposition [4] and the molecules are extremely stable in the oxidation states of interest. Surprisingly little is known about photoredox reactions involving these sensitizers [5-9]. For this reason, we have initiated extensive studies in this domain employing laser photolysis and continuous illumination technique as analytical tools. The present report deals with light initiated electron transfer reactions of the water soluble zincporphyrins **1** and **2**. A two component system will be presented that gives high yields of hydrogen in the presence of a redox catalyst.

Experimental part

Materials. Zinc tetra-*p*-sulfonatophenylporphyrin (**1**) (ZnTPPS) was prepared from tetra-*p*-sulfonatophenylporphyrin *(Strem)* by refluxing with a 3-fold excess of zinc acetate in water. The solvent was subsequently removed in a rotatory evaporator under vacuum. The substance was purified by passing through a *Dowex* 50 cation exchange column in the Na^+ form.

Zinc tetrapyridylporphyrin was prepared in an analogous manner from the free porphyrin *(Strem)* except that glacial acetic acid was used. To obtain the tetramethylpyridinio derivative (ZnTMPyP, **2**), 200 mg of the porphyrin were added to 25 ml of CH_3I. After 6 h of stirring, the solvent was filtered and purification of the crude product carried out by passing through a *Dowex* 2 anion exchange column in the Cl^- form.

The preparation and characteristics of the Pt catalyst have been described earlier [10]. EDTA *(Fluka)* and methylviologen *(BDH)* were reagent grade and were used as supplied. Deionized water was refluxed with $KMnO_4$ and subsequently distilled twice from a quartz still.

Apparatus. Steady state irradiations were carried out with 20 ml solutions using an *Osram* XBO 450-W lamp in conjunction with a 500 nm cut-off filter (*Schott*-GMBH). A ferrioxalate chemical dosimeter [11] was employed to mesure the photon flux. Hydrogen was analyzed by means of a *Gow-Mac* thermal conductivity detector with a limit of 0.1 µmol. The column used at 35° was a carbosieve-A. Laser photolysis experiments were performed with a *JK* frequency-doubled neodynium laser with a pulse width of 20 ns. The details of the detection method have been reported previously [12].

Results and discussion. - The short time kinetic investigations were carried out by laser photolysis technique. Data obtained from aqueous solutions of $ZnTMPyP^{4+}$ 10^{-5}M will first be discussed. Excitation was carried out at 530 nm and the spectral observations restricted to the 600-1000 nm wavelength domain. A 620 nm cut-off filter was placed between the cell and the analyzing light beam to avoid excitation of the porphyrin. *Figure 1* shows the end of pulse spectra obtained from three water soluble zincporphyrins which are assigned to T_1-T_n absorptions. For zincporphyrins, the quantum yield of triplet production usually exceeds 90% [13]. The spectra of the tetrasulfonate and tetracarboxylate derivatives resemble that of zinc tetraphenylporphyrin triplet which also has a maximum around 840 nm. $ZnTMPyP^{4+}$ is distinguished by a broad band in the red which extends up to 1100 nm.

In *Figure 2*, oscilloscope traces are presented showing the time course of the triplet decay at 840 nm. In the absence of quencher, one observes for $ZnTMPyP^{4+}$ an exponential decay function corresponding to a triplet lifetime of 1.3 ms. Addition of methylviologen (MV^{2+}) quenches the porphyrin triplet. Lifetimes decrease with increasing MV^{2+} concentration indicating pseudo first-order

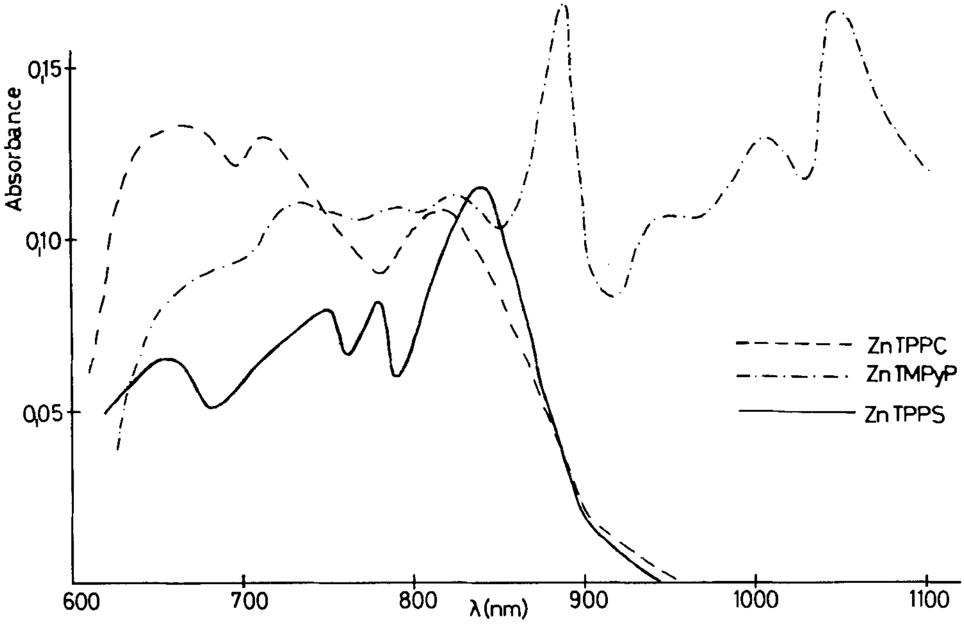

Fig. 1. *Transient absorption spectra of triplet excited state (end of laser pulse spectra) of Zn porphyrins (10^{-5}M) in water (pH 7),* (----) ZnTPPC (Zinc tetracarboxyphenyl porphyrin); (-·-·) ZnTMPyP; (——) ZnTPPS

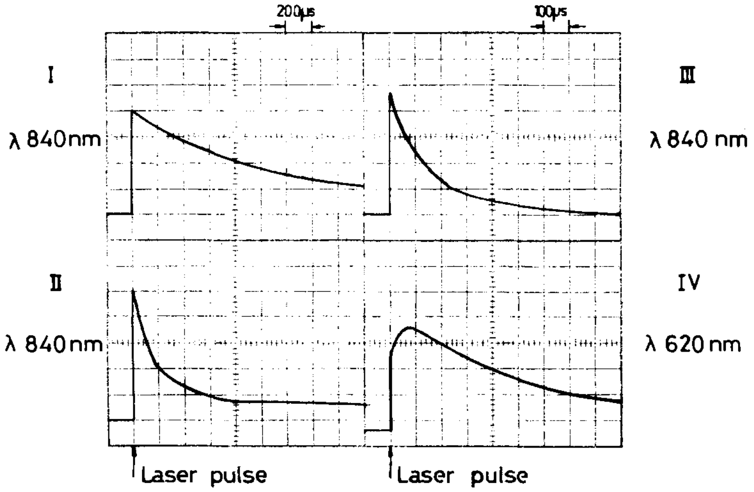

Fig. 2. *Quenching of cationic Zn porphyrin (ZnTMPyP) triplets in water by methyl viologen and by EDTA;* (ZnTMPyP) = 10^{-5}M. I: Decay of ZnTMPyP triplets alone (at λ = 840 nm); II: Decay of ZnTMPyP triplets (at λ = 840 nm) in the presence of 10^{-2}M EDTA. III: Decay of ZnTMPyP triplets (at λ = 840 nm) in the presence of 5×10^{-3}M MV^{2+}. IV: Growth and decay of MV^{+} radical (at λ = 620 nm).

behaviour. Concommitant with the triplet decay goes a build-up of absorption around 600 nm *(Fig. 2c)* where both the Π-cation of $ZnTMPyP^{4+}$ and reduced methylviologen have characteristic maxima [14] [15]. This indicates oxidative quenching:

$$^3ZnTMPyP^{4+*} + MV^{2+} \xrightarrow{k_1} MV^+ + ZnTMPyP^{5+} \qquad (1)$$

The kinetic evaluation yields $k_1 = (2 \pm 0.5) \times 10^6 \text{M}^{-1}\text{s}^{-1}$ at $5 \times 10^{-3}\text{M}$ MV^{2+} concentration.

Reductive quenching of the porphyrin triplet is observed in the presence of suitable electron donors such as EDTA [16]. In neutral aqueous solution the latter is present prominently in the monoprotonated form HY^{3-}. *Figure 2* (**II**) displays the 840 nm decay in the presence of $2 \times 10^{-2}\text{M}$ EDTA. The decay function in this case reaches a plateau arising from the monoreduced form of the porphyrin. The latter is apparently produced *via* the electron transfer reaction.

$$^3ZnTMPyP^{4+*} + HY^{3-} \xrightarrow{k_2} HY^{2-} + ZnTMPyP^{3+} \qquad (2)$$

The data in *Figure 2* yield $k_2 = (4 \pm 0.4) \times 10^5 \text{M}^{-1}\text{s}^{-1}$. Both k_1 and k_2 are dependent on ionic strength and hence refer to one particular quencher concentration.

Reaction (1) is important in that it provides the intermediate species MV^+ and $ZnTMPyP^{5+}$ that are thermodynamically capable of reacting with water to produce H_2 and O_2. Standard potentials are $E^0(MV^{2+/+}) = -0.45$ V [17] and $E^0(ZnTMPyP^{5+/4+}) = +1.2$ V [18]. In order to examine the H_2-generating channel separately, solutions containing $ZnTMPyP^{4+}$, MV^{2+} and EDTA were photolyzed in the presence of centrifuged, colloidal Pt-catalyst. In such a mixture, both reductive and oxidative quenching of the triplet porphyrin occurs, eq. (1) and (2), followed by the dark reactions:

$$ZnTMPyP^{5+} + HY^{3-} \longrightarrow HY^{2-} + ZnTMPyP^{4+} \qquad (3)$$

$$HY^{2-} \longrightarrow H^+ + Y^{3-} \qquad (4)$$

$$ZnTMPyP^{3+} + ZnTMPyP^{3+} \longrightarrow ZnTMPyP^{2+} + ZnTMPyP^{4+} \qquad (5)$$

$$ZnTMPyP^{3+} + MV^{2+} \longrightarrow MV^+ + ZnTMPyP^{4+} \qquad (6)$$

Furthermore, the EDTA radical Y^{3-}, having electron donating properties [19], may effect the reduction of both MV^{2+} and $ZnTMPyP^{4+}$ thus increasing the yields of the species MV^+ and $ZnTMPyP^{3+}$. In the presence of Pt catalyst, the reaction sequence 1–6 is followed by water reduction [20].

$$MV^+ + H_2O \xrightarrow{(Pt)} MV^{2+} + \tfrac{1}{2}H_2 + OH^- \qquad (7)$$

Figure 3 shows hydrogen production curves obtained from the illumination of porphyrin solution with visible light. The samples contained 10^{-5}M $ZnTMPyP^{4+}$, $2 \times 10^{-2}\text{M}$ EDTA and were buffered at pH 5. Catalyst concentration was 0.16 mg/100 ml ($8 \times 10^{-6}\text{M}$ Pt) as determined by atomic absorption spectroscopy. Irradiation conditions and geometry were kept constant. The figure illustrates the effect of methylviologen concentration on the hydrogen generation rate. In the

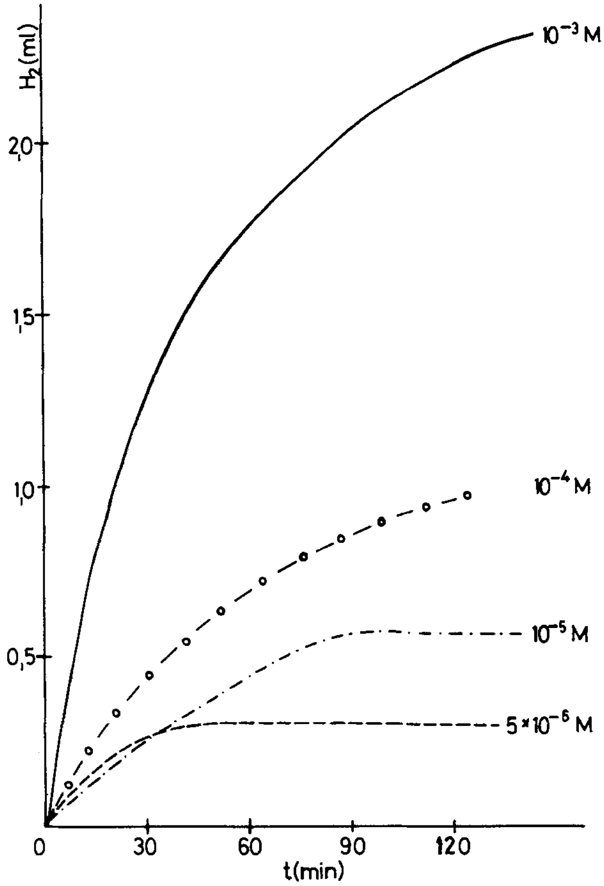

Fig. 3. *H_2-yields on photolysis ($\lambda \geq 500$ nm) of aqueous solutions (25 ml) of ZnTMPyP (10^{-4}M), EDTA (2×10^{-2}M), Pt-PVA catalyst (1 ml/ 25 ml), in pH 5.0 buffer solutions with different concentrations of methyl viologen (MV^{2+})* (---) 5×10^{-6}M; (- · -) 10^{-5}M; (- · -) 10^{-4}M; (——) 10^{-3}M

absence of MV^{2+} no hydrogen is obtained. Instead, one observes the irreversible reduction of the porphyrin under illumination. The intensity of the *Soret* band diminuishes, leaving weaker absorptions around 440 and 630 nm which presumably arise from dihydro or tetrahydroporphyrin derivatives [5] [6]. Similar effects have been observed in the photoinduced reduction of zinc uroporphyrin by EDTA [6]. The build up of reduction products is progressively suppressed as methylviologen is added to the solution and is replaced by hydrogen generation. A surprising feature emerging from *Figure 3* is the remarkably high initial H_2-evolution rates observed at very dilute MV^{2+} concentrations. A two hundred fold increase in [MV^{2+}] enhances hydrogen generation only by a factor of 5. However, the H_2 production in very dilute MV^{2+} solution tends to level off after 30 to 60 min photolysis.

One might be tempted to take the lack of H_2 formation, observed in the absence of MV^{2+}, as evidence that the $ZnTMPyP^{3+}$ radical is unable to transfer an electron to the Pt particle, thus inducing water reduction. In this respect, it would be different from other reducing radicals such as MV^+ [20], proflavine [21] and ketyl [22], where this process requires only 10^{-5} to 10^{-3}s. However, the Pt concentrations employed to achieve these rates were substantially higher than those used here. Indeed, upon increase of the Pt content to 12 mg Pt/l, hydrogen is generated efficiently even *in the absence of* MV^{2+}. Apparently, under these conditions the dismutation reaction (5) is intercepted by charge transfer from $ZnTMPyP^{3+}$ to the Pt-particles resulting in H_2 formation.

A further point concerns the astonishingly high activity of MV^{2+} electron relays in the low concentration range. Under conditions where $MV^{2+} < 10^{-3}$M reductive quenching of the porphyrin triplet will dominate over the oxidative pathway (eq. 1). The only way MV^{2+} can intervene in this case is through reaction (6). To be effective at low MV^+, the latter process must be considerably faster than the dismutation of the porphyrin radical, *i.e.* $k_6 \gg k_5$. A relatively low value for k_5 can be inferred also from the remarkably long lifetime of $ZnTMPy^{3+}$ which in neutral aqueous solution is at least 10 ms. Oxidative quenching of porphyrin triplets by MV^{2+} sets in only at $MV^{2+} \geq 10^{-3}$M where it contributes to the formation of MV^+ and hence H_2. Under these conditions, reaction (5) is completely suppressed rendering hydrogen generation cyclic with respect to the porphyrin sensitizer. The H_2 evolution rates observed here are impressively high, approaching the maximum output of the $Ru(bipy)_3^{2+}/MV^{2+}$ system [1] [10]. This astonishing result encourages further research to optimize solute concentrations and catalyst preparations. Thus the mere use of a very active Pt improves the H_2-output from 2 to 10 ml/h. It is likely that the intense absorption in the visible and the high triplet yield of the zinc-porphyrin are responsible for the efficient performance of this system.

Interested in exploring the effect of charge of the porphyrin on its photoredox behaviour, we also examined the reaction of $TPPS^{4-}$ with EDTA and methylviologen. The high negative charge of this chromophore is expected to favour oxidative quenching (eq. 1) while the reductive pathway (eq. 2) should be disfavoured. These conjectures are indeed borne out by experiment. In *Figure 4* are shown oscilloscope traces obtained from the laser photolysis of 10^{-5}M $ZnTPPS^{4-}$ in aqueous solution. The triplet lifetime as determined from the decay of the 840 nm absorbance is 1.5 ms in deaerated solutions. Addition of 5×10^{-4}M MV^{2+} or 10^{-2}M EDTA reduces it to 8 and 350 µs, respectively. This is attributed to quenching *via* the electron transfer reactions:

$$HY^{3-} + ZnTPPS^{4-} \longrightarrow HY^{2-} + ZnTPPS^{5-} \qquad (8)$$

and

$$MV^{2+} + ZnTPPS^{4-} \longrightarrow ZnTPPS^{3-} + MV^{+} \qquad (9)$$

for which we find $k_7 = 1.5 \times 10^5 M^{-1}s^{-1}$ and $k_8 = 1.4 \times 10^{10} M^{-1}s^{-1}$.

Interestingly, the coulombic attraction between MV^{2+} and $ZnTPPS^{4-}$ is sufficiently strong to cause the formation of charge transfer complexes. The onset of this effect is noticed already at low MV^{2+}-concentrations (10^{-5}M) where it produces static quenching of the porphyrin triplet states.

Comparison of the EDTA quenching rates with the positively and negatively charged porphyrins reveals that electrostatic effects can only play a minor role in

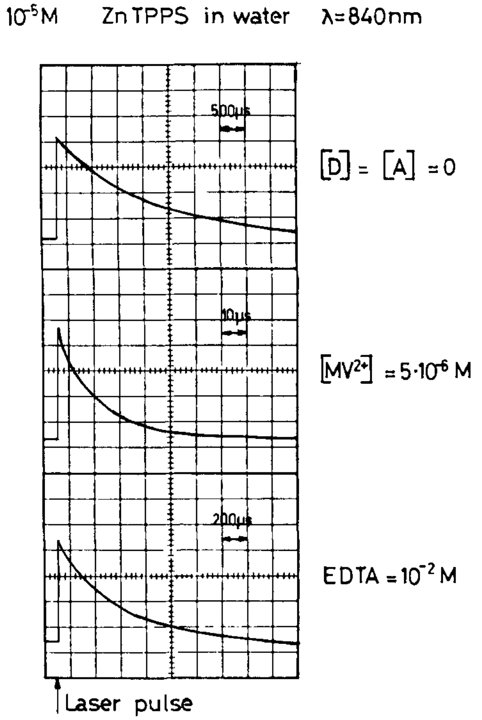

Fig. 4. *Quenching of anionic Zn porphyrin (ZnTPPS) triplets in water (pH 7) at* $\lambda = 840$ *nm by methyl viologen* (5×10^{-6}M) *and by EDTA* (10^{-2}M)

these reactions. In fact, the rate constant augments only by a factor of 3 when replacing the repulsive by the attractive porphyrin. In striking contrast to this behaviour are the quenching kinetics of methylviologen which are strongly affected by the charge of the sensitizer. Thus, the quenching rate constants k_1 and k_7 differ by four orders of magnitude. It is instructive to compare this finding to theoretical predictions for the rates of fast reactions involving ionic species in solution. These charge effects are expressed by the *Debye* factor $f = (L/r_{AB})/\exp(L/r_{AB}) - 1$ which contains the parameter $L = (Z_A \cdot Z_B e^2)/(\varepsilon kT)$ and the reaction radius r_{AB}. L is calculated as $\pm 5.6 \times 10^{-7}$ cm where the plus and minus sign apply to $ZnTMPyP^{4+}$ and $ZnTPPS^{4-}$, respectively. Assuming for the reaction radius a value of 10 Å one obtains $f_+ = 2 \times 10^{-2}$ and $f_- = 5.62$. Thus coulombic contributions account at most for a factor of 281 in the rate constants which is considerably smaller than the ratio of k_7/k_1 found experimentally. The difference may be attributed to substituent effects on the redox potential of the porphyrin. From the triplet energy of the porphyrin, $E_T \simeq 1.8$ V [9], and the standard potentials of the $ZnTMPyP^{4+/5+}$ and $MV^{2+/+}$-couples, a maximum driving force of only 150 mV for reaction (1) is derived. $ZnTPPS^{4-}$, on the other hand, is a much better reductant than the cationic porphyrin; the free energy of reaction (8) is more negative which renders the electron transfer practically diffusion controlled.

Preliminary experiments were also performed to test the ability of $ZnTPPS^{4-}$ to sensitize H_2-generation in an aqueous system which contained added Pt catalyst

MV^{2+} and EDTA as an electron donor. H_2-yields were surprisingly low and far inferior to the output of the system containing cationic porphyrin. An explanation for this effect may be sought in the high rate for the reverse electron transfer (eq. 8) and the low efficiency of EDTA in reducing $ZnTPPS^{3-}$.

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