

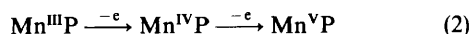
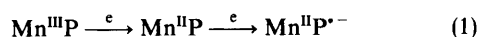
## Photochemistry of Manganese Porphyrins. Part 9.† Redox Reactions photosensitised by Diamagnetic Metalloporphyrins

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Photoredox processes employing diamagnetic metalloporphyrins as photosensitisers have been used to generate both oxidising and reducing radicals in aqueous solution. The reducing radicals reduce manganese(III) porphyrins to the corresponding manganese(II) porphyrins with high efficiency. Incorporating the manganese(III) porphyrin in a negatively charged micelle, vesicle, or microemulsion leads to a decrease in the efficiency of the reaction but reduction still occurs. Oxidation of either manganese-(II) or -(III) porphyrins by the oxidising radicals was not observed. The lifetime of the oxidising radical was kept short by primary reverse electron transfer and by reduction with impurities. The use of microheterogeneous media gave no real benefits for the oxidative cycle.

The primary functions of manganese in natural photosynthetic oxygen evolution remain obscure despite prolonged investigation. Almost certainly, the manganese complex involved acts as an electron-transferring agent but it is not known if it is the active catalyst for water oxidation or merely an intermediate member of the electron-transport chain that connects water to the specialised chlorophyll photosensitiser.<sup>1</sup> To help clarify this position, many model systems have been proposed<sup>2</sup> and we have identified manganese porphyrins (MnP) as promising model compounds for the natural manganese complex.<sup>3</sup> The manganese porphyrins undergo a series of well defined redox steps in which the stable Mn<sup>III</sup>P can be successively reduced [equation (1)]<sup>4</sup> or oxidised [equation (2)]. Thus, it is possible



to store many redox equivalents on one molecule and this should enable the manganese porphyrins to function as catalysts for multielectronic processes.<sup>5</sup> However, they are paramagnetic and possess very short excited-state lifetimes<sup>6</sup> which severely limits their potential as photosensitisers. To overcome this problem it is necessary to use a different compound as the photosensitiser and to use the manganese porphyrin as a ground-state electron relay. To this end, we have attempted to use diamagnetic metalloporphyrins to photo-reduce and photooxidise manganese porphyrins in aqueous solution and in microheterogeneous media. Photoreductions proceed smoothly but photooxidations have not been observed.

### Experimental

**Materials.**—The metalloporphyrins used were prepared and purified by established methods. The various manganese(III) derivatives were as described previously<sup>3</sup> whilst formation of the corresponding manganese(II) compounds was achieved by addition of stoichiometric amounts of sodium dithionite to N<sub>2</sub>-saturated solutions of the former.<sup>7</sup> A sample of protein-bound Mn<sup>III</sup>P was obtained by adapting the method of Hoffman and co-workers.<sup>8</sup> The haem molecules were extracted from haemoglobin and manganese(III) hematoporphyrin [7,12-bis(1'-hydroxyethyl)-3,8,13,17-tetramethylporphyrin-2,18-dipropionic acid] was inserted into the resultant cavities.

Full characterisation of this material will be given later. Preparation of the water-soluble zinc(II) and tin(IV) porphyrins has been described previously,<sup>9</sup> whilst surfactant porphyrins, based upon zinc(II) and manganese(III) complexes with *meso*-20-(*p*-dodecoxyphenyl)-5,10,15-triphenylporphyrin, were obtained by alkylation of the mono(hydroxyphenyl)porphyrins.<sup>10</sup> The various abbreviations used for the metalloporphyrins are given later. The different electron donors and acceptors were of the highest available grade except *N*-dodecyl-*N'*-methyl-1,4'-bipyridinium chloride and *NN'*-bis(3-sulphonatopropyl)-1,4'-bipyridine which were prepared according to refs. 11 and 12 respectively.

All aqueous solutions were prepared from deionised, doubly distilled water and contained sodium borate ( $5 \times 10^{-3}$  mol dm<sup>-3</sup>) to give pH 9.4. The solutions were purged thoroughly with N<sub>2</sub> prior to performing an experiment. The concentrations of metalloporphyrins were determined from the reported molar absorption coefficients (see refs. in Abbreviations) and were usually *ca.* 10<sup>-5</sup> mol dm<sup>-3</sup>. The oil-water microemulsion was prepared by the method of Mackay *et al.*<sup>13</sup> A cosurfactant, *n*-pentanol (10.8% w/w), and an oil, hexadecane (3.2% w/w), were mixed with sodium dodecyl sulphate (7.6% w/w) and the well dispersed mixture was diluted with water. Manganese(III) *meso*-5,10,15,20-tetrakis(*p*-tolyl)porphyrinate was dispersed in the microemulsion by stirring a solid sample in N<sub>2</sub>-purged solution for several hours in the dark until the porphyrin was fully dissolved. Negatively charged phosphatidylglycerol vesicles were prepared accordingly to the method of Wohlgemuth *et al.*<sup>14</sup> Samples of manganese(II) porphyrins and (where necessary) the surfactant zinc(II) porphyrin were dissolved in chloroform-methanol (1:1) and phospholipid (*ca.*  $3 \times 10^{-4}$  mol dm<sup>-3</sup>) was added from a stock solution. The solvent was removed under a stream of N<sub>2</sub> at room temperature and then the solid was pumped at 10<sup>-4</sup> Torr (*ca.*  $1.33 \times 10^{-2}$  Pa) overnight at 10 °C. Water was added to the residue and the mixture sonicated for 30 min at 4 °C.

In the presence of borate ( $5 \times 10^{-3}$  mol dm<sup>-3</sup>) the micro-heterogeneous media were stable for a few days but the addition of high concentrations of electrolyte (>0.1 mol dm<sup>-3</sup>) caused turbidity. The particle diameters of the microemulsions and vesicles were found to be 18 and 60 nm respectively by light-scattering experiments. From a few gel-filtration studies it was found that the positively charged water soluble complexes of SnCl<sub>2</sub><sup>2+</sup> and Zn<sup>2+</sup> with *meso*-5,10,15,20-tetrakis(*N*-methyl-4'-pyridinio)porphyrin tetrachloride were closely associated with the microheterogeneous media. More detailed studies on this effect have been published recently where it was found also that

† Part 8 is ref. 30.

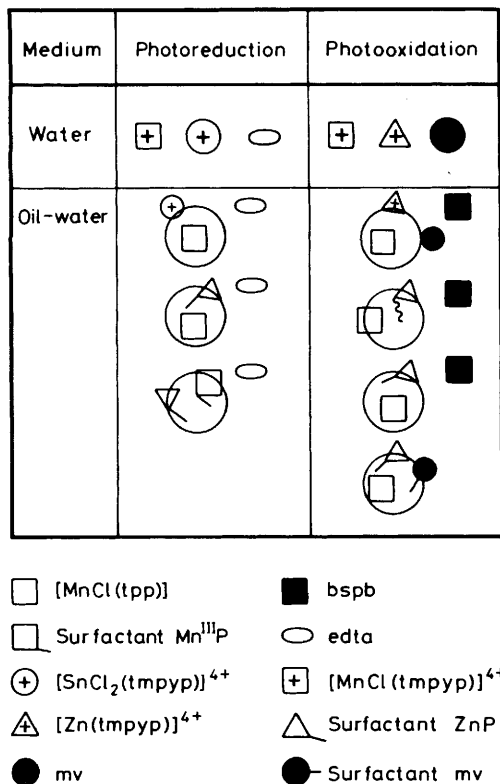


Figure 1. Arrangements of reactants in the various media used

1,1'-dimethyl-4,4'-bipyridinium dichloride was adsorbed onto vesicle surfaces.<sup>15</sup> The water-insoluble chloromanganese(III) *meso*-5,10,15,20-tetrakis(*p*-tolyl)porphyrinate and the surfactant metalloporphyrins were encapsulated into the microheterogeneous media so that several arrangements of the reactants are possible. The ones used in this study are shown diagrammatically in Figure 1.

**Methods.**—Absorption spectra were recorded with a Perkin-Elmer 554 spectrophotometer. Steady-state irradiations were performed with an Applied Photophysics UV30 950-W Xenon arc lamp, high radiance monochromator, and an i.r. filter. The solutions (7 cm<sup>3</sup>) were contained in spectrophotometric cells (1 cm<sup>2</sup>) and were purged thoroughly with N<sub>2</sub> before irradiation. The course of reaction was followed by absorption spectroscopy and light intensities were measured by ferrioxalate actinometry. Flash-photolysis studies were made with a conventional, frequency-doubled neodymium-glass laser set-up (pulse duration 15 ns) using N<sub>2</sub>-purged solutions. Fluorescence spectra were recorded with a Perkin-Elmer MPF4 spectrofluorimeter and were fully corrected.<sup>6</sup>

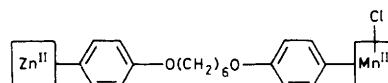
**Abbreviations.**—(a) *Media.* sds = Sodium dodecyl sulphate (Sigma), 5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; htac = hexadecyltrimethylammonium chloride (Sigma), 5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; Igepal, 3 × 10<sup>-2</sup> mol dm<sup>-3</sup>.

(b) *Redox agents.* mv = Methyl viologen (1,1'-dimethyl-4,4'-bipyridinium) dichloride (Sigma); dmbd = *N*-dodecyl-*N'*-methyl-1,4'-bipyridinium dichloride (see ref. 11); bspb = *NN'*-bis(3-sulphonatopropyl)-1,4'-bipyridine (see ref. 12); edta = ethylenediaminetetraacetate (disodium salt) (BDH), charge variable depending on pH.

(c) *Porphyrins.* ttp = *meso*-5,10,15,20-Tetrakis(*p*-tolyl)porphyrinate(2-) (see refs. 16 and 17 respectively for the complexes of Zn<sup>II</sup> and Mn<sup>III</sup>); tmpyp = *meso*-5,10,15,20-tetra-

Table 1. Photophysical data for the zinc porphyrins in different media

Compound	Medium	Φ <sub>F</sub>	τ <sub>T</sub> /ms
Surf ZnP <sup>*</sup>	Benzene	0.04	1.12
	Igepal CO634	0.04	7.4
	sds	0.01	2.6
	htac	< 0.005	0.79
	Microemulsion	0.025	3.4
[Zn(tmpyp)] <sup>4+</sup>	Vesicle	0.03	3.2
	Water	0.035	1.2
	Igepal CO634	—	1.2
	sds	—	0.17
	Microemulsion	—	0.35
	Vesicle	—	0.25



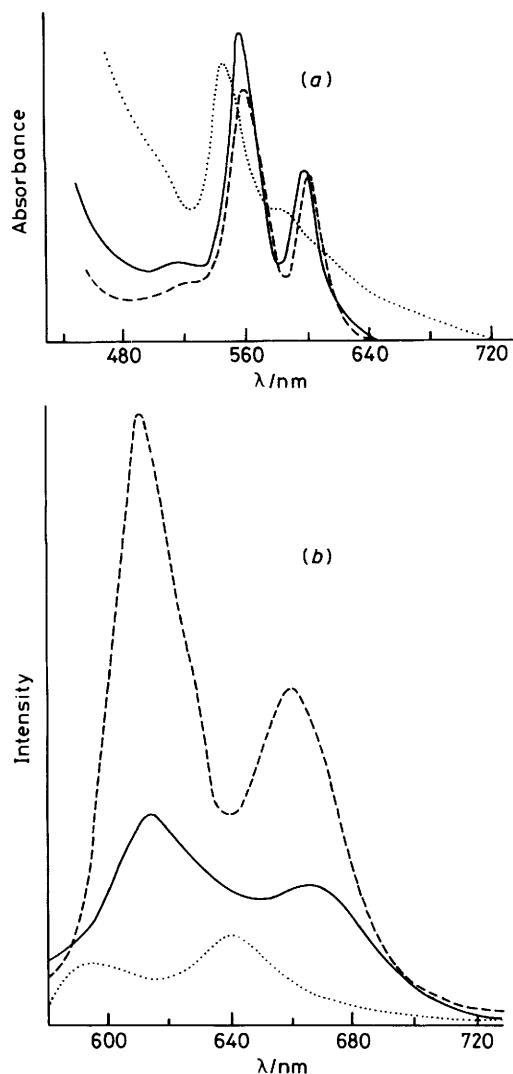
kis(*N*-methyl-4-pyridinio)porphyrin(2+) (see refs. 9, 7, and 18 respectively for the complexes of Zn<sup>II</sup>, Mn<sup>III</sup>, and Sn<sup>IV</sup>); Surf P = *meso*-20-(dodecoxyphenyl)-5,10,15-tris(*p*-tolyl)porphyrinate(2-); the ZnMn dimer is shown, where □ refers to *meso*-5,10,15-tris(*p*-tolyl)porphyrinate(2-).

## Results and Discussion

**Arrangement of Reactants.**—As shown by Figure 1, the use of microheterogeneous media permits the various reactants to be positioned at non-random sites. Water-insoluble reagents can be incorporated into charged or neutral micelles and, *via* the micelle-water interface, brought into close contact with water.<sup>19,20</sup> Similarly, water-soluble materials can be bound near the interface,<sup>15</sup> *via* electrostatic forces, and brought into contact with the organic phase. The general consequences of siting the reagents near the interface can be beneficial for achieving electron-transfer processes at low concentrations of reactants<sup>20</sup> but there could also be some deleterious effects. Thus, consider the case of surfactant zinc porphyrin. In outgassed benzene solution, this compound has a long triplet excited-state lifetime (τ<sub>T</sub>) and a modest fluorescence quantum yield (Φ<sub>F</sub>)<sup>21</sup> as shown by the data in Table 1. Incorporating the compound into neutral (Igepal CO634), negatively charged (sds), or positively charged (htac) micelles or microemulsion results in substantial changes in both τ<sub>T</sub> and Φ<sub>F</sub> (Table 1). Furthermore, the absorption and fluorescence spectra show pronounced perturbations (Figure 2) in the microheterogeneous media and in positively charged micelles the compounds are present in aggregated forms.<sup>22</sup> The use of phospholipid vesicles provides an environment similar to the microemulsion although the nature of the vesicle is more complex and several different binding sites can be identified.

Binding the metalloporphyrin to the micelle-water interface *via* electrostatic forces has a large effect upon the triplet lifetime of the porphyrin.<sup>15</sup> In outgassed aqueous solution at room temperature,<sup>9</sup> [Zn(tmpyp)]<sup>4+</sup> has a triplet lifetime of 1.2 ms and this remains essentially unaffected by the presence of neutral micelles. However, when the porphyrin is (partially) adsorbed onto the interface of a vesicle (τ<sub>T</sub> *ca.* 250 μs), microemulsion (τ<sub>T</sub> *ca.* 350 μs), or negatively charged micelle (τ<sub>T</sub> *ca.* 170 μs) the triplet lifetime is substantially lowered and the decay profile no longer fits a single exponential.<sup>15</sup> In addition, the transient absorption spectra showed the presence of porphyrin π-radical cations and anions which appear to arise from the triplet-triplet annihilation processes. Such effects have been reported recently for the vesicle-bound systems.<sup>15,23,24</sup>

It is easy to envisage some degrees of complexation between the central zinc ion and the polar head groups that form the



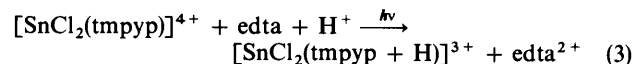
**Figure 2.** Absorption (a) and fluorescence spectra (b) of surfactant ZnP dissolved in vesicles (—), neutral micelles (---), and negatively charged micelles (···)

interface<sup>25</sup> but this is not the only factor responsible for the observed changes in the photophysical properties of the porphyrins. (Note, the metal-free porphyrins undergo similar effects.) Association of the metalloporphyrin with the interface appears to favour intermolecular porphyrin reactions. The normal consequence of such interactions is enhanced internal conversion<sup>26</sup> so that a lower triplet yield results. However, only a fraction of the porphyrin molecules will exist in the form of aggregates or clusters and the remainder should undergo intersystem crossing to form the triplet excited state. The longer intrinsic lifetime of the triplet state permits long-range electron-transfer reactions to occur so that porphyrin molecules spaced too far apart to undergo intermolecular singlet excited-state processes might still be subject to intermolecular triplet-state reactions.

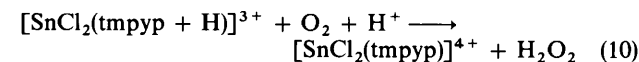
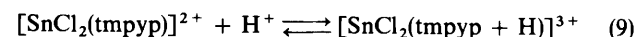
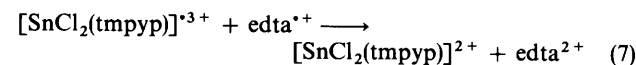
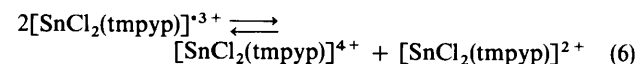
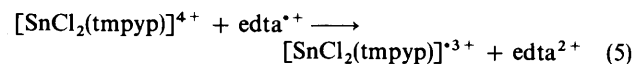
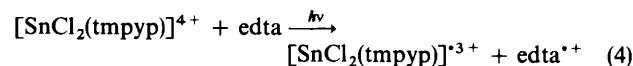
Previous work has shown that water-insoluble manganese(III) porphyrins can be solubilised in micellar and microheterogeneous media<sup>3</sup> without affecting their spectroscopic properties. The compounds used here were found to behave as described before.<sup>3</sup>

**Photoreduction of Manganese(III) Porphyrins.**—We reported previously that irradiation of water-soluble manganese(III)

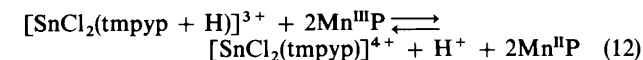
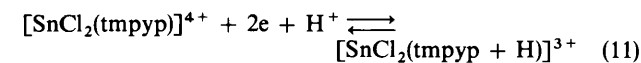
porphyrins in aqueous solution at pH > 8 containing an electron donor (e.g. edta or OH<sup>-</sup>) results in formation of the corresponding manganese(II) porphyrin.<sup>27</sup> Because the excited-state lifetimes of the paramagnetic manganese(III) porphyrins are extremely short ( $\tau_T$  < 20 ns) intermolecular photoreduction requires high concentrations of donor and the quantum yields are very low (typically in the order of 10<sup>-5</sup>). With diamagnetic metalloporphyrins, the long triplet lifetime ( $\tau_T$  ca. 1 ms) facilitates photoreduction at low donor concentration and the quantum yields can be high. Thus, irradiation of [SnCl<sub>2</sub>(tmpyp)]<sup>4+</sup> in aqueous solution at pH 9.4 containing edta (10<sup>-2</sup> mol dm<sup>-3</sup>) results in rapid formation of the tin(IV) phlorin ( $\lambda_{max}$ , 800 nm) (Figure 3).<sup>18</sup> The quantum yield for this



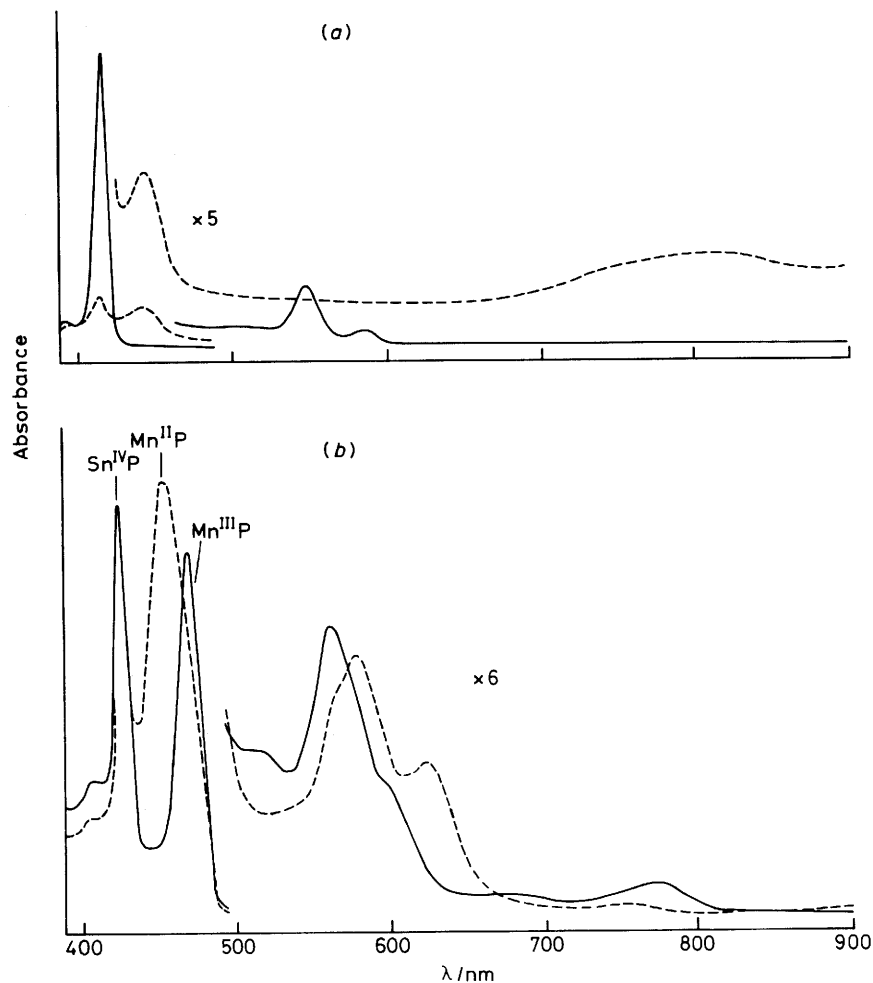
process was found to be 0.80 ± 0.07 using monochromatic light of  $\lambda$  418 nm. This is a two-electron reduction of the metalloporphyrin and it proceeds *via* intermediate formation of the  $\pi$ -radical anion, as monitored by flash photolysis [equations (4)–(9)].<sup>18</sup> The phlorin is stable in aqueous alkaline solution in the absence of oxygen but it is quantitatively oxidised to the original metalloporphyrin upon aeration of the solution [equation (10)].<sup>18</sup> If colloidal Pt or protons are added to the outgassed solution there is partial conversion of the phlorin into the chlorin. The chlorin ( $\lambda_{max}$ , 622 nm) is an irreversible product since it cannot be reoxidised to the porphyrin except by drastic chemical methods.



The phlorin is a modest reductant [equation (11),  $E_{\ddagger} = -0.40$  V at pH 7] and, in the presence of Pt, it will liberate H<sub>2</sub> from water in slightly acidic solution. It will also reduce manganese(III) porphyrins to the corresponding manganese(II) porphyrins, as shown by addition of an outgassed solution of a manganese(III) porphyrin to a solution of the phlorin [equation (12)]. The same overall process can be achieved *in situ*. Thus,

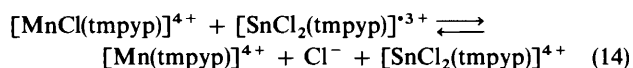
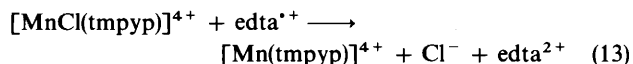


irradiation of [SnCl<sub>2</sub>(tmpyp)]<sup>4+</sup> with light of  $\lambda$  418 nm in aqueous solution at pH 9.4 containing edta (10<sup>-2</sup> mol dm<sup>-3</sup>) and [MnCl(tmpyp)]<sup>4+</sup> resulted in formation of [Mn(tmpyp)]<sup>4+</sup> as shown in Figure 3. The thermodynamic driving force for reaction (12) is about -40 kJ mol<sup>-1</sup> and the quantum yield for



**Figure 3.** Absorption spectral profiles showing the course of reaction upon irradiation of  $[\text{SnCl}_2(\text{tmpyp})]^{4+}$  ( $3 \times 10^{-6} \text{ mol dm}^{-3}$ ) in water at pH 9.4 containing edta ( $10^{-2} \text{ mol dm}^{-3}$ ) in the absence (a) and in the presence (b) of  $[\text{MnCl}(\text{tmpyp})]^{4+}$  ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ). (—),  $t = 0$ ; (---),  $t = 2 \text{ min}$

formation of  $[\text{Mn}(\text{tmpyp})]^{4+}$  was found to be 1.50. For the *in situ* case, other processes for reduction of the manganese(III) porphyrin must be considered [equations (13) and (14)].



Similar photoreductions were observed when the manganese(III) porphyrin was encapsulated into a vesicle, an oil-water microemulsion, or a negatively charged micelle, although the quantum yields for formation of the manganese(II) porphyrin were markedly lower than found in aqueous solution (Table 2). All the microheterogeneous media used possess negatively charged interfaces so that reaction (13) will be inhibited by electrostatic forces. On the other hand, the positively charged photosensitiser should be closely associated with the interface and reaction (14) can proceed unhindered. Association of the photosensitiser with the interface is accompanied by a reduction in the triplet excited-state lifetime<sup>15</sup> and in the yield of triplet and these factors, together with repulsion of the edta quencher, combine to give a low yield for the primary photoreaction [reaction (4)]. Other negatively charged electron donors gave similar low quantum yields (Table 2) and

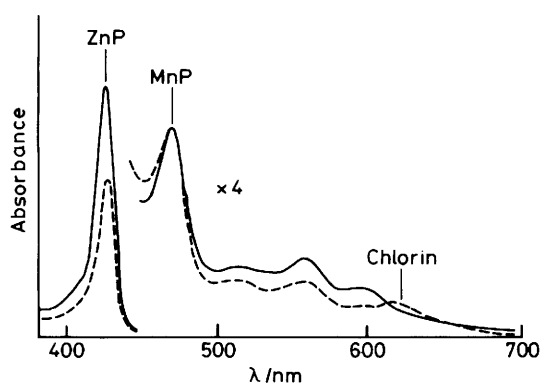
flash-photolysis studies confirmed that, under such conditions, the triplet excited state of the photosensitiser was only partially quenched by reaction with the donor. Thus, the low quantum yields found with microheterogeneous media are caused by association of the photosensitiser at the interface and not by inaccessibility of the manganese(III) porphyrin. Justification for this latter statement can be found by replacing  $[\text{MnCl}(\text{tmpyp})]^{4+}$  with a surfactant manganese(III) porphyrin which will reside at the interface of the microheterogeneous unit. As shown by Table 2, the two systems give comparable quantum yields.

When a surfactant photosensitiser is used in place of  $[\text{SnCl}_2(\text{tmpyp})]^{4+}$  the sensitiser is held near the interface and the quantum yield for formation of manganese(II) porphyrin is very low ( $<10^{-4}$ ). Again, this is most probably due to inefficient quenching of the triplet excited state by edta, which is repelled by the interface. Despite the long lifetime of the triplet state in microheterogeneous media, the potential barrier at the interface is sufficiently strong to inhibit quenching by edta and the triplet lifetime remains almost unaffected by high concentrations of edta. Prolonged irradiation does result in some photoreduction but the observed product was the chlorin of the surfactant zinc porphyrin rather than the manganese(II) porphyrin. Thus, with the surfactant photosensitiser, reaction (14) does not proceed to any significant extent.

To account for this phenomenon it is necessary to consider that the surfactant zinc porphyrin resides in the micro-

**Table 2.** Quantum yields for formation of manganese(II) porphyrin upon irradiation of a diamagnetic metalloporphyrin in the presence of an electron donor ( $10^{-2}$  mol  $\text{dm}^{-3}$ )

System	Photosensitiser	Manganese(III) porphyrin	Donor	$\lambda_{\text{ex}}/\text{nm}$	$\Phi(\text{Mn}^{\text{II}})$ ( $\pm 5\%$ )	
Aqueous	$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{tmpyp})]^{4+}$	edta	418	1.50	
Protein-bound	$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$\text{Mn}^{\text{III}}\text{P}$ -myoglobin	edta	418	0.15	
Vesicle	$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	edta	418	0.12	
	$[\text{Zn}(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	edta	437	0.094	
	$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	Surf $\text{MnCl}^{\text{III}}\text{P}$	edta	418	0.096	
	$[\text{Zn}(\text{tmpyp})]^{4+}$	Surf $\text{MnCl}^{\text{III}}\text{P}$	edta	437	0.12	
	Surf ZnP	$[\text{MnCl}(\text{ttp})]$	edta	420	$10^{-4}$	
	Surf ZnP	Surf $\text{MnCl}^{\text{III}}\text{P}$	edta	420	$<10^{-4}$	
	Surf ZnP	$[\text{MnCl}(\text{ttp})]$	$\text{KNO}_2$	420	$<10^{-4}$	
	Surf ZnP	$[\text{MnCl}(\text{ttp})]$	$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$	420	$<10^{-4}$	
	Microemulsion	$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	edta	418	0.17
		$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	$\text{KNO}_2$	418	0.0046
$[\text{SnCl}_2(\text{tmpyp})]^{4+}$		$[\text{MnCl}(\text{ttp})]$	$\text{NaSCN}$	418	0.0033	
$[\text{SnCl}_2(\text{tmpyp})]^{4+}$		Surf $\text{Mn}^{\text{III}}\text{P}$	edta	418	0.14	
$[\text{Zn}(\text{tmpyp})]^{4+}$		$[\text{MnCl}(\text{ttp})]$	edta	437	0.13	
Surf ZnP		$[\text{MnCl}(\text{ttp})]$	edta	420	$<10^{-4}$	
sds		$[\text{SnCl}_2(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	edta	418	0.064
	$[\text{Zn}(\text{tmpyp})]^{4+}$	$[\text{MnCl}(\text{ttp})]$	edta	437	0.057	
	Surf ZnP	$[\text{MnCl}(\text{ttp})]$	edta	420	$<10^{-4}$	
Microemulsion	ZnMn Dimer	Dimer	edta	420	$<10^{-4}$	

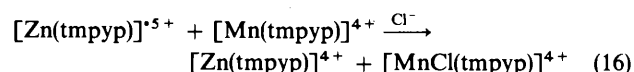
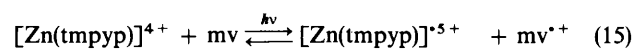
**Figure 4.** Absorption spectral profiles showing the formation of zinc chlorin upon irradiation of the ZnMn dimer ( $10^{-5}$  mol  $\text{dm}^{-3}$ ) in oil-water microemulsion in the presence of edta ( $10^{-2}$  mol  $\text{dm}^{-3}$ ) at pH 9.4. (—),  $t = 0$ ; (---),  $t = 50$  min

heterogeneous medium near to the interface but on the organic side.<sup>19</sup> This would explain the extremely poor quenching with edta. However, upon reduction the  $\pi$ -radical anion of the porphyrin is formed<sup>28</sup> and, being negatively charged, it might be expelled somewhat from the organic phase. This would expose the  $\pi$ -radical anion to the aqueous solution where it can collect a second electron (from an  $\text{edta}^{\cdot-}$  radical) to form the chlorin. {Note, unlike  $[\text{SnCl}_2(\text{tmpyp})]^{4+}$ , zinc porphyrins tend to form chlorins rather than phlorins, except at high pH.} Partial expulsion of the  $\pi$ -radical anion would inhibit reduction of a manganese(III) porphyrin held within the organic phase of the micelle. Even when the manganese(III) porphyrin was attached directly to the surfactant zinc porphyrin *via* a medium-length alkoxy-chain the preferred reduction product was the zinc chlorin and no manganese(II) porphyrin could be observed (Figure 4).

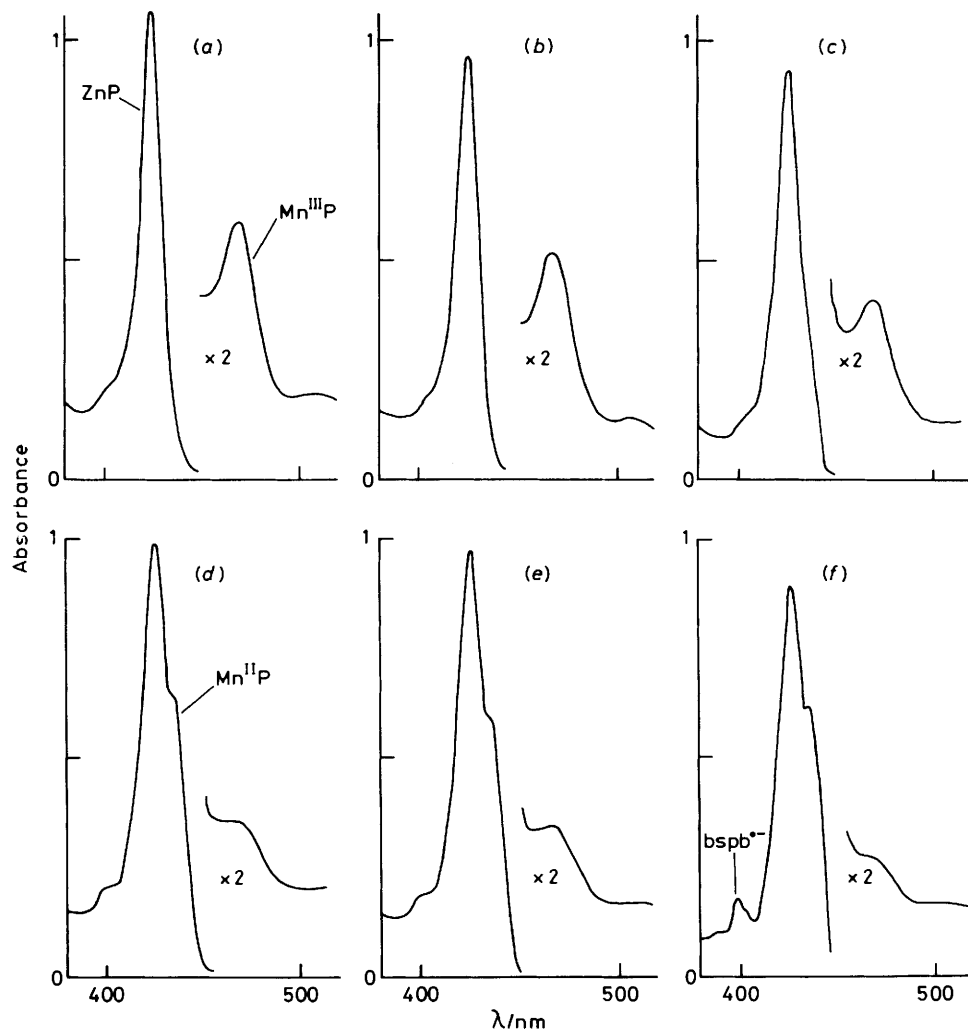
A manganese(III) porphyrin was used to replace the haem molecule in myoglobin<sup>8</sup> and this protein-bound porphyrin was also reduced by  $[\text{SnCl}_2(\text{tmpyp} + \text{H})]^{3+}$ . The quantum yield for formation of manganese(II) porphyrin was found to be only 10% of that found with water-soluble  $[\text{MnCl}(\text{tmpyp})]^{4+}$  under

identical experimental conditions (Table 2). This suggests that the protein provides a barrier to electron transfer, possibly by keeping the reactants at long distance. However, it is possible that the redox potential for reduction of the protein-bound manganese(III) porphyrin is lower than that of the water-soluble analogue so that the equilibrium position for reaction (12) lies further to the left-hand side.

**Photooxidation of Manganese(II) Porphyrins.**—Manganese(II) porphyrins are oxidised readily<sup>7</sup> to the corresponding manganese(III) porphyrins by  $\text{O}_2$  and it is necessary to conduct all experiments at pH  $> 8$  in order to avoid acid-catalysed demetallation of the manganese(II) porphyrin. These manganese(II) porphyrins are somewhat more photoactive than the manganese(III) porphyrins<sup>4</sup> and their absorption spectra are too similar to those of tin(IV) and zinc(II) porphyrins to be able selectively to excite one compound in the presence of the other. Therefore, there are experimental difficulties associated with photosensitising the oxidation of manganese(II) porphyrins with a diamagnetic metalloporphyrin. Steady-state irradiation of  $[\text{Zn}(\text{tmpyp})]^{4+}$  in aqueous solution at pH 9.4 containing  $[\text{Mn}(\text{tmpyp})]^{4+}$  and mv ( $5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) gave no change in the absorption spectrum of the mixture. Flash-photolysis studies showed that electron transfer did occur but it was highly reversible [equation (15)]. The rate of reverse electron transfer ( $\Delta G^\circ = -157$  kJ  $\text{mol}^{-1}$ ) occurs at the diffusion-controlled rate limit ( $k = 6.4 \times 10^8$   $\text{dm}^3$   $\text{mol}^{-1}$   $\text{s}^{-1}$ ) and it is too fast for the manganese(II) porphyrin to intercept it by reducing  $[\text{Zn}(\text{tmpyp})]^{5+}$ . From the flash-photolysis studies, the rate constant for this reaction [equation (16)] must be less than  $10^6$   $\text{dm}^3$   $\text{mol}^{-1}$   $\text{s}^{-1}$  despite the favourable thermodynamic driving force ( $\Delta G^\circ = -116$  kJ  $\text{mol}^{-1}$ ).

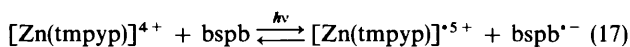


When water-insoluble manganese(II) porphyrins contained within oil-water microemulsions or negatively charged micelles were used in place of  $[\text{Mn}(\text{tmpyp})]^{4+}$ , formation of the



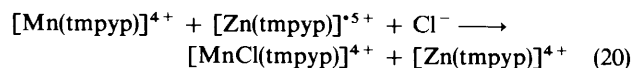
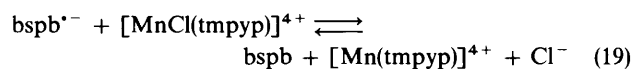
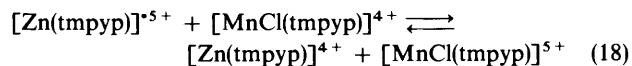
**Figure 5.** Absorption spectral profiles showing the course of reaction upon irradiation of the ZnMn dimer ( $10^{-5}$  mol  $\text{dm}^{-3}$ ) in oil-water microemulsion in the presence of bspb ( $10^{-2}$  mol  $\text{dm}^{-3}$ ).  $t = 0$  (a), 10 (b), 30 (c), 45 (d), 60 (e), and 90 min (f)

manganese(III) porphyrin could not be observed. Replacing mv with the neutral viologen bspb should prevent adsorption at the interface and, since electron transfer will produce a negatively charged viologen radical [equation (17)], there should be some inhibition of reverse electron transfer.<sup>14,29</sup> However, we were still unable to observe photooxidation of manganese(II) to -(III) porphyrin. The use of surfactant metalloporphyrins and protein-bound manganese(III) porphyrin gave similar negative results and in no case were we able to observe net photooxidation of a manganese(II) porphyrin.



**Photooxidation of Manganese(III) Porphyrins.**—Prolonged steady-state irradiation of  $[\text{Zn}(\text{tmpyp})]^{4+}$  in aqueous solution at pH 9.4 containing bspb ( $5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) and  $[\text{MnCl}(\text{tmpyp})]^{4+}$  gave no apparent changes in absorption spectrum. Flash-photolysis studies showed that electron transfer occurred, in accordance with reaction (17), but the rate constant for the reverse electron-transfer step ( $\Delta G^\circ = -150$  kJ  $\text{mol}^{-1}$ ) was  $(5 \pm 2) \times 10^9$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .<sup>30</sup> There was no evidence for intermediate formation of manganese(IV) porphyrin, although the thermodynamics are favourable ( $\Delta G^\circ = -37$  kJ  $\text{mol}^{-1}$ ), so that the rate constant for this step

[equation (18)] must be less than  $10^5$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . However, the flash-photolysis records showed that inefficient reduction occurred [equation (19)] with a rate constant of *ca.*  $5 \times 10^7$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . Reaction between the manganese(II) porphyrin and oxidised zinc porphyrin restored the ground-state equilibrium [equation (20)]. There is a large thermodynamic driving force ( $\Delta G^\circ = -116$  kJ  $\text{mol}^{-1}$ ) for this reaction although we were not able to determine an accurate rate constant.



Thus, it appears that manganese(III) porphyrins are more easily reduced than oxidised in aqueous solution. The standard free-energy changes  $\Delta G^\circ$  for the oxidation and reduction steps are  $-37$  and  $-34$  kJ  $\text{mol}^{-1}$  respectively so that the

preference for reduction is for kinetic reasons not thermodynamic ones. The large Coulombic repulsion forces between the reactants in reaction (20) is of obvious importance in this respect although we still failed to observe oxidation with a neutral manganese(III) porphyrin [manganese(III) meso-tetrakis(4-pyridyl)porphyrinate]. Recent electrochemical studies<sup>31</sup> have also shown the reluctance of manganese(III) porphyrins to be oxidised in aqueous solution at pH < 12, but pulse-radiolytic experiments<sup>32</sup> have shown that manganese(IV) porphyrins can be formed in neutral solution when a strong oxidant is employed.

It should be possible to use the microheterogeneous media to inhibit the reduction step whilst promoting the oxidation process.<sup>20</sup> Recent work by Calvin and co-workers<sup>14,29</sup> has suggested that a negatively charged vesicle will repel bspb<sup>•-</sup> sufficiently for the reduction step to be surpassed by the oxidation process. We could not confirm this finding. In our experiments with bspb in the aqueous phase, a water-insoluble manganese(III) porphyrin [MnCl(tp)] dispersed within a vesicle, oil-water microemulsion, or a negatively charged micelle and water-soluble [Zn(tmpyp)]<sup>4+</sup> adsorbed at the interface, we always observed the reduction of the manganese(III) porphyrin. This effect is shown by Figure 5 and in no case was Mn<sup>IV</sup> detected even as a transient species. With these various microheterogeneous systems the quantum yields for formation of [Mn<sup>II</sup>(tp)] were found to be around  $5 \times 10^{-3}$ .

Using surfactant zinc and manganese(III) porphyrins in conjunction with bspb and the microemulsion or vesicle systems gave identical qualitative results to the above. In all cases, steady-state irradiation (at a wavelength where only the zinc porphyrin absorbs) resulted in formation of the manganese(II) porphyrin and there was no apparent involvement of the manganese(IV) porphyrin, even as a transient with a lifetime longer than 10  $\mu$ s. Identical results were found with the covalently linked zinc-manganese(III) porphyrin dimer dissolved in the microemulsion, as shown in Figure 5, and the quantum yield for formation of manganese(II) porphyrin was 0.02 for this system. With a surfactant viologen in place of bspb and using [Zn(tmpyp)]<sup>4+</sup> and [MnCl(tp)] in the microemulsion medium, the photoreaction was very slow but even so after long irradiation times there was some formation of [Mn<sup>II</sup>(tp)].

As shown by Figure 5, before irradiation the B bands of [Zn(tmpyp)]<sup>4+</sup> ( $\lambda = 437$  nm) or [Zn(tp)] ( $\lambda = 420$  nm) and manganese(III) porphyrin ( $\lambda = 478$  nm) are well resolved although the Q bands ( $\lambda$  500–620 nm) overlap too strongly to be resolved. Irradiation at 437 or 420 nm results in electron transfer from triplet zinc porphyrin to bspb, according to reaction (17). Reverse electron transfer occurs but the negatively charged interface provides some repulsive forces to slow down approach of bspb<sup>•-</sup>. Consequently, the primary photo-products are stabilised against reverse electron transfer relative to aqueous solution. The zinc porphyrin  $\pi$ -radical cation is a strong oxidant<sup>33</sup> and it is readily reduced by many organic species, including alcohols.<sup>30</sup> As monitored by flash photolysis, most of the zinc porphyrin  $\pi$ -radical cations produced in the flash decayed *via* second-order, reverse electron transfer but a substantial fraction (*ca.* 30%) decayed *via* a first-order process. This latter reaction resulted in restoration of ground-state porphyrin and is most probably due to reduction by impurities or constituents in the microheterogeneous media. The residual bspb<sup>•-</sup> reduces manganese(II) porphyrin and, when this reaction is complete, bspb<sup>•-</sup> begins to accumulate in solution. Eventually, the concentration of accumulated bspb<sup>•-</sup> is sufficient for reverse electron transfer to compete with the reduction process and, at this point, a photostationary state is attained.

Consequently, the use of manganese porphyrins to store redox equivalents produced in photochemical systems does not

look too promising at the present time. Perhaps, the direction to take is to replace the zinc-manganese porphyrin dimer that was used here with a similar compound in which the two porphyrins are held closer together. This might assist electron transfer between the zinc porphyrin  $\pi$ -radical cation and the manganese porphyrin. We will report on such systems at a later stage.

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