Coordination Chemistry Reviews, 44 (1982) 83–126
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

METAL PHTHALOCYANINES AND PORPHYRINS AS PHOTOSENSITIZERS FOR REDUCTION OF WATER TO HYDROGEN

JAMES R. DARWENT, PETER DOUGLAS, ANTHONY HARRIMAN, GEORGE PORTER and MARIE-CLAUDE RICHOUX

Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS (Gt. Britain)

(Received 21 May 1981)

CONTENTS

A. INTRODUCTION

Interest in solar energy storage devices has increased dramatically in the last decade and, currently, this is an extremely active area of scientific research. Many different approaches have been advocated but it is worth considering that one of the very few systems capable of the collection and storage of sunlight on a practical scale is the natural photosynthetic process. This natural process functions by coupling together two separate photochemical reactions. The first reaction, photosystem I (PS I), concerns the fixation and reduction of CO_2 to the level of carbohydrate, which is the plant's fuel,

0010-8545/82/0000–0000/$11.00

whilst the second reaction, PS II, involves the photo-oxidation of water to O_2. Although this process provides the best possible template for laboratory models, carbohydrate is not a suitable fuel for our present needs and, instead, many research workers have proposed H_2 as a more applicable fuel. Consequently, in recent years there have been numerous attempts to construct laboratory models that are capable of a modified version of PS I, that is the photoreduction of water to H_2 using visible light excitation.

Perhaps the simplest method for photogeneration of H_2 from water involves irradiation of a low valence metal ion at a wavelength corresponding to a charge-transfer-to-solvent (CTTS) transition [1]. This has the effect of transferring an electron from the metal ion on to a water molecule.

$$*M^{n+} + H_2O \rightarrow M^{(n+1)+} + \tfrac{1}{2}H_2 + OH^- \quad (1)$$

Many metal ions are capable of this reaction [2–5] and, often, the quantum yields for formation of H_2 are very high ($\phi_{H_2} > 0.2$), as for example with Fe^{2+}, Cr^{2+}, or Eu^{2+}. Unfortunately, the CTTS absorption band is normally found in the high energy UV region and it is only with Eu^{2+} that H_2 production occurs upon irradiation with light of $\lambda > 350$ nm [6].

There are several metal ions which will reduce water to H_2 in the presence of a suitable catalyst.

$$M^{n+} + H_2O \xrightarrow{Pt} M^{(n+1)+} + \tfrac{1}{2}H_2 + OH^- \quad (2)$$

If an electron donor (D) is added to the system then the overall reaction can be made cyclic with respect to the metal ion and, furthermore, if a coloured compound is used for this purpose, the low valence metal ion can be produced by photochemical means [1].

$$D^* + M^{(n+1)} \rightarrow D^+ + M^{n+} \quad (3)$$

There are several important examples of reaction (3), using tris(2,2′-bipyridyl) ruthenium(II) ($(bipy)_3Ru^{2+}$) as the electron donor [7,8] but, although in principle this process should result in formation of H_2, no gaseous products have been detected. The absence of H_2 is due to reverse electron transfer

$$D^+ + M^{n+} \rightarrow D + M^{(n+1)+} \quad (4)$$

which normally occurs with extremely high efficiency [1].

Several interesting systems have been proposed to minimize the importance of reverse electron transfer. Experiments have shown that useful results are obtained if a weak reductant is added to the system. Thus, upon irradiation with visible light, acridine orange will transfer an electron to methyl viologen.

$$*AO + MV^{2+} \rightarrow AO^+ + MV^+ \quad (5)$$

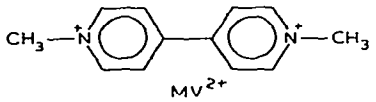
Normally, reverse electron transfer proceeds rapidly but in the presence of EDTA the oxidized form of the dye participates in a second redox reaction [9].

$$AO^+ + EDTA \rightarrow AO + EDTA^+ \quad (6)$$

The oxidized form of EDTA is a weak oxidant and undergoes irreversible decomposition rather than reaction with MV^+. This allows high concentrations of MV^+ to build-up and it is well established that catalysts, such as Pt or hydrogenase, can be used to catalyse the reaction between MV^+ and water [10].

$$2\,MV^+ + 2\,H_2O \xrightarrow{\text{Catalyst}} 2\,MV^{2+} + H_2 + 2\,OH^- \quad (7)$$

It has been reported by Bolton et al. [11] that this overall system allows a steady production of H_2 using visible light although quantum yield data are not available.



Recent studies have used modifications of this reaction scheme. Thus, a paper by Shilov et al. [12] presents a most interesting method for photogeneration of H_2 from water. In this system, an acridine dye (A) was photoreduced by an electron donor, e.g. cysteine or EDTA, in aqueous solution. Addition of V^{3+} or Eu^{3+} salicylates caused reoxidation of the reduced dye and H_2 was formed when small amounts of Pt were added to the solution [12].

$$\begin{matrix} EDTA^+ \\ EDTA \end{matrix} \Big) \quad \Big(\begin{matrix} h\nu\, A^- \\ A \end{matrix} \Big) \quad \Big(\begin{matrix} M^{3+} \\ M^{2+} \end{matrix} \Big) \quad \Big(\begin{matrix} Pt\, H_2 \\ H_2O \end{matrix} \quad (8)$$

Upon 450 nm irradiation, the primary photoredox reaction produces the semireduced dye (A^-) which is capable of reducing the metal ions to the divalent state. Oxidation of M^{2+} at the surface of a Pt catalyst leads to formation of H_2 and the quantum yields were estimated to be about 0.01 [12]. In fact, the semireduced dye has a redox potential suitable for H_2 formation without involvement of the metal ions and, in the presence of a homogeneous catalyst, it was found that water was reduced directly by A^- [12].

In a slight modification of this scheme, methyl viologen (MV^{2+}) was used in place of the metal salts. The semireduced form of MV^{2+} has a characteristic absorption spectrum [13] showing strong bands around 600 nm and can be monitored easily in model systems. Using EDTA as reducing agent, the

quantum yield for formation of MV^+ was estimated to be about 0.55 [12].

$$A^* + EDTA \rightarrow A^- + EDTA^+ \quad (9)$$

$$A^- + MV^{2+} \rightarrow A + MV^+ \quad (10)$$

Again, addition of a Pt catalyst allowed evolution of H_2.

That these systems produce H_2 at the expense of consumption of some organic substrate, such as EDTA, should be noted since this limits the utility of the overall process. However, it should be possible to link these H_2 producing systems with similar ones capable of the photo-oxidation of water to O_2, in much the same way as green plants unite PS I and PS II. The linking together presents severe experimental problems but once the two "half-reactions" have been optimized, as regards their photochemical efficiency, and the general principles involved have been understood it should be possible to construct a system capable of the overall photodissociation of water into H_2 and O_2 [14]. Before this can happen, however, it is necessary to optimize the two "half-reactions" and the authors are now close to achieving this situation with the H_2 producing step.

In the last few years, there has been a proliferation of reports describing modified versions of the above "Shilov system" [15–25]. These systems, which all involve a sacrificial electron donor, can be described as oxidative or reductive cycles; the nomenclature refers to the primary photoredox step with respect to the chromophore. Thus, in an oxidative cycle the excited state of the chromophore (S*) donates an electron to an acceptor (A) and the oxidized form of the chromophore is reduced subsequently by a donor (D).

$$S^* + A \rightarrow S^+ + A^- \quad (11)$$

$$S^+ + D \rightarrow S + D^+ \quad (12)$$

In the corresponding reductive cycle, the primary photochemical reaction results in reduction of the chromophore.

$$S^* + D \rightarrow S^- + D^+ \quad (13)$$

$$S^- + A \rightarrow S + A^- \quad (14)$$

Such systems have been refined to a high degree although with few exceptions the chromophore has been either an acridine dye or $(bipy)_3Ru^{2+}$ [15–25]. These sensitizers are photostable and give good yields of H_2 upon prolonged irradiation but they are capable of collecting only a modest fraction of the solar spectrum. Obviously, before they can be proposed as practical devices for storage of solar energy it is necessary that the sensitizer absorbs a considerable fraction of the incident sunlight and we have concentrated our attention on photosensitizers that absorb throughout the visible region and preferably into the near IR. As such, porphyrins and

phthalocyanines appear to be most attractive candidates.

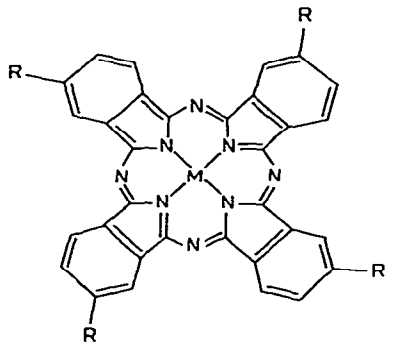
The desired properties of a good sensitizer are: (1) Good solubility in water. (2) Intense absorption in the visible region, preferably extending into the near IR. (3) Good stability upon prolonged storage in aqueous solution. (4) No side-photoreactions. (5) High triplet yield. (6) Efficient production of separated ion products upon irradiation in the presence of an electron donor or acceptor.

The above points are self-explanatory but perhaps some comment is required about the need for a high triplet yield. It has been known for a long time that the triplet state of many porphyrins and phthalocyanines will readily undergo net electron-transfer with suitable redox couples, forming the separated ion products [26]. However, there is growing evidence that, in most cases, despite the high quenching rate constants, the singlet excited state does not yield ion products [27]. This effect has been explained in terms of spin selection rules [28] and it appears that only in special cases [29] will redox products occur from the singlet excited state of a sensitizer. Thus, a necessary requirement for a good chromophore is that the triplet state is populated in high yield.

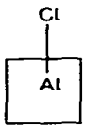
Porphyrins and phthalocyanines possess most, if not all, of the desired properties for a photosensitizer for generation of H_2 from a sacrificial system and in this review the authors describe their findings on this subject. Although we have concentrated on work carried out in our laboratory, we have attempted to include all relevant work arising from other groups.

B. PHTHALOCYANINES

Phthalocyanines

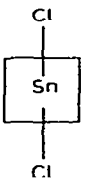


R = H MPc
R = SO_3^- $MPcTS^{4-}$
R = CO_2^- $MPcTC^{4-}$



AlPcCl

where □ refers to the phthalocyanine ring



$SnPcCl_2$

(i) General properties

One important requirement for a photosensitizer capable of the reduction of water to H_2 is that it must harvest a large fraction of the solar spectrum. Phthalocyanines are particularly attractive in this respect since they possess intense absorption in the near IR region such that, when used in conjunction with additional chromophores that absorb in the blue–green region (e.g. porphyrins, carotenes), they can collect up to 50% of the energy available in the solar spectrum (Fig. 1).

In addition to attractive absorption spectra, phthalocyanines are extremely resistant to chemical degradation and they can be synthesized by convenient routes [30], although the inherent insolubility of the products makes routine purification difficult, and water-soluble derivatives such as $MPcTS^{4-}$ and $MPcTC^{4-}$ or *N*-alkylated porphyrazines [31] are readily available.

Such compounds are readily soluble in water but formation of dimers and higher order aggregates [32] is a common occurrence with the sulphonates and carboxylates ($AlPcTS^{4-}$ being an unusual exception). Equilibrium constants for dimerization

$$2MPc \rightleftharpoons (MPc)_2 \qquad (15)$$

usually lie within the range 10^5–10^7 M^{-1} and follow the order $Cu^{II} > H^I > Fe^{II} > VO > Zn^{II} > Co^{II} > Al^{III}$ [33]. The rate of internal conversion from the first excited singlet state of a dimer greatly exceeds that of the corresponding

Fig. 1. Absorption spectrum of ZnPc in pyridine solution (------) and a typical solar emission spectrum (————).

monomer [34] so that when the dimers are excited by red light no useful photochemistry can be brought about. Consequently, such aggregation must be avoided and this can be achieved by adding low concentrations of organic solvents (e.g. 5% w/w pyridine) or by incorporating the phthalocyanine into micelles. The effect of such additives is quite striking, as shown in Fig. 2, where addition of a positively charged micelle forming agent (CTAC) to an aqueous solution of $ZnPcTS^{4-}$ converts the spectrum from that of the dimer ($\lambda_{max} \sim 635$ nm) to the characteristic spectrum of the monomer ($\lambda_{max} \sim 680$ nm) [35].

(ii) Photophysical properties

Table 1 summarizes the available photophysical properties for a series of metal phthalocyanines. Most of the data reported in this table concern chloronaphthalene or aqueous solutions and, in general, the photophysical properties of these compounds are relatively independent of the nature of the solvent provided that the MPc is present in the monomeric form. For the purposes of this review, the most relevant properties are excited-state lifetimes and energies, especially those measured in fluid solution at ambient temperature. However, there is a scarcity of room temperature triplet excited-state lifetimes so that, in many cases, Table 1 records the phosphorescence lifetimes (τ_p), measured at 77 K, for comparison.

Table 1 shows that MPcs possess very intense absorption in the region of 680 nm ($\epsilon > 10^5$ l mol^{-1} cm^{-1}), which is blue shifted towards 640 nm for the heavy metal phthalocyanines (e.g. Pt^{II}, Ir^{III}). An unfortunate consequence of

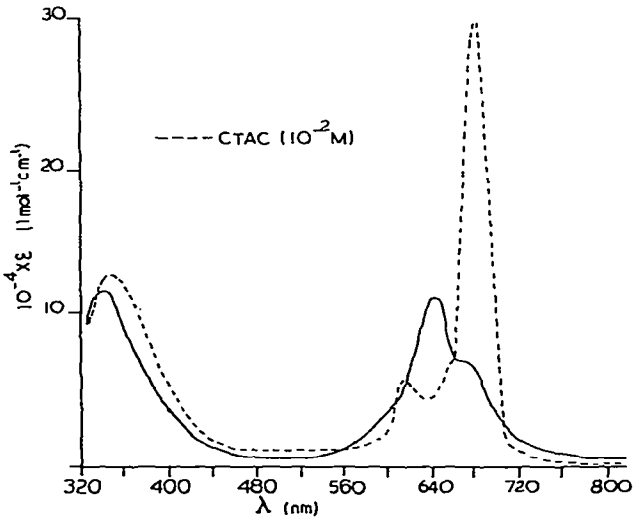


Fig. 2. The effect of cationic micelles on the absorption spectrum of $ZnPcTS^{4-}$ in aqueous solution (ref. 35).

TABLE I

Photophysical properties of some metal phthalocyanines

Compound	λ_{max} (nm)	log ϵ	τ_S (ns)	ϕ_F	τ_P^{77K} (ms)	τ_T^{300K} (μs)	ϕ_T	E_T (eV)	E_S (eV)
Pc	698 [a]	5.21 [a]	6 [b]	0.7 [c]	–	140 [d]	0.14 [d]	1.24 [c]	1.77 [d]
$PcTS^{4-}$	702 [e]	–	9.8 [e]	0.62 [e]	–	170 [e]	0.22 [e]	–	1.76 [e]
MgPc	675 [a]	4.94 [a]	7.2 [f]	0.6 [c]	1.0 [c]	–	–	1.12 [c]	1.82 [c]
ZnPc	672 [a]	5.45 [a]	3.8 [f]	0.3 [c]	1.1 [c]	–	–	1.13 [c]	1.83 [a]
$ZnPcTS^{4-}$	690 [g]	5.47 [e]	2.9 [e]	0.32 [e]	2 [e]	245 [e]	0.56 [e]	1.12 [e]	1.81 [g]
CdPc	700 [h]	4.16 [h]	–	0.05 [c]	0.35 [c]	–	–	1.13 [c]	1.79 [c]
AlPcCl	680 [h]	5.1 [h*]	6.8 [i]	0.58 [i]	–	500 [g]	0.4 [i]	–	1.80 [g]
$AlPcTS^{4-}$	675 [g]	5.2 [g]	5.3 [g]	–	–	500 [g]	–	1.2 [g]	1.81 [g]
CrPc	689 [j]	4.92 [j]	–	–	–	0.02 [k]	–	–	1.79 [j]
CuPc	678 [a]	5.34 [a]	–	–	–	0.035 [m]	>0.7 [m]	1.15 [n]	1.83 [a]
$CuPcTS^{4-}$	670 [e]	–	–	$<10^{-4}$	<0.5 [e]	0.065 [e]	0.92 [e]	1.16 [e]	1.85 [e]
PdPc	660 [l]	4.77 [l]	–	–	0.025 [l]	–	–	1.25 [l]	1.87 [l]
PtPc	650 [l]	4.86 [l]	–	–	0.006 [l]	–	–	1.31 [l]	1.90 [h]

[a] M.J. Whalley, J. Chem. Soc., (1961) 866. [b] W.F. Kosonocky and S.E. Harrison, J. Appl. Phys., 37 (1966) 4789. [c] P.S. Vincett, E.M. Voight and K.E. Rieckhoff, J. Chem. Phys., 55 (1971) 4131. [d] J.G. Villar and L. Lindquist, C.R. Acad. Sci. Paris, Ser. B, 264 (1967) 1807. [e] Ref. 44. [f] A.T. Gradyushko, A.N. Sevchenko, K.N. Solovyou and M.P. Tsvirko, Photochem. Photobiol., 11 (1970) 387. [g] Ref. 45. [h] D.B. Berezin, Russ. J. Phys. Chem., 36 (1962) 258. [i] J.H. Brannon and D. Madge, J. Am. Chem. Soc., 102 (1980) 62. [j] J.A. Elvidge and A.B.P. Lever, J. Chem. Soc., (1961) 1257. [k] Ref. 36. [l] E.R. Menzal, K.E. Rieckhoff and E.M. Voight, J. Chem. Phys., 58 (1973) 5726. [m] Ref. 37. [n] A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy and K. Magnell, J. Am. Chem. Soc., in press.

this intense absorption is that the radiative lifetimes of the lowest excited singlet states of these compounds are short (~ 12 ns). This results in high fluorescence quantum yields (ϕ_F) and short excited singlet-state lifetimes (τ_S). This situation limits the utility of the excited singlet states since it necessitates very high concentrations of quencher before intermolecular quenching can compete with the intrinsic deactivation of the excited singlet state and it also results in relatively low quantum yields for formation of the excited triplet state (ϕ_T). The nature of the central metal ion has a great effect upon ϕ_F and ϕ_T and heavy metal ions or paramagnetic metal ions enhance the yield of the triplet state, as shown in Fig. 3. Inevitably, this shortens the lifetime of the excited state (τ_T). In particular, phthalocyanines having a central paramagnetic transition metal ion possess very short τ_T values (e.g. $Cr^{III}Pc$, $\tau_T = 20$ ns [36]; $Cu^{II}Pc$, $\tau_T = 35$ ns [37]) which imposes a severe limitation upon their subsequent use as photosensitizers.

The final two columns in Table 1 show the energy available in the excited singlet (E_S) and triplet (E_T) states. As these data show, the energy loss associated with using the triplet rather than the singlet excited state of a MPc is about 0.6 eV. This effect is illustrated in Fig. 4 where energy level diagrams for ZnPc and zinc(II) meso-tetraphenylporphine (ZnTPP) are compared. The energy loss for ZnTPP is not so great but it is still serious, especially when the excited state is used as a sensitizer for a redox reaction.

As mentioned in the Introduction, in almost all cases where a phthalocyanine or porphyrin has been used to sensitize a photoredox reaction it is the triplet excited state that is the active sensitizer [26–29]. In this respect, the longer lifetime of the triplet relative to the singlet state is a considerable advantage since at a given concentration of quencher the number of diffusional encounters between a molecule in an excited state and a quencher molecule increases as the lifetime of the excited state increases. More

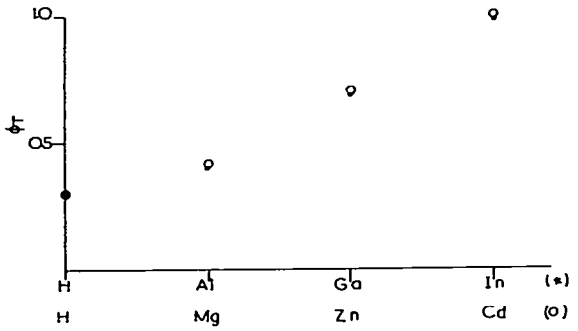


Fig. 3. The influence of atomic number of the central metal ion on the quantum yield for formation of the triplet excited state for some metal phthalocyanines.

importantly, recent work has established that separation of photoredox products is more efficient for a triplet process than for the analogous singlet process [28]. Thus, no redox products were observed when the fluorescent

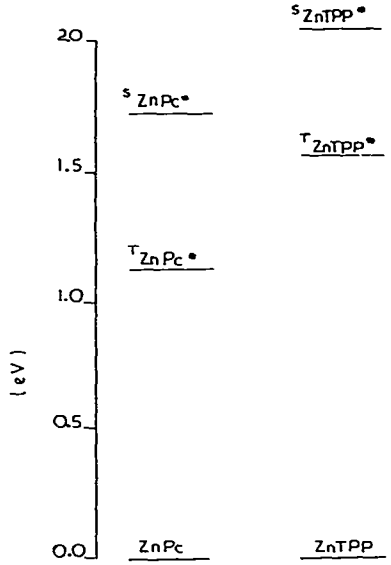


Fig. 4. Energy level diagrams for ZnPc and ZnTPP.

state of chlorophyll was quenched by quinones since reverse electron transfer within the solvent cage (k_3 in Fig. 5) was spin-allowed [27]. In contrast, quenching of the triplet excited state of chlorophyll by duroquinone led to formation of redox products with an estimated efficiency of about 48% [38]. In this latter case, spin reorientation within the solvent cage (k_6 in Fig. 6) must occur before the thermodynamically favoured reverse electron transfer step (k_3 in Fig. 5) can take place. As a result, the redox products may escape from the solvent cage (k_4 in Figs. 5 and 6). Reverse electron transfer between the separated products S^+ and A^- is now a diffusion controlled bimolecular process (k_5 in Fig. 5) and should be comparatively slow. If k_4 is particularly favourable, e.g. where there is some degree of electrostatic repulsion between

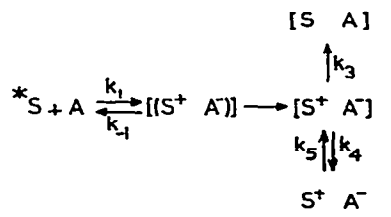


Fig. 5. General scheme for intermolecular photoinduced electron transfer.

the products which enhances charge separation, the yield of redox products can approach 100%, as found for reaction between triplet chlorophyll and MV^{2+} [39].

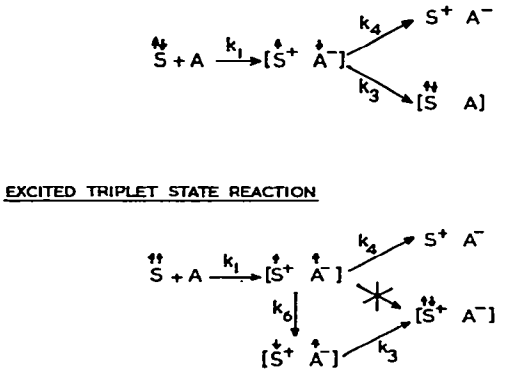


Fig. 6. Intermolecular electron transfer processes for excited singlet and triplet state reactions.

(iii) Thermodynamic requirements for H_2 production

As described briefly in the Introduction, the excited state of a chromophore can function as an electron donor or as an electron acceptor [26].

$$S^* + A \rightarrow S^+ + A^- \tag{16}$$

$$S^* + D \rightarrow S^- + D^+ \tag{17}$$

Consequently, excited states have distinct redox properties and, in general, these are related to the ground-state redox potentials by the appropriate excitation energy [40]. Thus, the redox potential for the process

$$S^+ + e^- \rightarrow S^* \qquad E(S^+/S^*) \tag{18}$$

can be obtained from the difference between the redox potential for the corresponding ground-state reaction ($E(S^+/S)$) and the energy of the excited state (E_S or E_T) whilst the redox potential for the process

$$S^* + e^- \rightarrow S^- \qquad E(S^*/S^-) \tag{19}$$

can be obtained from the sum of the redox potential for the ground-state process and the energy of the excited state. Thus, for a singlet excited-state reaction

$$E(S^+/S^*) = E(S^+/S) - E_S \tag{20}$$

$$E(S^*/S^-) = E(S/S^-) + E_S \tag{21}$$

These equations have been discussed in detail by other authors [26,40,41]. They involve a small approximation in that no allowance is made for changes in the entropy of the excited state relative to the ground state but they agree quite well (± 50 mV) with experimental findings [40,41].

Using the above equations, excited-state redox potentials for a series of metal phthalocyanines have been estimated (Table 2). It should be noted that the authors have made no allowance for solvent effects, which can change the given redox potentials by a considerable amount, so that the trends shown in Table 2 must be regarded with some caution. For the compounds described in Table 2, the first oxidation and reduction potentials involve formation of π-radical cations and anions, respectively, where the charge is located primarily upon the phthalocyanine ring [42]. The redox potentials ($E(P^+/P)$ and $E(P/P^-)$) lie around $+1.0$ and -0.5 V versus NHE, respectively, although they are sensitive to the nature of the central metal ion. This effect is even more pronounced when the central metal ion can undergo a change in oxidation state (e.g. CoPc, FePc) but these compounds possess extremely short excited-state lifetimes and are unlikely to be useful photosensitizers.

For a redox couple to reduce water, it is necessary that the redox potential of the couple is more negative than that of the proton

$$E(H^+/\tfrac{1}{2}\,H_2) = 0 - 0.059\ \text{pH} \tag{22}$$

and, in order to overcome kinetic barriers, there must be some degree of overpotential. With favourable reactants and efficient catalysts, these overpotentials can be quite small. For example, the redox couple

$$MV^{2+} + e^- \rightarrow MV^+ \tag{23}$$

has a redox potential of -0.45 V [43], which is only 40 mV more negative than that required to liberate H_2 from water at pH 7 but, in the presence of colloidal Pt, the reaction

$$2\,MV^+ + 2\,H_2O \xrightarrow{Pt} 2\,MV^{2+} + H_2 + 2\,OH^- \tag{24}$$

occurs with high efficiency [10]. For this reason, considerable attention has focused upon the use of MV^{2+} as an electron relay for reduction of water to H_2.

In a conventional three-component system, reduction of MV^{2+} is accompanied by oxidation of a sacrificial electron donor [15–25], e.g. cysteine, EDTA, triethanolamine. As described earlier, this can occur by oxidative (I)

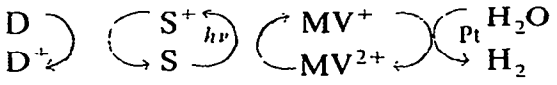
TABLE 2

Redox potentials for some ground and excited state phthalocyanines (measured in eV vs. NHE) where P_T^* refers to the triplet excited state and P_S^* refers to the singlet excited state

Compound	$E(P^+/P)$	$E(P/P^-)$	$E(P^+/P_T^*)$	$E(P_T^*/P^-)$	$E(P^+/P_S^*)$	$E(P_S^*/P^-)$
Pc	+1.34 [a]	−0.42 [b]	+0.10	+0.82	−0.43	+1.35
MgPc	+0.85 [c]	−0.7 [c]	−0.27	+0.42	−0.97	+1.12
ZnPc	+0.92 [c]	−0.65 [c]	−0.21	+0.48	−0.91	+1.18
CdPc	+0.78 [c]	−0.93 [c]	−0.35	+0.20	−1.01	+0.86
AlPcCl	+1.18 [c]	−0.42 [c]	−0.02	+0.78	−0.63	+1.39
CuPc	+1.22 [a]	−0.6 [c]	+0.07	+0.55	−0.61	+1.23
$CuPcTS^{4-}$	+1.11 [a]	−0.49 [a]	−0.05	+0.67	−0.63	+1.36

[a] A. Wolberg and J. Manassen, J. Am. Chem. Soc., 92 (1970) 2982. [b] L.D. Rollman and R.I. Iwamoto, J. Am. Chem. Soc., 90 (1968) 1455. [c] D. Lexa and M. Reix, J. Chim. Phys., 71 (1974) 511.

or reductive (II) cycles



(25)

(I)

(26)

(II)

In an oxidative cycle the sensitizer (S) is used to photoreduce MV^{2+} directly and for this process to occur the respective redox potentials must fulfil the requirement

$$E(S^+/S^*) < E(MV^{2+}/MV^+) \tag{27}$$

under the experimental conditions employed. For a reductive cycle the excited state of the sensitizer reacts with the sacrificial electron donor to form S^- and D^+ and it is the reduced form of the sensitizer that is used to reduce MV^{2+}. With this system, the respective redox potentials must fulfil the requirement

$$E(S/S^-) < E(MV^{2+}/MV^+) \tag{28}$$

In both cases, the oxidized form of the sacrificial electron donor D^+ is irreversibly decomposed so that the sensitizer is used to drive the overall reaction

$$D + MV^{2+} \rightarrow D^+ + MV^+ \tag{29}$$

Comparison of the data provided in Table 2 with the above redox potential requirements allows selection of some phthalocyanines that may be suitable for the reduction of MV^{2+} in aqueous solution. In an oxidative cycle, none of the above phthalocyanines are expected to photoreduce directly MV^{2+} via the phthalocyanine triplet excited state. However, this is a gross oversimplification since the redox potentials used in construction of Table 2 have taken no account of concentration, solvent, or electrostatic factors. Even so, the trends established by Table 2 may be useful in that they suggest that an oxidative cycle will be inefficient. In contrast, reductive cycles look quite promising and MgPc, ZnPc, CdPc, and CuPc should be capable of reducing MV^{2+} following reductive quenching of the excited triplet state by a suitable electron donor.

(iv) Photochemical systems

Inspection of the data compiled in Table 2 suggests that the singlet excited state of most phthalocyanines should be capable of the reduction of MV^{2+}

but, for reasons described earlier, the yield of redox products expected from a singlet state reaction is low. In fact, fluorescence quenching experiments have shown that MV^{2+} quenched the excited singlet state of $ZnPcTS^{4-}$ [44] and $AlPcTS^{4-}$ [45], the bimolecular quenching rate constants are given in Table 3. Despite the high quenching efficiency (the quenching rate constants are essentially diffusion controlled) the reactions gave no observable redox products. Presumably, the high degree of electrostatic attraction between the reactants (and expected products) favours recombination of the redox products within the solvent cage (k_3 in Fig. 5).

In an attempt to find a method of overcoming this strong electrostatic attractive force, recent attention has focused upon the use of a positively charged magnesium porphyrazine [46] ($MgPz^{4+}$) as a singlet state photosensitizer for reduction of MV^{2+} in aqueous solution. The structure of the sensitizer used for these studies is shown in Fig. 7, although it should be noted that the synthetic route used results in production of several structural isomers. As seen from Table 3, the rate constant for quenching the excited singlet state of the porphyrazine ($MgPz^{4+}$) was comparatively low, due to the strong electrostatic repulsion between the reactants [46]. Despite this low quenching efficiency, flash photolysis studies showed that net electron transfer products were formed under conditions where the triplet excited state was not expected to participate in the reaction [46]. However, the concentration of MV^{+} so produced was very low, even at extremely high quencher concentration and upon steady-state irradiation in the presence of EDTA, as sacrificial electron donor, and colloidal Pt no H_2 could be observed. Thus, this system seems to have little application to H_2 producing processes, at the present time.

A similarly discouraging picture emerges for the corresponding photoreduction of MV^{2+} via a triplet sensitized oxidative cycle. Although MV^{2+} quenched the triplet excited state of $ZnPcTS^{4-}$ in aqueous pyridine solution, the quenching rate constant was very low and prolonged irradiation of

TABLE 3

Bimolecular rate constants for quenching the excited singlet state of some metal phthalocyanines by MV^{2+} in aqueous solution

Compound	$10^{-9} \times k$ ($M^{-1}\,s^{-1}$)	Ref.
$ZnPcTS^{4-}$	10	44
$AlPcTS^{4-}$	20	45
$MgPz^{4+}$	0.045	46

$ZnPcTS^{4-}$ in the presence of MV^{2+}, EDTA, and colloidal Pt did not result in production of H_2 [44,47]. Replacement of EDTA with other sacrificial electron donors (cysteine, H_2S, or triethanolamine) and adjustment of the

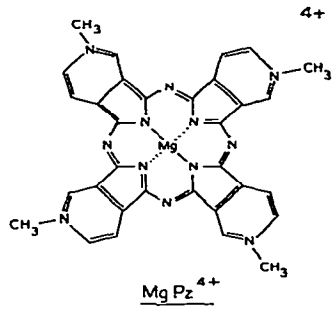


Fig. 7. Structure of $MgPz^{4+}$.

solution pH and concentration of reagents all failed to give a detectable yield of H_2 [44,47].

The corresponding photoreduction of MV^{2+} via a triplet sensitized reductive cycle is at a somewhat more advanced stage. Recent work has demonstrated that ZnPc dispersed in neutral or cationic micelles was photoreduced by cysteine or EDTA [35]. When MV^{2+} was present in the aqueous phase, irradiation resulted in formation of MV^+ as shown in Fig. 8. Identical effects were observed with $ZnPcTS^{4-}$ dispersed in cationic micelles [35] and, for this system, the overall reaction mechanism was found to correspond to the

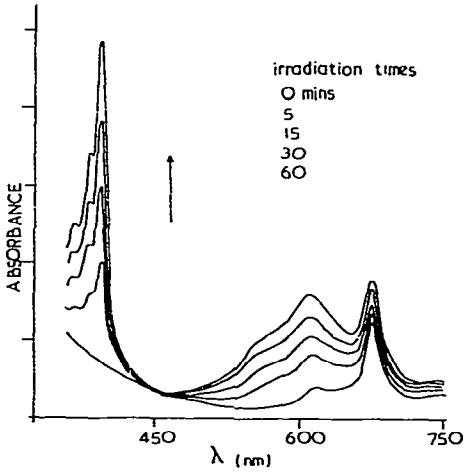


Fig. 8. Absorption spectral profile showing the build-up of MV^+ (λ_{max} 395 and 605 nm) from the $ZnPcTS^{4-}/MV^{2+}$/cysteine system (ref. 35).

following scheme.

$$*ZnPcTS^{4-} + cysSH \rightarrow ZnPcTS^{5-} + cysSH^{+\cdot} \quad (30)$$

$$ZnPcTs^{5-} + cysSH^{+\cdot} \rightarrow ZnPcTS^{4-} + cysSH \quad (31)$$

$$cysSH^{+\cdot} \rightarrow cysS^{\cdot} + H^{+} \quad (32)$$

$$2\ cysS^{\cdot} \rightarrow cysS - Scys \quad (33)$$

$$ZnPcTS^{5-} + MV^{2+} \rightarrow ZnPcTS^{4-} + MV^{+} \quad (34)$$

Under similar experimental conditions MgPc dispersed in neutral micelles was found to reduce MV^{2+} following reductive quenching of the excited triplet state with cysteine whilst no reaction was observed when AlPcCl or $SnPcCl_2$ were used [48].

In separate experiments, it was found that the reduced form of a phthalocyanine could be used to reduce water to H_2 directly, without involvement of an electron relay such as MV^{2+}. However, the quantum yield for formation of H_2 from such a system was extremely low ($\phi_{H_2} < 10^{-4}$) and there was extensive decomposition of the phthalocyanine [44].

$$2\ ZnPcTS^{5-} + 2H^{+} \xrightarrow{Pt} 2\ ZnPcTS^{4-} + H_2 \quad (35)$$

Detailed investigations by Lever et al. [49] have screened a wide range of MPcs for their ability to photoreduce MV^{2+} in aqueous tetrahydrofuran containing triethanolamine. In some cases (e.g. Mg^{II}, Zn^{II}, Fe^{II}, Ru^{II}, Cr^{II}, Mn^{II}, and Rh^{III}) MV^{+} was produced as a photoproduct but the quantum yields were low ($\sim 10^{-3}$) whilst, in several instances, irradiation of trivalent Pc derivatives (e.g. Fe^{III}) resulted in photoreduction to the divalent state which functioned as a photosensitizer for reduction of MV^{2+}. Although no attempts were made to produce H_2 under these experimental conditions, the presence of organic solvents may inhibit this step, the work is extremely useful in that it correlates thermodynamic and kinetic parameters for the photochemical processes of Pc derivatives.

Recently, it was shown that particles of metal-free phthalocyanine dispersed in positively charged micelles photoreduced oxygen to superoxide [50]. In view of the high reducing power of the conduction band of these compounds, which can be regarded as possessing semiconductor properties, such particles should be capable of the reduction of water to H_2. Indeed, experiments have shown that particles of CuPc, upon which Pt had been deposited, were able to photoreduce water using EDTA as the electron donor [51]. Although the quantum yield for this process was again extremely low ($\phi_{H_2} < 10^{-4}$), these findings do suggest an interesting area for further study.

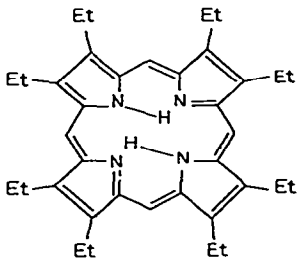
In conclusion, although phthalocyanines are not ideal chromophores,

since triplet yields and energies are low and there are problems with solubility and aggregation, some modest success has been achieved in the photochemical production of H_2 from three component systems. The long wavelength absorption characteristics and the low cost of these compounds merit further work in this field.

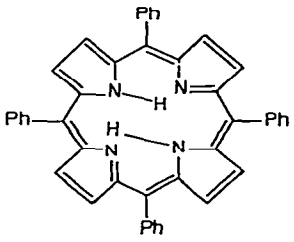
C. PORPHYRINS

(i) General properties

The basic porphine skeleton is the foundation stone for construction of a wide variety of porphyrins, chlorins, phlorins, phthalocyanines, etc. As regards synthetic ease, the most commonly encountered compounds are symmetrically substituted porphyrins such as octaethylporphine (OEP) and tetraphenylporphine (TPP) and an exceptionally wide range of metal complexes of these two ligands has been reported.



OEP



TPP

(Et ≡ C_2H_5; Ph = C_6H_5)

There is a multitude of porphyrins and metalloporphyrins, and there are a number of excellent reviews that have compiled the synthesis [52], characterization [53,54], and properties [55,56] of these compounds. For the purposes of this review, we have restricted our attention to OEP and TPP complexes although necessity has forced us to refer to several other types of porphyrin.

There is a wide range of synthetic routes available for preparation of porphyrins and metalloporphyrins [52], although many of the metalloporphyrins are acid labile and undergo demetallation [57]. As described for the phthalocyanines, water soluble porphyrins can be prepared by sulphonation or carboxylation or by alkylation of *N*-pyridyl compounds [58] (Fig. 9). The resulting compounds are readily soluble in water and do not suffer from aggregation problems to the same extent as the phthalocyanines, although the negatively charged porphyrins exhibit fairly high dimerization constants [53]. The *N*-alkyl salts favour monomeric species and appear to be particu-

larly attractive as possible photosensitizers for reduction of water.

The absorption spectral features of porphyrins are not so attractive as those of the corresponding phthalocyanines since the absorption does not

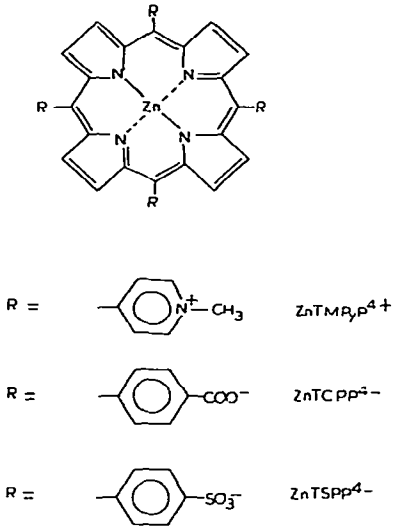


Fig. 9. Structure of the water-soluble porphyrins.

extend so far into the near IR region. This is particularly true for metalloporphyrins, where the lowest energy absorption maximum is usually found at $\lambda < 620$ nm. Figure 10 gives absorption spectra for TPP, ZnTPP, and PdTPP and it is seen that the nature of the central metal ion has a marked effect upon the absorption profile.

The absorption spectra of many metal-free porphyrins have been described in detail by other authors [59]. The fairly weak bands in the visible region are normally termed Q bands whilst the most intense band in the absorption spectrum is the B band which is the origin of the second singlet excited state and normally occurs at about 420 nm. As seen in Fig. 10, the Q region of the absorption spectrum for a metalloporphyrin often consists of two bands, the lowest energy band being the origin of the first excited singlet state whilst the second band is its vibrational overtone. Both the energy (E_Q) and the oscillator strength (f_Q) of the lowest energy absorption band depend upon the central metal ion [60] and they can be used as a simple measure of the degree of interaction between the metal ion and the porphyrin π-system [61]. Thus, with increased interaction the energy is raised and there is a reduction in the oscillator strength. This effect is illustrated in Fig. 11 which relates E_Q and f_Q for a series of metal TPP complexes [62]. The figure infers that there is very little interaction between the metal ion and the porphyrin

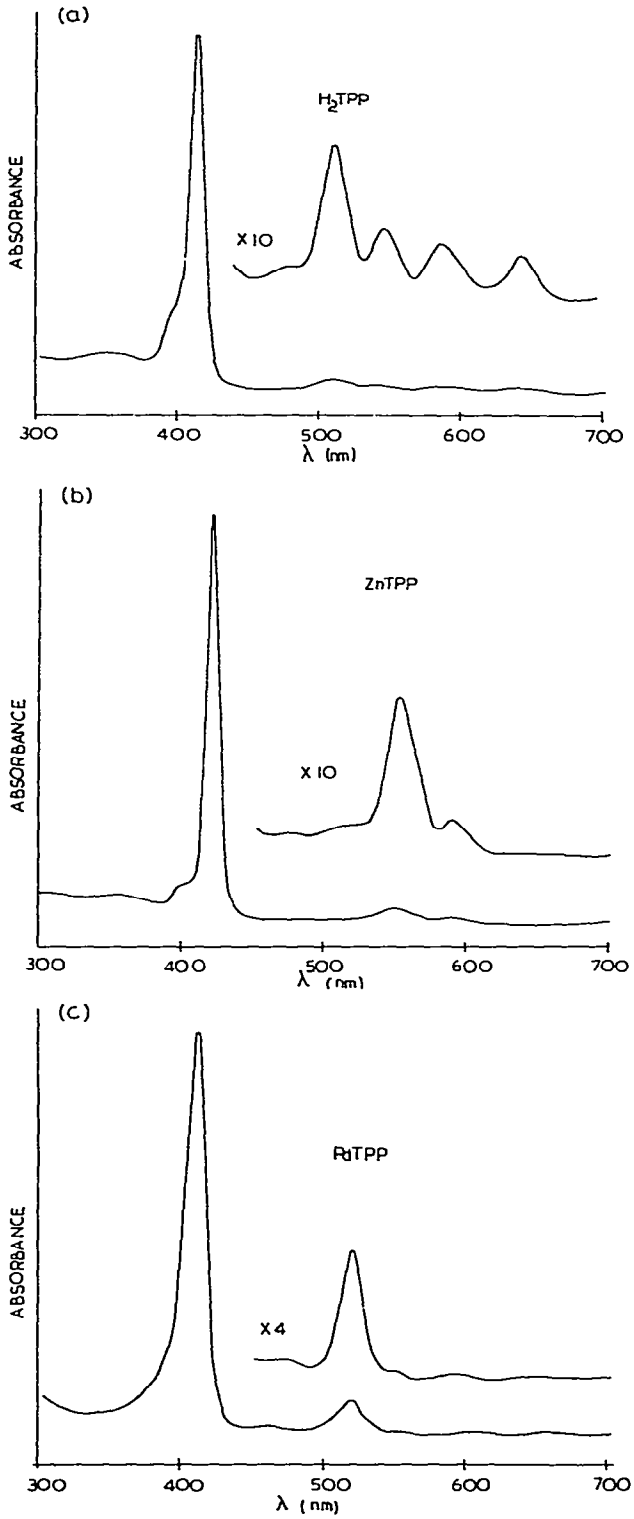


Fig. 10. Absorption spectra of (a) H_2TPP, (b) ZnTPP and (c) PdTPP recorded in benzene solution.

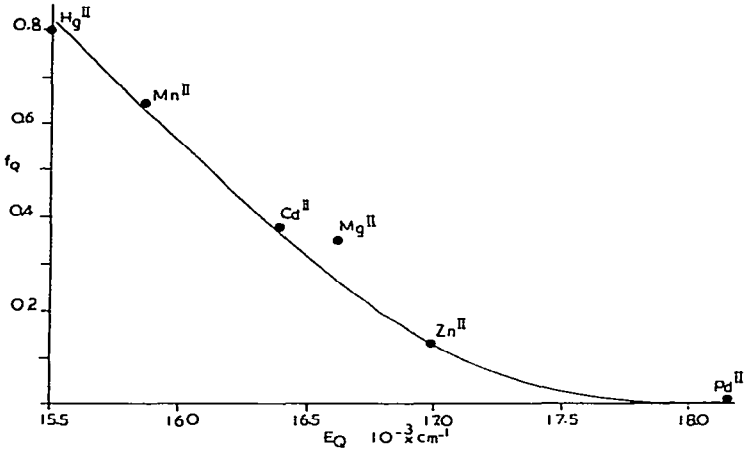


Fig. 11. Relationship between the oscillator strength (f) and the energy (E) of the lowest energy absorption band for some metal TPPs.

π-system for HgTPP whilst for PdTPP the interaction is quite strong. The extent of interaction is controlled by a combination of several factors, including the size of the metal ion, the geometry of the metalloporphyrin and electrostatic and inductive effects but, even so, Fig. 11 provides a useful fingerprint for comparison of the relative efficiency with which orbitals on the metal ion interact with the porphyrin π-system.

Although not as useful as phthalocyanines, porphyrins and metalloporphyrins are still capable of collecting a considerable fraction of the solar spectrum. In particular, TPP can absorb about 46% of the energy available in the solar spectrum. Metalloporphyrins always have their lowest energy absorption bands to the blue of the corresponding metal-free porphyrin but when the extent of interaction between the metal ion and the porphyrin π-system is fairly weak (e.g. MgTPP) the metalloporphyrin can collect about 40% of the energy available in the solar spectrum. This value is reduced for strongly interacting metalloporphyrins but, even so, PdTPP can absorb some 25% of the solar spectrum.

(ii) Photophysical properties

Table 4 contains a summary of the available photophysical properties for a series of metalloporphyrins. The symbols used in this table follow from Table 1 and, wherever possible, the data refer to room temperature measurements. In general, metalloporphyrins exhibit lower ϕ_F values than the corresponding phthalocyanines and there is a substantial increase in the

TABLE 4

Photophysical properties of some metalloporphyrins

Compound	ϕ_F	τ_S (ns)	ϕ_T	τ_T^{300K} (μs)	τ_T^{77K} (ms)	E_T (eV)	E_S (eV)
H_2TPP	0.13 [a]	13.6 [a]	0.82 [a]	1380 [a]	6 [a]	1.43 [a]	1.86 [a]
MgTPP	0.15 [b]	9.2 [b]	–	1350 [b]	45 [b]	1.48 [b]	2.03 [b]
ZnTPP	0.04 [b]	2.7 [b]	0.88 [c]	1200 [b]	26 [b]	1.59 [b]	2.05 [b]
CdTPP	4×10^{-4} [b]	6.5×10^{-2} [b]	–	260 [b]	2.4 [b]	1.54 [b]	2.03 [b]
HgTPP	$<10^{-3}$ [b]	–	–	32 [b]	0.2 [b]	1.46 [b]	1.92 [b]
AlTPP	0.11 [d]	5.1 [d]	–	1140 [d]	30 [d]	1.61 [d]	2.07 [d]
PdTPP	2×10^{-4} [b]	2×10^{-2} [b]	~1 [e]	380 [b]	2.8 [b]	1.79 [b]	2.25 [b]
PtTPP	$<10^{-3}$ [e]	–	–	–	0.3 [f]	1.90 [f]	2.31 [f]
CuTPP	$<10^{-3}$ [e]	–	~1 [e]	0.09 [g]	0.6 [g]	1.66 [g]	2.13 [g]
ZnOEP	0.04 [h]	2.2 [h]	–	–	57 [h]	1.76 [h]	2.14 [h]
SnOEP	8×10^{-3} [i]	0.5 [j]	0.8 [j]	–	30 [j]	1.79 [j]	2.15 [j]
CuOEP	$<10^{-3}$ [j]	–	1.0 [j]	0.12 [k]	0.075 [l]	1.83 [l]	2.19 [l]
PdOEP	$<10^{-3}$ [j]	–	1.0 [j]	300 [d]	2 [d]	1.88 [d]	2.24 [d]
H_2ETIO [m]	0.17 [n]	21.2 [n]	–	–	20 [p]	1.59 [p]	2.00 [n]
MgETIO	0.25 [n]	12.4 [n]	–	–	130 [p]	1.73 [p]	2.12 [n]
ZnETIO	0.04 [n]	2.3 [n]	–	–	57 [p]	1.76 [p]	2.15 [n]
H_2MESO [o]	0.12 [c]	19 [c]	0.8 [c]	~500 [c]	14 [p]	1.65 [p]	2.00 [p]
MgMESO	0.20 [c]	11 [c]	0.62 [c]	~500 [c]	–	1.72 [p]	2.12 [p]
ZnMESO	0.05 [c]	2 [c]	0.86 [c]	~500 [c]	83 [p]	1.77 [p]	2.16 [p]
CdMESO	–	–	–	–	7 [p]	1.71 [p]	2.13 [p]

[a] Ref. 61. [b] Ref. 62. [c] G.P. Gurinovich and B.M. Dzhagarov, Izv. Akad. Nauk. SSSR, 37 (1973) 383. [d] A. Harriman, unpublished work. [e] G.P. Gurinovich and B.M. Dzhagarov, in F. Williams (Ed.), Luminescence of Crystals, Molecules and Solutions. Plenum, London, 1973, p. 196. [f] D. Eastwood and M. Gouterman, J. Mol. Spectrosc., 35 (1970) 359. [g] A. Harriman, J. Chem. Soc., Faraday Trans. 1, 77 (1981) 369. [h] A.T. Gradyushko and M.P. Tsvirko, Opt. Spectrosc., 31 (1971) 548. [i] M. Gouterman, F.D. Schwarz, P.D. Smith and D. Dolphin, J. Chem. Phys., 59 (1973) 676. [j] D. Madge, M.W. Windsor, D. Holten and M. Gouterman, Chem. Phys. Letts., 29 (1974) 183. [k] M.P. Tsvirko, K.N. Solovev and V.V. Sapunov, Opt. Spectrosc., 36 (1974) 335. [l] Ref. 59. [m] ETIO, etioporphyrin I. [n] A.T. Gradyushko and M.P. Tsvirko, Opt. Spectrosc., 31 (1971) 291. [o] MESO, dimethyl ester of mesoporphyrin IX. [p] J.B. Allison and R.S. Becker, J. Phys. Chem., 67 (1963) 2669.

quantum yields for formation of the excited triplet state. A further generalization that appears from Tables 1 and 4 is that the triplet state lifetimes, at both 77 and 293 K, are longer for the porphyrins than for the phthalocyanines, presumably because the triplet energy of the porphyrin always exceeds that of the phthalocyanine. Thus, although the porphyrins cannot collect as high a fraction of the solar spectrum as the phthalocyanines, the excited triplet states of the porphyrins seem to be more amenable for use as photosensitizers.

The relative trends found for the excited-state lifetimes of the metal phthalocyanines hold for the metalloporphyrins. Thus, the paramagnetic transition metal porphyrins (e.g. CuTPP, FeTPP) have very short excited-state lifetimes, which essentially preclude their use as sensitizers in fluid solution at ambient temperatures. The heavy metal ion porphyrins (e.g. HgTPP) possess ϕ_T values that approach unity [62] but still retain relatively long triplet-state lifetimes and these diamagnetic porphyrins look very promising photosensitizers. From a comparison of the triplet-state properties described in Table 4 with the stability figures given in ref. 57 the authors have selected the following metalloporphyrins as potential photosensitizers

H^{I}; Mg^{II}; Zn^{II}; Pd^{II}; Cd^{II}; Pt^{II}; Al^{III}; Sn^{IV}

although both Mg^{II} and Cd^{II} porphyrins are susceptible to acid catalysed demetallation.

(iii) Redox potentials

Table 5 lists the one electron oxidation and reduction potentials for ground-state and excited-state metalloporphyrins, measured in organic solvents. The list is limited to the metalloporphyrins cited above as being promising sensitizers; for further information about the ground-state redox potentials there are several excellent reviews [63,64]. Relative to the phthalocyanines, the excited-state redox potentials of the metalloporphyrins are more amenable for photoreduction of water to H_2, either by oxidative or reductive cycles. Following the discussion given earlier, we would expect most of the metalloporphyrins to reduce MV^{2+} (or water) by oxidative and reductive cycles upon excitation to the triplet state. Again, these considerations must be treated with some caution since no attempt has been made to take into account the effects of solvent, concentration, or electrostatic factors and these effects may involve considerable changes in the apparent thermodynamics of the process.

However, a recent study [65] has measured oxidation potentials for some water-soluble zinc(II) porphyrins in aqueous solution and the observed values are collected in Table 6. It can be seen that the oxidation potential of

TABLE 5

Ground and excited state redox potentials (eV vs. NHE) for some metalloporphyrins in organic solvents (E^0 values from ref. 63)

Compound	$E(P^+/P)$	$E(P/P^-)$	$E(P^+/P_{T\bullet})$	$E(P^+/P_S^*)$	$E(P_T^*/P^-)$	$E(P_S^*/P^-)$
H_2TPP	+1.19	−0.81	−0.24	−0.67	+0.62	+1.05
MgTPP	+0.78	−1.11	−0.70	−1.25	+0.37	+0.92
ZnTPP	+0.95	−1.11	−0.64	−1.10	+0.48	+0.94
CdTPP	+0.87	−1.01	−0.67	−1.16	+0.53	+1.02
PdTPP	+1.26	−0.76	−0.53	−0.99	+1.03	+1.49
PtTPP	+1.07	−1.22	−0.83	−1.20	+0.68	+1.09
CuTPP	+1.14	−0.96	−0.52	−0.99	+0.70	+1.17
H_2OEP	+1.05	−1.22	−0.56	−0.95	+0.39	+0.78
MgOEP	+0.78	−1.44	−0.95	−1.34	+0.29	+0.68
ZnOEPqa+0.87		−1.37	−0.89	−1.27	+0.39	+0.77
CdOEP	+0.79	−1.28	−0.92	−1.34	+0.43	+0.85
PdOEP	+1.06	−1.29	−0.82	−1.18	+0.59	+0.95
PtOEp	+0.99	–	−0.95	−1.31	–	–
CuOEP	+1.03	−1.22	−0.80	−1.16	+0.61	+0.97
PbOEP	+0.92	−1.06	−0.85	−1.21	+0.71	+1.07

TABLE 6

One electron oxidation potentials for some water-soluble zinc porphyrins in aqueous solution (from ref. 65)

Compound	E^0(eV vs. NHE)
$ZnTSPP^{4-}$	+0.87
$ZnTCPP^{4-}$	+0.80
$ZnTMPyP^{4+}$	+1.18

$ZnTMPyP^{4+}$ is similar to that of the unsubstituted ZnTPP measured in organic solvents but the negatively charged porphyrins have considerably lower oxidation potentials. This finding is in agreement with the hypothesis that the positive charges of $TMPyP^{4+}$ are located primarily at the pyridyl *N*-atoms whilst the negative charges of the sulphonate and carboxylate derivatives are delocalized over the entire porphyrin ring [66]. Using the above oxidation potentials it would be expected that the negatively charged zinc porphyrins would be good triplet excited-state photosensitizers for the reduction of MV^{2+} via an oxidative cycle but the positively charged compound appears to be close to the thermodynamic limit.

Earlier work [67] has established that substituents can have an important effect upon the redox potential of a porphyrin or metalloporphyrin. For substitution in the 4-position of the phenyl rings of TPP, the effect upon the redox potential (E^0) correlates with the Hammett constant of the substituent. This correlation holds for both oxidation and reduction potentials and provides a very useful method for tuning the redox potentials of a porphyrin for any particular application [67]. In fact, the substituent has an even greater effect upon E^0 when it is positioned directly on the pyrrole ring [68] but the synthesis of such compounds can be difficult.

(iv) Photochemical systems involving zinc(II) porphyrins

Three separate laboratories have reported that positively-charged, water-soluble zinc porphyrins function as efficient photosensitizers for the reduction of water to H_2. Kalyanasundaram and Gratzel [22] found that $ZnTMPyP^{4+}$ was a particularly effective photosensitizer for the reduction of MV^{2+} in aqueous solution and in the presence of EDTA, as sacrificial electron donor, and colloidal Pt irradiation of the system with visible light resulted in formation of H_2 with high yield. These findings were confirmed by McLendon and Miller [69] who also reported that H_2 production was observed when $ZnTSPP^{4-}$ was used as the photosensitizer. A recent report

from the authors' laboratory [70] gave further confirmation of Kalyanasundaram and Gratzel's results whilst providing a more quantitative evaluation of the system.

Two of the above reports concluded that the triplet excited state of the zinc porphyrin was the active photosensitizer [22,70] but McLendon and Miller [69] preferred a singlet-state reaction mechanism. However, flash photolysis studies [22,70] have provided strong evidence that the reaction involves the triplet excited state of the metalloporphyrin. These latter studies allowed a full evaluation of the reaction mechanism and this is described below, based on the findings of Harriman et al. [70].

Using spectroscopic data, the energy levels of the excited singlet and triplet states of $ZnTMPyP^{4+}$ were located at 198 and 152 kJ mol^{-1}, respectively. The photophysical properties measured for $ZnTMPyP^{4+}$ in aqueous solution are collected in Table 7 and it was found that the addition of high concentrations of MV^{2+} and EDTA had no effect upon either the ground-state absorption spectrum or the fluorescence yield [70]. From these studies, it was estimated that the bimolecular rate constants for quenching the excited singlet state by these quenchers must be $< 3 \times 10^7$ M^{-1} s^{-1}. Under similar conditions, the triplet state was quenched by both MV^{2+} and EDTA and the quenching rate constants are collected in Table 8. These values appear to be in poor agreement with those reported previously by Kalyanasundaram and Gratzel [22] but this discrepancy may be due to differences in the ionic strength (μ) of the medium. Classical kinetic theory relates the observed rate of electron transfer between ions A and B of charge Z to the ionic strength of the medium by the equation

$$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu} \tag{36}$$

where k_0 refers to electron transfer at zero μ. For reaction between triplet $ZnTMPyP^{4+}$ and MV^{2+}, the product $Z_A Z_B$ is $+8$ so that the rate of reaction should show a sharp increase with increased μ. In contrast, the rate of reaction between triplet $ZnTMPyP^{4+}$ and EDTA at pH 5 should decrease with increased μ since EDTA is present in ionized form. Thus, since Harriman et al. used a much higher μ value than that of Kalyanasundaram

TABLE 7

Photophysical properties of $ZnTMPyP^{4+}$ in aqueous solution at pH 5 (data from ref. 70)

Φ_F	τ_S (ns)	Φ_T	τ_T^{300K} (μs)	E_T (eV)
0.025	1.4	0.9	655	1.57

TABLE 8

Bimolecular rate constants for quenching the triplet excited state of $ZnTMPyP^{4+}$ in aqueous solution

Quencher	$10^{-5} \times k$ (ref. 70)	$M^{-1} s^{-1}$ (ref. 22)
EDTA	1.7 ± 0.3	4.0 ± 0.4
MV^{2+}	180 ± 20	20

and Gratzel, it would be expected that their rate constants be higher for quenching by MV^{2+} and lower for quenching by EDTA, as observed.

When MV^{2+} was present in high concentration, flash spectroscopy showed the formation of radical ion products consistent with the reaction [70]

$$*ZnTMPyP^{4+} + MV^{2+} \rightarrow ZnTMPyP^{5+\cdot} + MV^{+} \quad (37)$$

The radical ions were reasonably long-lived ($t_{1/2} \sim 300\ \mu s$) and decayed via a second order kinetic process, presumably due to diffusional recombination (see Fig. 5).

$$ZnTMPyP^{5+\cdot} + MV^{+} \rightarrow ZnTMPyP^{4+} + MV^{2+} \quad (38)$$

Despite the high efficiency of this recombination process the quantum yield for production of $ZnTMPyP^{5+\cdot}$ was estimated to be (0.75 ± 0.08) [70].This value is very high and means that practically all of the triplet state can be converted into redox products under these conditions. In fact, the quantum yield for formation of redox products (ϕ_{IONS}) can be considered as the product of three probabilities

$$\phi_{IONS} = \phi_T \times \phi_Q \times \phi_S \quad (39)$$

where ϕ_T is the quantum yield for formation of the triplet state and ϕ_Q is the probability of quenching the triplet state by a particular concentration of quencher.

$$\phi_Q = k(MV^{2+})/\left(k(MV^{2+}) + \tau_T^{-1}\right) \quad (40)$$

Under the conditions employed, $\phi_T = (0.9 \pm 0.1)$ and $\phi_Q = 1.0$ so that the probability of the quenching act leading to the formation of separated ion products (ϕ_S) must be about 0.8. This is surprisingly high for a photoredox reaction and must reflect the high degree of electrostatic repulsion between the products within the solvent cage. In this respect, it is of interest to note that ϕ_{IONS} for reaction between $ZnTSPP^{4-}$ and MV^{2+} was found to be < 0.01 under similar conditions [70].

The observation that the triplet excited state of $ZnTMPyP^{4+}$ undergoes oxidative quenching in the presence of MV^{2+} appears to be at variance with the measured redox potential of the ground-state molecule. Thus, E^0 for the $ZnTMPyP^{5+/4+}$ couple has been reported [65] as 1.18 V which together with the observed phosphorescence maximum of 1.58 eV gives a redox potential for the triplet state of -0.40 V compared to the formal redox potential for the $MV^{2+/+}$ couple of -0.45 V. As stated earlier, there are important limitations in the calculations used to estimate E^0P^+/P_T^* but, even so, it appears that there is a minimal thermodynamic driving force for electron transfer from the triplet excited state of $ZnTMPyP^{4+}$ to MV^{2+}, especially since coulombic repulsion forces must be overcome, and this may be manifest in the modest triplet quenching rate constant found for this process. Even allowing for coulombic interactions between the reactants, the quenching rate constant is still some way short of the diffusion controlled limit. For $ZnTSPP^{4-}$ the calculated redox potential of the triplet excited state (based upon the triplet energy of $ZnTMPyP^{4+}$) is -0.7 V so that there is a reasonably high thermodynamic driving force and, here, quenching of the triplet excited state with MV^{2+} occurs at the diffusion controlled limit. Thus, the type of water solubilizing group has a marked effect upon the kinetics and overall efficiency of charge separation for these systems and these effects are worthy of detailed investigation.

At high concentrations of EDTA, flash spectroscopy showed the formation of a long-lived intermediate that was attributed to $ZnTMPyP^{3+}$ [70].

$$*ZnTMPyP^{4+} + EDTA \rightarrow ZnTMPyP^{3+} + EDTA^{+} \quad (41)$$

The transient decayed via disproportionation

$$2\,ZnTMPyP^{3+} \rightleftharpoons ZnTMPyP^{4+} + ZnTMPyP^{2+} \quad (42)$$

and there was extensive bleaching of the chromophore. Since the triplet quenching rate constants exhibited by MV^{2+} and EDTA were quite dissimilar, it was possible to control the reactant concentrations so that the photochemistry occurred exclusively via an oxidative cycle. The redox products produced by this process were sufficiently long-lived for EDTA to intercept reverse electron transfer and so stabilize the MV^+ and it was found that with concentrations of EDTA $> 10^{-2}$ M most, if not all, of the initially produced MV^+ was stabilized.

$$*ZnTMPyP^{4+} + MV^{2+} \rightarrow ZnTMPyP^{5+} + MV^{+} \quad (43)$$

$$ZnTMPyP^{5+} + EDTA \rightarrow ZnTMPyP + EDTA^{+} \quad (44)$$

$$EDTA^{+} \rightarrow \text{products} \quad (45)$$

In fact, irradiation of an outgassed solution containing $ZnTMPyP^{4+}$ ($2\times$

10^{-5} M), MV^{2+} (8×10^{-3} M) and EDTA (15×10^{-3} M) in water at pH 5 resulted in the formation of MV^{+} as a permanent product and the quantum yield for production of MV^{+} was found to be (0.75 ± 0.10) [70].

As described earlier, MV^{+} is able to reduce water to H_2 when a suitable catalyst is added to the system and irradiation of the above solution in the presence of a colloidal Pt catalyst resulted in production of H_2 [19,69,70]. Under the above experimental conditions and using a Pt concentration of $\sim 10^{-5}$ M, the quantum yield for production of H_2 (ϕ_{H_2}) was found to be 0.30 under optimum conditions (Fig. 12). This optimum value decreased with longer irradiation times, possibly due to competitive absorption of light by unreacted MV^{+} [70] although it is also known that MV^{2+} can be hydrogenated under these conditions [71]. When the optimum concentrations of reactants were employed, it was possible to obtain a high turnover with respect to the chromophore and also a modest turnover with respect to MV^{2+} and Pt. In this experiment, the total concentration of evolved H_2 corresponded to a turnover with respect to $ZnTMPyP^{4+}$, MV^{2+}, and Pt of 6000, 7, and 200, respectively.

Experiments carried out in the absence of MV^{2+} demonstrated that H_2 was produced [22,70,72] but in relatively low yield. As described earlier, irradiation of $ZnTMPyP^{4+}$ in outgassed aqueous solution containing EDTA resulted in bleaching of the porphyrin and the quantum yield for the bleaching process (ϕ_{BL}) was found to be 0.08 [72]. In the presence of a Pt catalyst, ϕ_{BL} was lowered, as shown in Fig. 13, although it required very high Pt concentrations for complete inhibition of the photoreduction reaction. When the catalyst was present, H_2 was detected as a reaction product and the observed quantum yields (ϕ_{H_2}) are also given in Fig. 13. At moderate concentrations of Pt, there is a rough correlation between ϕ_{BL} and ϕ_{H_2} in

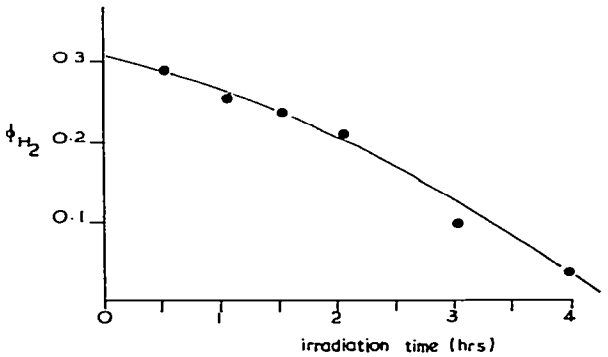


Fig. 12. Quantum yield for formation of hydrogen (ϕ_{H_2}) from the $ZnTMPyP^{4+}$/MV^{2+}/EDTA system (ref. 70).

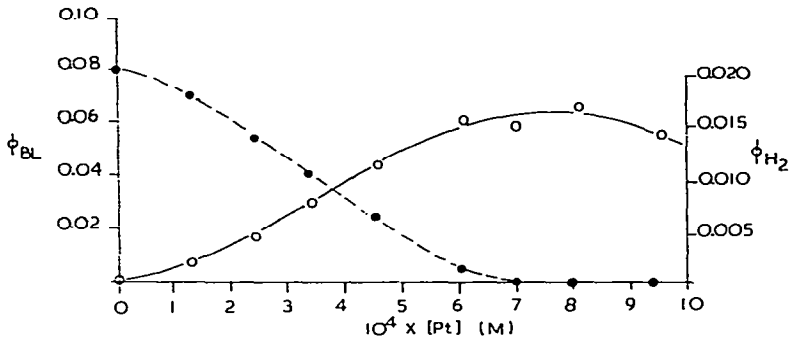


Fig. 13. The effect of Pt concentration upon the quantum yields for bleaching (●) and H_2 formation (○) from the $ZnTMPyP^{4+}$/EDTA system (ref. 72).

that more H_2 is produced as the bleaching process is inhibited. At very high Pt concentrations, the observed ϕ_{H_2} falls but this may be due to adsorption of H_2 onto the catalyst surface. In the absence of either Pt, EDTA, or $ZnTMPyP^{4+}$, there was no H_2 produced [72] and addition of Pt to a photolysed solution did not lead to generation of H_2. Thus, Pt must intercept one of the intermediate species involved in the bleaching reaction and mediate H_2 production from water using this intermediate.

From flash photolysis studies, it was found that the presence of Pt did not affect the yield of $ZnTMPyP^{3+\cdot}$ but it did shorten its lifetime [72]. This effect is shown in Fig. 14 and demonstrates clearly that the species responsible for production of H_2 is the one electron reduction product of the zinc porphyrin (cf. $ZnPcTS^{4-}$ described earlier). In the absence of Pt, the half-life of $ZnTMPyP^{3+\cdot}$ was quite short, due to the dismutation reaction (reaction (45)), so that the radical had a limited time in which to reach a Pt particle. Consequently, in order to ensure that the majority of the $ZnTMPyP^{3+\cdot}$ radicals produced in the photochemical step are used for H_2 generation it is necessary to use a high concentration of Pt. In this respect, this system compares unfavourably with the corresponding system containing MV^{2+} since in the latter system the species responsible for H_2 generation ($MV^{+\cdot}$) had a lifetime in excess of 1 h and, hence, low concentrations of Pt could be used.

Of the total amount of Pt in the solution most is present in an inactive form since only the Pt that is freely exposed to the solution can form an active site. Thus, an active site can be viewed as a small exposed region of a large particle. Unfortunately, the particle size of the Pt catalyst used in the above study [72] was quite large with an effective radius of about 30 nm (the particles were supported on poly(vinyl alcohol) and it is realized that this support does not favour small particles [73]). For this radius, the aggregation

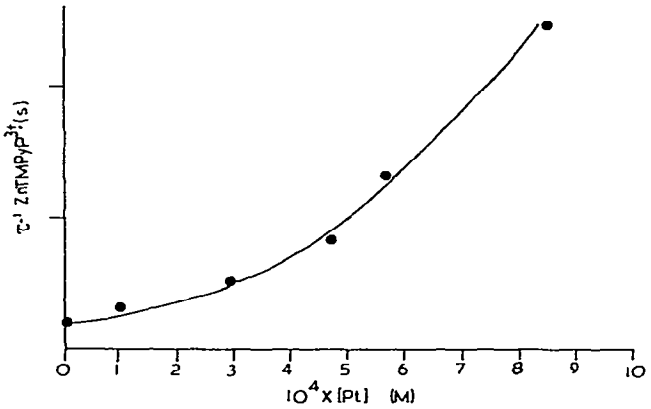


Fig. 14. The effect of Pt concentration upon the half-life of $ZnTMPyP^{3+}$ for the $ZnTMPyP^{4+}$/EDTA system (ref. 72).

number (n) was calculated to be 7×10^6 so that the molar concentration of Pt particles can be expressed as

$$(Pt) = C_0/n \tag{46}$$

where C_0 is the total concentration of Pt in the solution (measured in moles per liter). The rate of diffusion for an organic radical, such as $ZnTMPyP^{3+}$, and a Pt particle of radius 30 nm is about 2.5×10^{11} (molar particles)$^{-1}$ s^{-1} so that in order for the Pt particle to compete favourably with the dismutation reaction by intercepting $ZnTMPyP^{3+}$ the total concentration of Pt present in the above solution must exceed 5×10^{-4} M. In fact, as shown in Figs. 13 and 14, efficient production of H_2 requires somewhat higher concentrations of Pt so that $ZnTMPyP^{3+}$ must, on average, encounter several Pt particles before it finds an active site.

The high concentration of Pt required for the $ZnTMPyP^{4+}$/EDTA system is a serious drawback to applying the system to a practical solar energy device. The major problem with such two-component reductive cycles is that the lifetime of the reduced sensitizer is very short and, consequently, the Pt particle has only a short time period in which to locate and react with the radical. In order to extend the utility of these systems, it is necessary that the lifetime of the reduced sensitizer is increased dramatically (say > 10 s) or else the rate of diffusion between the radical and the Pt catalyst must be increased. The former situation may be achieved by the use of micelles or similar ordered structures or by restricting the disproportionation reaction via the use of steric or electrostatic factors. To achieve the latter situation, it is necessary to produce Pt particles with small radii, so that for a given concentration of Pt there will be more particles present in the solution, and

such preparations are now available [74,75].

The above discussion illustrates that the positively charged $ZnTMPyP^{4+}$ functions as a very efficient sensitizer for the photoreduction of water to H_2. In fact, it is the authors understanding that $ZnTMPyP^{4+}$ is the most efficient photosensitizer reported to date, as regards the optimum ϕ_{H_2} value. However, other zinc porphyrins have been used to photoreduce MV^{2+} in aqueous solution and, in several cases, H_2 has been observed as an overall reaction product.

Kalyanasundaram and Gratzel [22] found that MV^{2+} quenched the triplet excited state of $ZnTSPP^{4-}$ in aqueous solution ($k \sim 1 \times 10^{10}$ M^{-1} s^{-1}) although their work was somewhat hampered by ground-state complexation between the reactants. Both McLendon and Miller [69] and Okura et al. [76] have reported subsequently that $ZnTSPP^{4-}$ photosensitized H_2 production from three-component reductive cycles and for the $ZnTSPP^{4-}/MV^{2+}/EDTA/Pt$ system a ϕ_{H_2} of about 2×10^{-3} was given [69]. Okura and Thuan [77] also reported that ZnTPP dispersed in micelles could be used for H_2 production, using mercaptoethanol as sacrificial electron donor and hydrogenase as catalyst, whilst under identical conditions zinc protoporphyrin was ineffective.

If the extremely high yield of redox products found for the $ZnTMPyP^{4+}/MV^{2+}$ system is due to strong electrostatic repulsion between the products within the solvent cage, then it would be expected that a very low yield of redox products from the $ZnTSPP^{4-}/MV^{2+}$ system would be found. In fact, this hypothesis has been substantiated by flash photolysis studies [70] and although MV^{2+} quenched the triplet excited state of $ZnTSPP^{4-}$ at the diffusion controlled limit, the quantum yield for formation of redox products was less than 0.01. In contrast, reductive quenching of the triplet excited state of $ZnTSPP^{4-}$ with EDTA (and probably mercaptoethanol) leads to efficient formation of redox products despite the low quenching rate constants involved [70]. Since H_2 is also formed by reductive quenching of triplet $ZnTSPP^{4-}$, in the absence of MV^{2+}, the relative concentrations of electron donor and MV^{2+} will determine the relative importance of oxidative and reductive quenching mechanisms and also the quantum yield for formation of H_2. These findings suggest that H_2 formed from the $ZnTSPP^{4-}$ systems referred to above probably arises from a reductive cycle, especially where low concentrations of MV^{2+} were used,

(v) Photochemical systems with other metalloporphyrins

Because of its special involvement in the natural photosynthetic process, chlorophyll has been the subject of intensive investigation over a prolonged period of time. It is now well established that both singlet and triplet excited

states of chlorophyll undergo electron transfer quenching in fluid solution and this subject has been reviewed, in some detail, by Seely [26]. However, one recent report from the authors' laboratory should be highlighted here since it describes the photoreduction of MV^{2+} using triplet chlorophyll as the sensitizer [78].

Thus; it was found that steady-state irradiation of chlorophyll, dispersed in neutral micelles, in the presence of MV^{2+} and cysteine resulted in formation of reduced viologen [78]. From continuous irradiation and flash photolysis studies, the overall reaction mechanism was found to follow an oxidative cycle, as shown below.

$$Chl^* + MV^{2+} \rightarrow Chl^{+\cdot} + MV^{+} \quad (47)$$

$$Chl^{+\cdot} + cysSH \rightarrow Chl + cysH^{+\cdot} \quad (48)$$

$$cysSH^{+\cdot} \rightleftharpoons cysS^{\cdot} + H^{+} \quad (49)$$

$$2\ cysS^{\cdot} \rightarrow cysS - Scys \quad (50)$$

The relevant rate constants for this scheme, and the analogous one in which the micellar medium was replaced with ethanol, are collected in Table 9. The quantum yield for formation of MV^{+} was found to be 0.28 ± 0.05 [78], a value very close to the quantum yield for formation of triplet chlorophyll in the micellar medium. Therefore, practically all of the chlorophyll triplets could be converted into redox products by this system [78].

The authors have recently extended this system by replacing the sacrificial electron donor (cysteine) with hydroquinone [79]. In this case the oxidized electron donor, i.e. quinone, could be used in a second photocycle with water

TABLE 9

Summary of rate constants for electron transfer in neutral micelles and in ethanol (from ref. 78)

Reaction	Ethanol	Igepal CO-630 micelles (5 mM, pH 7)
$^*Chl_T \rightarrow Chl$ normal decay	$1.3\times10^{3}\ s^{-1}$	$1.0\times10^{3}\ s^{-1}$
$^*Chl_T + MV^{2+} \rightarrow Chl^{+\cdot} + MV^{+}$		
From triplet decay	$(2\pm1)\times10^{9}\ M^{-1}\ s^{-1}$	$1.4\times10^{6}\ M^{-1}\ s^{-1}$
From MV^{+} growth	$(7\pm3)\times10^{8}\ M^{-1}\ s^{-1}$	$0.8\times10^{6}\ M^{-1}\ s^{-1}$
$Chl^{+\cdot} + MV^{+} \rightarrow Chl + MV^{2+}$		
At Chl^{+} maximum (668 nm)	$(8\pm2)\times10^{8}\ M^{-1}\ s^{-1}$	$5.5\times10^{8}\ M^{-1}\ s^{-1}$
At MV^{+} maximum (395 nm)	$(5\pm2)\times10^{8}\ M^{-1}\ s^{-1}$	$2.2\times10^{8}\ M^{-1}\ s^{-1}$
$Chl^{+\cdot} + cysSH \rightarrow Chl + cysSH^{+\cdot}$	$(4\pm0.5)\times10^{8}\ M^{-1}\ s^{-1}$	$2.8\times10^{6}\ M^{-1}\ s^{-1}$
$^*Chl_T + cysSH \rightarrow Chl^{-} + cysSH^{+\cdot}$	$2\times10^{4}\ M^{-1}\ s^{-1}$	$<10^{3}\ M^{-1}\ s^{-1}$

as the eventual electron donor. This is not possible with sacrificial donors which undergo irreversible processes following the loss of an electron.

Several other metalloporphyrins have been used for the photosensitized reduction of MV^{2+}. Thus, Young et al. [80] found that the excited triplet state of PdOEP was quenched by MV^{2+} in isobutyronitrile solution and that the quenching act resulted in formation of net electron transfer products.

$$PdOEP^* + MV^{2+} \rightarrow PdOEP^{+} + MV^{+} \quad (51)$$

Although the triplet quenching rate constant was very high ($k = 1.5 \times 10^9$ M^{-1} s^{-1}) the rate constant for reverse electron transfer was diffusion controlled so that the steady-state yield of MV^{+} was low.

$$PdOEP^{+} + MV^{+} \rightarrow PdOEP + MV^{2+} \quad (52)$$

No attempt was made to minimize the reverse electron transfer step by addition of a sacrificial electron donor nor to use water-soluble Pd porphyrins.

A brief report has alluded to the use of a Sn^{IV} porphyrin for photosensitized H_2 production. Thus, irradiation of Sn^{IV} porphyrins in the presence of amines, water, and PtO_2 was claimed to result in H_2 formation [81]. In the absence of PtO_2, the reaction involved reductive addition of the amine to the porphyrin skeleton yielding chlorin products and the overall reaction mechanism was believed to involve electron transfer from the amine to the Sn^{IV} porphyrin, followed by proton transfer and coupling of the radicals [81]. In the presence of PtO_2, a lower yield of chlorin was obtained, suggesting that the catalyst intercepted one of the redox intermediates, and some H_2 was detected as a reaction product. No quantum yields or mechanistic details were given but it seems probable that the reaction is similar to that described for the $ZnTMPyP^{4+}$/EDTA system.

Okura and Thuan [82] have reported that several porphyrins and metalloporphyrins can be used for H_2 generation. In particular, hematoporphyrin was found to sensitize the photoreduction of MV^{2+}, the reaction involved a reductive cycle in which the excited state of hematoporphyrin was reduced by a sacrificial electron donor (mercaptoethanol, NADH, triethanolamine, or glutathione) and the reduced form of the porphyrin reduced MV^{2+} in a secondary step [82]. Similar studies have shown that Ru^{II} porphyrins function as photosensitizers for reduction of MV^{2+} [83] although in this case the reaction involved an oxidative cycle. In all cases, the MV^{+} product could be used to reduce water to H_2 upon addition of a suitable catalyst. Few quantitative details were provided for these studies and ϕ_{H_2} values were not given.

Carnieri and Harriman [84] have reported recently that water-soluble

Mn^{III} porphyrins can be used to photoreduce MV^{2+} in aqueous solution. The yield of MV^{+} so produced was extremely low but the reaction was somewhat unusual in that it involved coupling together two separate photochemical reactions. Thus, flash photolysis studies showed that $Mn^{III}TPyP$ did not directly photoreduce MV^{2+} but, instead, inefficient photoreduction of the porphyrin occurred.

$$Mn^{III}TPyP^{*} + OH^{-} \rightarrow Mn^{II}TPyP + OH^{\cdot} \quad (53)$$

In contrast, the Mn^{II} porphyrin photoreduced MV^{2+} but the products were unstable with respect to reverse electron transfer.

$$Mn^{II}TPyP^{*} + MV^{2+} \rightarrow Mn^{III}TPyP + MV^{+} \quad (54)$$

$$Mn^{III}TPyP + MV^{+} \rightarrow Mn^{II}TPyP + MV^{2+} \quad (55)$$

Consequently, the steady-state yield of MV^{+} remained low [84] but, as shown in Fig. 15, prolonged irradiation of $Mn^{III}TPyP$ in aqueous solution containing MV^{2+} resulted in a build-up in the concentration of MV^{+}. However, the final concentration of MV^{+} was extremely low and the pH required to bring about reaction (53) with even modest efficiency was far too high for the reduced viologen to be used for H_2 generation.

Finally, recent work from the authors laboratory suggests that water-soluble $CdTMPyP^{4+}$ behaves in a similar fashion to $ZnTMPyP^{4+}$ in that steady-state irradiation of the porphyrin in aqueous solution containing MV^{2+} and a sacrificial electron donor resulted in formation of MV^{+} [85]. So far, these experiments are at a preliminary stage and, as noted before, there are problems with the stability of Cd porphyrins at $pH < 7$ but the results look encouraging [85]. Thus, the triplet excited state of $CdTMPyP^{4+}$ in water at pH 7.0 ($\tau_T = 0.17$ ms) was quenched by MV^{2+} ($k \sim (2.3 \pm 1.0) \times 10^{6}$

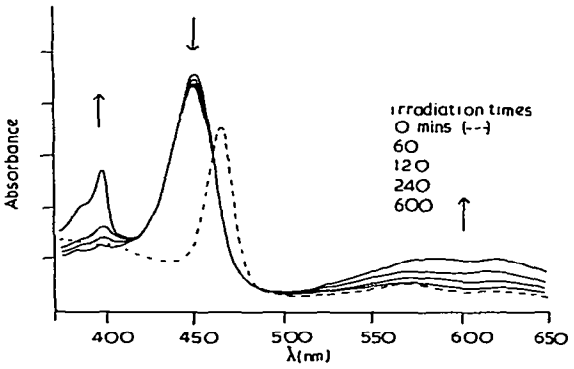


Fig. 15. Absorption spectral profile showing the build-up of MV^{+} for the $MnTPyP/MV^{2+}$ system (ref. 84).

M^{-1} s^{-1}) and in the presence of morpholinoethane sulphonic acid as sacrificial donor, the reaction resulted in a build-up in the concentration of MV^+.

There have been many other reports of photoinduced electron transfer reactions involving porphyrins and metalloporphyrins. These systems have been reviewed recently by other authors and need not be elaborated upon here [26,86].

D. CONCLUSIONS

The preceding discussion has pointed out that metalloporphyrins, especially $ZnTMPyP^{4+}$, can function as very efficient photosensitizers for the reduction of water to H_2 using either oxidative or reductive cycles. So far, most work has involved zinc(II) porphyrins but now that the principles of these photoreactions have been established it seems probable that many other metalloporphyrins will be used in the near future. The fraction of the solar spectrum that can be collected by a zinc porphyrin is in the order of 30% whilst the optimum quantum efficiency for formation of H_2 is about 60% [70]. Thus, in this respect, the overall performance of zinc porphyrins is most encouraging. In contrast, phthalocyanines do not appear to be good photosensitizers for reduction of water. This is an unfortunate finding because the absorption characteristics of phthalocyanines, together with their cheap syntheses, makes these compounds particularly attractive for large scale use. Whenever a phthalocyanine has been used as sensitizer for an oxidative or reductive cycle, the observed quantum yields for formation of H_2 have been very low ($< 10^{-4}$) so that these compounds compare most unfavourably with the corresponding metalloporphyrins.

Although considerable success has been realized over the past few years, the above systems suffer from many problems that must be overcome before they can be proposed as practical devices for the collection and storage of solar energy. In particular, attention must be given to the following points: (1) ϕ_{H_2} must be increased. (2) The fraction of sunlight collected by the sensitizer must be increased. (3) The susceptibility towards atmospheric oxygen must be decreased. (4) The longevity of the system must be improved. (5) The sacrificial electron donor must be replaced with a non-sacrificial redox couple [79]. (6) The H_2 producing system must be coupled to an analogous one capable of the photo-oxidation of water to O_2.

To a large extent, these problems are closely interrelated and the final two points are crucial to the development of practical devices [79]. However, these latter two points are outside the field of this review, here the authors have attempted only to describe sacrificial H_2 producing systems, but some comments can be made concerning the first four points.

To achieve a high efficiency for a photoredox reaction in homogeneous solution it seems most probable that a triplet-state mechanism must be used [26]. Consequently, as mentioned earlier, it is necessary that the triplet excited state of the sensitizer is formed with unit efficiency and, for a metalloporphyrin, this can be achieved by careful choice of the central metal ion. For zinc porphyrins ϕ_T is about 0.9 but this can be improved by using heavier metal ions and, since the porphyrin must retain a reasonably long excited triplet state lifetime, the most promising compounds appear to be Pd^{II} and Cd^{II} porphyrins, although the latter compounds are susceptible towards acid catalysed demetallation. Thus, a promising system for the photoreduction of water to H_2 by a sacrificial process involves electron transfer from triplet $PdTMPyP^{4+}$ to MV^{2+}. So far, this reaction has not been reported and the authors wait with considerable interest to find if the ϕ_S term for $PdTMPyP^{4+}/MV^{2+}$ is comparable to that found for $ZnTMPyP^{4+}/MV^{2+}$ [70]. If so, then the use of Pd^{II} porphyrins could lead to a minor increase in ϕ_{H_2} relative to Zn^{II} porphyrins.

One unfortunate consequence of replacing Zn^{II} with Pd^{II} is that the absorption spectrum undergoes a blue shift (see Fig. 10) so that a smaller fraction of the solar spectrum is collected. This fraction can be increased by using a different porphyrin skeleton but the nature of the skeleton affects the photophysical properties of the molecule. This effect is shown in Table 10 where the fluorescence quantum yields and excited singlet-state lifetimes for some zinc(II) porphyrins are listed together with the maximum fraction of the solar spectrum that can be collected by the compound (ζ). As these data show compounds possessing a high ζ value also have a high ϕ_F value (and consequently a decrease in the yield of the excited triplet state). To what degree replacing Zn^{II} with the heavier Pd^{II} ion overcomes this problem is not

TABLE 10

Fluorescence quantum yields and excited singlet state lifetimes for some zinc porphyrins in chloronaphthalene solution (A. Harriman, unpublished work)

Compound [a]	ϕ_F	τ_S (ns)	ζ (%)
ZnOEP	0.04	2.3±0.3	35.0
ZnTPP	0.04	2.7±0.2	39.0
ZnTBP	0.25	4.2±0.4	46.6
ZnPc	0.32	3.8±0.5	51.8
ZnNc	0.50	5.2±1.5	64.3

[a] TBP, tetrabenzoporphine; Nc, naphthalocyanine.

known, as yet, since the corresponding data for Pd porphyrins have not been reported.

Other means of increasing ζ are worthy of study. For example, the absorption spectrum of Cr^{III} porphyrins shows a long tail stretching out as far as about 800 nm. This tail has been assigned to direct absorption to the excited triplet state [87] and the extinction coefficient is sufficiently high for the tail to contribute significantly to the overall absorbance even at modest concentrations of porphyrin. If the photophysical properties of Cr^{III} porphyrins are not complicated by the presence of low-lying *dd* or charge transfer states, it may be possible to use water-soluble Cr^{III} porphyrins as photosensitizers for the reduction of water. Such studies are now in progress [88].

A further means of increasing ζ would be to use the excited singlet state of the metallöporphyrin, as mentioned earlier. However, before the excited-singlet state can be used it is necessary to overcome the problems associated with the poor charge separation inherent in singlet-state reactions and also to circumnavigate the problem of the short excited singlet-state lifetime. The first problem may be solved, at least to some extent, by invoking electrostatic factors [46] but the short lifetimes of the excited singlet states mean that very high concentrations of quencher must be used before the quenching act can compete with radiative and non-radiative deactivation of the excited singlet state. Recent work from the authors' laboratory [89] suggests that this problem may be overcome by attaching the electron donor or acceptor directly to the metalloporphyrin via covalent bonds. Thus, the fluorescence quantum yields and excited singlet-state lifetimes were measured for a series of substituted TPP derivatives (Fig. 16) in outgassed benzene solution (Table 11). For some of the substituents (II, III, VIII and IX) there was virtually no fluorescence quenching but for the porphyrins with good electron accepting groups (IV, V and XI) there was a substantial reduction in both ϕ_F and τ_S (Table 11). Electron donating substituents (VI and X) also resulted in reductions in ϕ_F and τ_S.

The fluorescence of TPP (I) was quenched by the presence of electron donor and acceptor molecules in the solution [26,89]. For these systems, the bimolecular quenching rate constants (k_Q) were determined from the Stern–Volmer relationship and are collected in Table 12. In some cases the rate constants approach the diffusion controlled limit and in all cases the quenching mechanism was believed to involve charge transfer [89]. Comparison of these k_Q values with the quenching effects of the substituted porphyrins shows the high quenching efficiency obtained by fixing the quencher at an intramolecular site. Thus, for (XI) the effective concentration of 1,4-benzoquinone is about 0.11 M based on the reduction in ϕ_F. This observation may account for the high efficiency of the primary photoredox reaction of

photosynthetic organisms, where the reactants are held in close proximity by proteins. It may be possible to design a suitable porphyrin/donor or porphyrin/acceptor unit whereby the excited singlet state of the porphyrin can be used to reduce water to H_2.

Oxygen is a notorious inhibitor of photochemical processes and it presents many serious problems in the work described in this review. All laboratory experiments have been carried out with deaerated solutions and, in our experience, the presence of oxygen results in a dramatic reduction in the yield of H_2 obtained from any particular system. In principle, the harmful effects of oxygen can be regarded as a kinetic problem and if the rates for the individual processes that lead up to H_2 evolution can be increased to very high levels then the inhibition by oxygen will be minimized. Such a situation requires well-ordered systems wherein the reactants have been designed carefully. Possibly, linking together the reactants so that long range mass diffusion is avoided may be a useful tool in this area [50,90].

For any of the above systems to be used on a practical scale, it is necessary that all of the components in the reaction mixture are stable. So far, very high turnovers have not been reported and this is especially true for

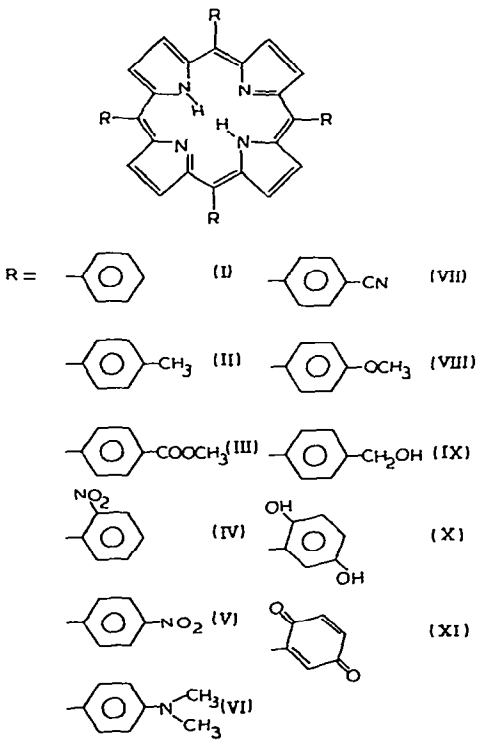


Fig. 16. Structures of substituted TPPs.

TABLE 11

Fluorescence properties of some substituted tetraphenylporphyrins in outgassed benzene (from ref. 87)

Compound	ϕ_F	τ_S (ns)
I	0.13	15.7
II	0.15	14.0
III	0.13	13.9
IV	0.02	6.4
V	0.045	8.3
VI	0.025	8.4
VII	0.064	12.2
VIII	0.15	12.3
IX	0.11	13.4
X	0.030	7.5
XI	0.007	2.5

MV^{2+} which is known to undergo hydrogenation upon prolonged storage in H_2-saturated water at ambient temperatures [71]. Porphyrins and phthalocyanines, whilst being fairly resistant to oxidative attack, undergo irreversible photoreduction and this must be avoided. However, the observation that green plants can achieve turnovers with respect to chlorophyll in the order of 10^6 encourages the belief that these problems may be overcome in the near future, although the solution may involve the use of protective agents. Certainly, it will be necessary to design carefully the system for maximum efficiency and, to the authors, it appears that this is best achieved by linking

TABLE 12

Bimolecular rate constants for quenching the fluorescence of tetraphenylporphine in ethanol solution (from ref. 87)

Quencher	$k_Q(M^{-1}\,s^{-1})$
1,4-Benzoquinone	9.6×10^9
1,3-Dinitrobenzene	3.3×10^9
1,4-Benzohydroquinone	2.7×10^8
N,*N*-Dimethylaniline	1.6×10^8
1,4-Dimethoxybenzene	6×10^7
Cyanobenzene	7×10^6
Benzyl alcohol	$<10^6$
Methyl benzoate	$<10^6$

together the various components, either by covalent bonds or by adsorption.

As regards more speculative further work, it would be of great interest to learn if metalloporphyrins can sensitize H_2 production using dispersions of semiconductor powders. Thus, very recently it was reported that dispersions of TiO_2 particles possessing Pt and RuO_2 surface sites gave efficient cleavage of water into H_2 and O_2 upon band gap illumination [91]. When these particles were coated with surfactant $(bipy)_3Ru^{2+}$ dyes, the dye acted as a sensitizer and cleavage of water was observed at sub-band gap illumination [91]. Perhaps metalloporphyrins can function in a similar manner. In addition, it might be possible to construct micro-photoelectrochemical cells for photoreduction of water to H_2. Such cells would consist of very fine Pt particles coated with a layer of surfactant metalloporphyrin.

Finally, the authors introduced this review by referring to the natural photosynthetic process and it is clear that there is still a great deal to be learned from natural processes. In this context, further work into attempting to mimic the primary photoredox reactions of green plant and bacterial photosynthetic organisms should be undertaken. At the moment, it appears that the primary reaction involves electron transfer from a specialized form of chlorophyll (possibly a dimer) to a pheophytin or a monomeric chlorophyll molecule. This reaction, which is an excited singlet-state process, is remarkable in that almost all of the excitation energy is stored in the redox products and it seems to be a very promising initial step for model systems aimed at the collection and storage of solar energy.

ACKNOWLEDGEMENTS

We thank the Science Research Council, the European Economic Community and General Electric (Schenectady) for financial support.

REFERENCES

1 A. Harriman and J. Barber, in J. Barber (Ed.), Topics in Photosynthesis, Vol. 3. Elsevier, Amsterdam, 1979, Chap. 8.
2 L.J. Heidt and A.F. McMillan, J. Am. Chem. Soc., 76 (1954) 2135.
3 F.S. Dainton, E. Collinson and M.A. Malati, Trans. Faraday Soc., 55 (1959) 2096.
4 L.J. Heidt, M.G. Mullin and W.B. Martin, J. Phys. Chem., 66 (1962) 336.
5 H.B. Gray, K.R. Kent, N.S. Lewis, V.M. Miskowski, D.R. Erwin and G.S. Hammond, J. Am. Chem. Soc., 99 (1977) 5525.
6 D.D. Davis, K.L. Stevenson and G.K. King, Inorg. Chem., 16 (1977) 670.
7 N. Sutin, C. Creutz, M. Chou, W. Bottcher and C.T. Lin, J. Am. Chem. Soc., 98 (1976) 6536.
8 M. Chou, C. Creutz and N. Sutin, J. Am. Chem. Soc., 99 (1977) 5615.
9 A.A. Krasnovsky, in J. Barber (Ed.), Topics in Photosynthesis, Vol. 3. Elsevier, Amsterdam, 1979, Chap. 9.

10 D.E. Green and L.H. Stickland, Biochem. J., 28 (1934) 898.
11 J.R. Bolton, S. Markiewicz, M.S. Chan, R.H. Sparks and C.A. Evans, International Conference on Photochemical Conversion and Storage of Energy, Univ. of Western Ontario, Canada, 1976.
12 A.E. Shilov, B.V. Koryakin and T.S. Dzhabiev, Dokl. Akad. Nauk. SSSR, 233 (1977) 620.
13 J.A. Farrington, M. Ebert and E.J. Land, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 665.
14 K. Kalyanasundaram and M. Gratzel, Angew. Chem., Int. Edn. Engl., 18 (1979) 701.
15 J.M. Lehn and J.P. Sauvage, Nouv. J. Chim., 1 (1977) 449.
16 K. Kalyanasundaram, J. Kiwi and M. Gratzel, Helv. Chim. Acta, 61 (1978) 2720.
17 E. Amouyal, P. Keller and A. Moradpour, Nouv. J. Chim., 2 (1978) 547; Chem. Commun., (1980) 1019.
18 A.I. Krasna, Photochem. Photobiol., 29 (1979) 267; 31 (1980) 75.
19 J. Kiwi and M. Gratzel, J. Am. Chem. Soc., 101 (1979) 7214; Nature (London), 281 (1979) 657.
20 M. Kirch, J.M. Lehn and J.P. Sauvage, Helv. Chim. Acta, 62 (1979) 1345.
21 K. Kalyanasundaram and M. Gratzel, Chem. Commun., (1979) 1137.
22 K. Kalyanasundaram and M. Gratzel, Helv. Chim. Acta, 63 (1980) 478.
23 M.W.W. Adams, K.K. Rao and D.O. Hall, Photobiochem. Photobiophys., 1 (1980) 33.
24 M.P. Pileni, A.M. Braun and M. Gratzel, Photochem. Photobiol., 31 (1980) 423.
25 M.M. Rosen and A.I. Krasna, Photochem. Photobiol., 31 (1980) 259.
26 G.R. Seely, Photochem. Photobiol., 27 (1978) 639.
27 D. Holten, M. Gouterman, W.W. Parson, M.W. Windsor and M.G. Rockley, Photochem. Photobiol., 23 (1976) 415.
28 M. Gouterman and D. Holten, Photochem. Photobiol., 25 (1977) 85.
29 D. Holten, M.W. Windsor, W.W. Parson and M. Gouterman, Photochem. Photobiol., 28 (1978) 951.
30 A.B.P. Lever, Adv. Inorg. Chem. Radiochem., 7 (1965) 27.
31 J.E. Scott, Histochemie, 32 (1972) 191.
32 H. Sigal, P. Waldmeier and B. Prijs, Inorg. Nucl. Chem. Lett., 90 (1968) 1455.
33 K. Bernauer and S. Fallab, Helv. Chim. Acta, 162 (1961) 287.
34 P.G. Bowers and G. Porter, Proc. R. Soc. London, 296 (1967) 435
35 J.R. Darwent, Chem. Commun., (1980) 805.
36 M.C. Spaeth and W.R. Sooy, J. Chem. Phys., 48 (1968) 2315.
37 J. McVie, R.S. Sinclair and T.G. Truscott, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 1870.
38 J.M. Kelly and G. Porter, Proc. R. Soc. London, 319 (1970) 319.
39 A.K. Chibisov, Photochem. Photobiol., 10 (1969) 331.
40 V. Balzani, F. Bolletta, M.T. Gandolf and M. Maestri, Top. Curr. Chem., 75 (1978) 1.
41 C. Creutz and N. Sutin, Adv. Chem. Ser., 168 (1978) 1.
42 P. George, D.J.E. Ingram and J.E. Bennett, J. Am. Chem. Soc., 79 (1957) 1870; L.D. Rollmann and R.I. Iwamoto, J. Am. Chem. Soc., 90 (1968) 1455; A. Wolberg and J. Manassen, J. Am. Chem. Soc., 92 (1970) 2982; D.W. Clark and J.R. Yandle, Inorg. Chem., 11 (1972) 1738; D.W. Clack, N.S. Hush and I.S. Woolsey, Inorg. Chim. Acta, 19 (1976) 129.
43 R.M. Elofson and R.L. Edsberg, Can. J. Chem., 35 (1957) 646.
44 A. Harriman, G. Porter and M.C. Richoux, J. Chem. Soc., Faraday Trans. 2, 76 (1980) 1618.
45 J.R. Darwent and I. McCubbin, unpublished work.
46 A. Harriman, G. Porter and M.C. Richoux, J. Chem. Soc., Faraday Trans. 2, 77 (1981) 1175.

47 A. Harriman and M.C. Richoux, J. Photochem., 14 (1980) 253.
48 J.R. Darwent, Ph.D. Thesis, University of London, 1982.
49 A.B.P. Lever, S. Licoccia, B.S. Ramaswamy, A. Kandil and D.V. Stynes, Inorg. Chim. Acta, in press.
50 J.R. Harbour and M.L. Hair, Photochem. Photobiol., 28 (1978) 721; J.R. Harbour, J. Trump and M.L. Hair, J. Am. Chem. Soc., 102 (1980) 1874.
51 J.R. Darwent, J. Chem. Soc., Faraday Trans. 2, 77 (1981) 1703.
52 J.W. Buchler, in D. Dolphin (Ed.), The Porphyrins, Vol. 1. Academic Press, New York, 1977, Chap. 10.
53 P. Hambright in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins. Elsevier, New York, 1976, Chap. 6.
54 H. Brockmann, in D. Dolphin (Ed.), The Porphyrins, Vol. 2. Academic Press, New York, 1978, Chap. 9.
55 J.H. Fuhrhop, in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins. Elsevier, New York, 1976, Chaps. 14 and 15.
56 F.R. Longo, Porphyrin Chemistry Advances, Ann Arbor Science, Ann Arbor MI, 1979.
57 J.W. Buchler, in K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, New York, 1976, Chap. 5.
58 A. Harriman and G. Porter, J. Chem. Soc., Faraday Trans. 2, 75 (1979) 1532.
59 M. Gouterman, in D. Dolphin (Ed.). The Porphyrins, Vol. 3. Academic Press, New York, 1978, Chap. 1.
60 M. Gouterman, J. Chem. Phys., 30 (1959) 1139.
61 A. Harriman, J. Chem. Soc., Faraday Trans. 1, 76 (1980) 1978.
62 A. Harriman, J. Chem. Soc., Faraday Trans. 2, 77 (1981) 1281.
63 R.H. Felton, in D. Dolphin (Ed.), The Porphyrins, Vol. 5. Academic Press, New York, 1978 Chap. 3.
64 D.G. Davis, in D. Dolphin (Ed.), The Porphyrins, Vol. 5. Academic Press, New York, 1978, Chap. 4.
65 M. Neumann-Spallart and K. Kalyanasundaram. Z. Naturforsch., Teil B, 36 (1981) 596.
66 A. Harriman and G. Porter, J. Chem. Soc., Faraday Trans. 2, 75 (1979) 1543.
67 A. Wolberg, Isr. J. Chem., 12 (1974) 1031.
68 H.J. Callot, A. Giraudeau and M. Gross, J. Chem. Soc., Perkin Trans. 2, (1975) 1321.
69 G. McLendon and D.S. Miller, Chem. Commun., (1980) 533.
70 A. Harriman, G. Porter and M.C. Richoux, J. Chem. Soc. Faraday Trans. 2, 77 (1981) 833.
71 P. Keller, A. Moradpour, E. Amouyal and H. Kagan, J. Mol. Catal., 7 (1980) 539.
72 A. Harriman and M.C. Richoux, J. Photochem., 15 (1981) 335.
73 A. Henglein, J. Phys. Chem., 83 (1979) 2209.
74 J. Turkevich and G. Kim, Science, 169 (1970) 873.
75 P.A. Brugger, P. Cuendet and M. Gratzel, J. Am. Chem. Soc., 103 (1981) 2923.
76 I. Okura and N.K. Thuan, J. Mol. Catal., 5 (1979) 311; I. Okura, S. Nakamura, N.K. Thuan and K. Nakamura, Ibid., 6 (1979) 261.
77 I. Okura and N.K. Thuan, J. Mol. Catal., 6 (1979) 227; J. Chem. Res. (s), (1979) 344.
78 K.Kalyanasundaram and G. Porter, Proc. R. Soc. London, Ser. A, 364 (1978) 29.
79 J.R. Darwent, K. Kalyanasundaram and G. Porter, Proc. R. Soc. London, Ser. A, 373 (1980) 179.
80 R.C. Young, J.K. Nagle, T.J. Meyer and D.G. Whitten, J. Am. Chem. Soc., 100 (1978) 4773.
81 D.G. Whitten, Acc. Chem. Res., 13 (1980) 83.
82 I. Okura and N.K. Thuan, J. Chem. Soc., Faraday Trans. 1, 76 (1980) 2209.

83 I. Okura and N.K. Thuan, Chem. Commun., (1980) 84.
84 N. Carnieri and A. Harriman, J. Photochem., 15 (1981) 341.
85 P. Douglas, unpublished work.
86 F.R. Hopf and D.G. Whitten, in D. Dolphin (Ed.), The Porphyrins, Vol. 2. Academic Press, New York, 1977, Chap. 6.
87 M. Gouterman, L.K. Hansen, G.E. Khalil, W.R. Leenstra and J.W. Buchler, J. Chem. Phys., 62 (1975) 2343.
88 N. Searle and A. Harriman, unpublished work.
89 R.J. Hosie and A. Harriman, J. Chem. Soc., Faraday Trans. 2, 77 (1981) 1695.
90 J.R. Darwent and G. Porter, Chem. Commun., (1981) 145.
91 E. Borgarello, J. Kiwi, E. Pellizetti, M. Visca and M. Gratzel, Nature (London), 289 (1981) 158.