

## Photoredox Properties of Tetra-2,3-pyridinoporphyrazines (29*H*,31*H*-Tetrapyrido[2,3-*b*:2',3'-*g*:2'',3''-*l*:2''',3'''-*q*]porphyrazine)

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Tetra-2,3-pyridinoporphyrazines (29*H*,31*H*-tetrapyrido[2,3-*b*:2',3'-*g*:2'',3''-*l*:2''',3'''-*q*]porphyrazine) (1) and the corresponding water-soluble *NN'N''N'''*-tetramethylated quaternized tetracationic forms (2) with different central metal atoms were prepared and their photoredox activities investigated. The synthesis of (2; M = Zn, Cu) leads to mixtures of different constitutional isomers, which were isolated and characterized. The photoredox activities of (1) upon irradiation with visible light in the presence of EDTA and methylviologen (MV<sup>2+</sup>) are comparable with those of phthalocyanines. The photochemical reaction of (2) with different donors works clearly through a reductive quenching mechanism. Reaction with EDTA proceeds by a two-step sensitization to the dicationic species of (2).

Synthetic porphyrins and phthalocyanines are interesting as sensitizers for the conversion of visible light into chemical energy not only through their relationship to chlorophyll, but also because they absorb throughout the visible region, preferably into the near-i.r. Both water-soluble and water-insoluble porphyrins were investigated in photoredox reactions (e.g. ref. 1—13). The aim of these investigations is the photolysis of water by visible light. A water-soluble tetracationic zinc porphyrin is the most effective one yet reported for the photo-generation of molecular hydrogen from water in a sacrificial process.<sup>2,13</sup>

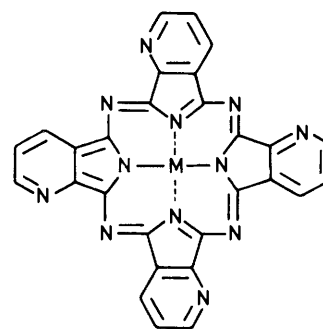
The investigation of different porphyrins is important to clarify their behaviour as sensitizers towards donors and acceptors and to enlarge the wavelength range of light-energy conversion through their absorptions in different wavelength regions.

In this paper, tetra-2,3-pyridinoporphyrazines (29*H*,31*H*-tetrapyrido[2,3-*b*:2',3'-*g*:2'',3''-*l*:2''',3'''-*q*]porphyrazines) (1), soluble in organic solvents, and water-soluble *NN'N''N'''*-tetramethyltetra-2,3-pyridinoporphyrazines (2) were characterized by simple photochemical reactions. These compounds differ from phthalocyanines due to the presence of the annulated electron-withdrawing pyridine ring. Compounds (2) have an advantage over tetrasulphophthalocyanines, since the macrocycles of (2) do not aggregate in aqueous solution<sup>14,15</sup> which would prevent photochemical redox activities.

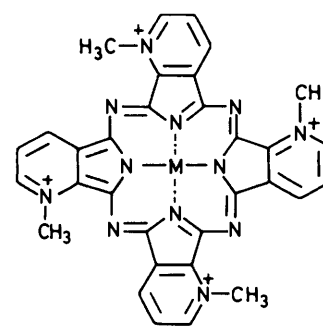
### Results and Discussion

*Tetra-2,3-pyridinoporphyrazines* (1).—As is the synthesis of phthalocyanines, compounds (1) are prepared from pyridine-2,3-dicarboxylic acid<sup>15–20</sup> or 2,3-dicyanopyridine.<sup>21,22</sup> Synthesis starting with the carboxylic acid in the presence of a metal salt, urea, and a catalyst has the disadvantage of using concentrated acids for further purification. During this process, (1; M = Mg, Cd, Zn) is demetallized.

Hence, compounds (1) have been prepared beginning with 2,3-dicyanopyridine. Compounds (1; M = Cd, Zn, Cu) have been prepared by the method of Brach *et al.*<sup>23</sup> at 130 °C (reaction of 2,3-dicyanopyridine in *NN*-dimethylaminoethanol by addition of a metal salt and bubbling of ammonia through the solution). Synthesis of metal-free (1) has been accomplished analogously by omitting the addition of a metal salt. The preparation of [1; M = Mg, Al(OH)] succeeded through the reaction of 2,3-



(1)



(2)

dicyanopyridine with Mg or Al powder in a sealed ampoule at higher temperatures. Synthesis of (1; M = Mg) from pyridine-2,3-dicarboxylic acid by the method of Harriman<sup>20</sup> was not successful probably due to the low chelation tendency of magnesium. Furthermore, the characterization in the literature does not permit exact statements.

The i.r. spectra of (1) show a metal-dependent frame vibration at 885–905 cm<sup>-1</sup>. This vibration is a measure of the strength of the interaction between metal and ligand.<sup>24,25</sup> For different metals these vibrations are: Cd (885 cm<sup>-1</sup>); Mg, Zn (895 cm<sup>-1</sup>); Al(OH), Cu (905 cm<sup>-1</sup>). This sequence is confirmed by the fact that only [1; M = Al(OH) or Cu] can be reprecipitated from concentrated sulphuric acid without being demetallized.

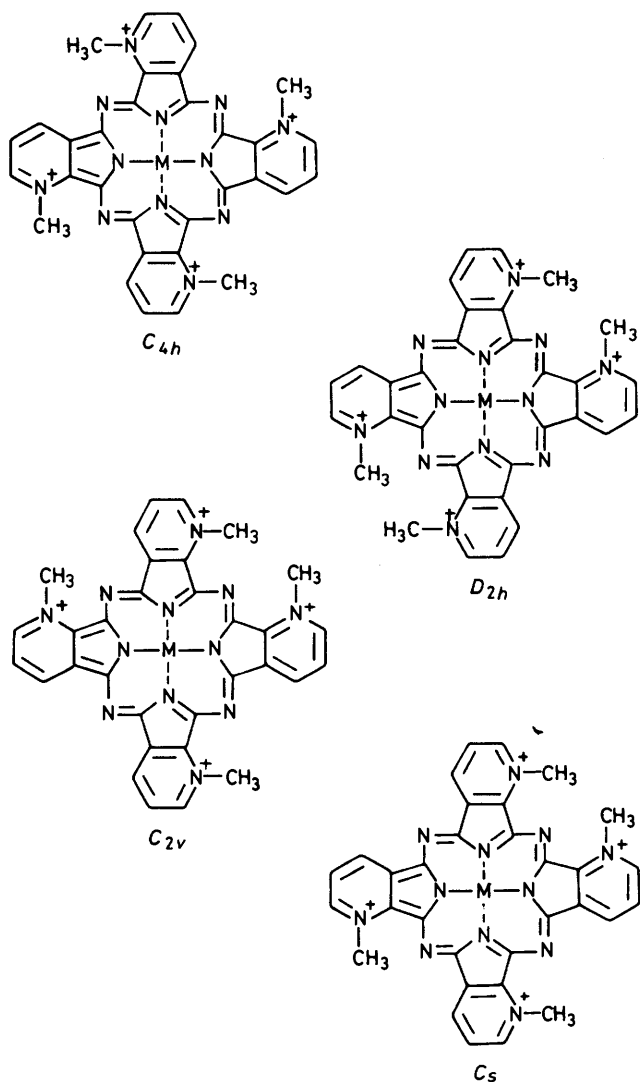


Figure 1. Possible constitutional isomers of (2)

Compounds (1) absorb at  $\lambda$  ca. 640 nm (in DMF) with  $\epsilon$  ca.  $10^5$  (see Table 1). The long-wave band structure resembles that of the phthalocyanines, but is shifted to shorter wavelengths. Compound (1;  $M = 2H$ ) possesses long-wave band structure as does metal-containing (1) with  $C_{4h}$  symmetry. The electron-withdrawing effect of the annelated pyridine ring increases the acidity of the inner N-H bonds, so that the dissociated dicationic ligand is present in DMF solution. The visible spectra of metal-free (1) in non-basic 1-chloronaphthalene show expected long-wave band structure of the neutral form with  $C_{2v}$  symmetry (Table 1).

**Quaternized Tetra-2,3-pyridinoporphyrazines (2).**—For the preparation of (2), alkylation of (1) with dimethyl sulphate was carried out in DMF according to Scott.<sup>15,26</sup> Reported yields of ca. 80% were not obtained although reaction conditions were varied (Table 1). In the case of (1;  $M = Mg, Cd$ ), demetallization occurred during quaternization (contrary to the report in ref. 20), resulting in (2;  $M = 2H$ ). Attempts to alkylate (1) with methyl iodide under varying reaction conditions resulted in yields of ca. 1.7% of (2). With  $M = Cu$  or  $Zn$  a DMF-soluble (2b) and a DMF-insoluble fraction (2a) were isolated. By  $^1H$  n.m.r. spectra we were able to prove that (2a and b) are

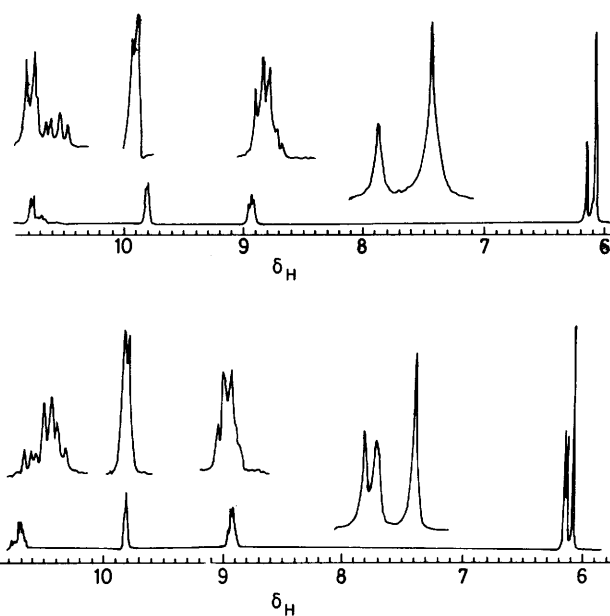


Figure 2. 360 MHz  $^1H$  N.m.r. spectra of (2a) (upper) and (2b) (lower) ( $M = Zn$ ) in  $D_2O$

mixtures of constitutional isomers. As far as we know, this is the first time that constitutional isomers of porphyrazines (phthalocyanines and their analogues) have been proven to exist. No fractions of other compounds (2) could be isolated due to their similar solubilities. The four possible constitutional isomers have the symmetries  $C_{4h}$ ,  $D_{2h}$ ,  $C_{2v}$ ,  $C_s$  (Figure 1). The existence of isomers contradicts the assumption of Scott<sup>26</sup> that isomers are not possible due to electrostatic repulsion and steric hindrance.

The n.m.r. and u.v.-visible spectra of (2a and b) differ although the metal content and the degree of alkylation (determined by electrophoresis,<sup>27</sup> buffered at pH 1.5) are the same. This leads to the conclusion that constitutional isomers are present. Compound (1) must also exist as mixtures of constitutional isomers but this is not detectable due to the poor solubility of (1) in organic solvents.

Alkylated zinc tetra-2,3-pyridinoporphyrazine shows several signals for the methyl groups at the pyridine nitrogens. In (2a), the methyl resonance consists of two signals and in (2b) three signals are observed (Figure 2). Since this number of signals cannot be due to H,H coupling this has to be explained by the existence of different mixtures of constitutional isomers. Depending on the isomer, the following numbers of singlets are to be expected for the different methyl groups:

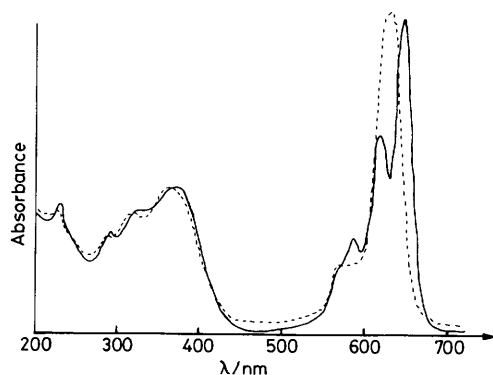
Symmetry	$^1H$ N.m.r. singlets
$C_{4h}$	1
$D_{2h}$	1
$C_{2v}$	2
$C_s$	4 (or less due to minimal magnetic differences between the different methyl groups)

Isomer  $C_{4h}$  should be produced in the highest amount for electrostatic and steric reasons. Hence, the largest signal corresponds to the methyl groups of the  $C_{4h}$  isomer. Since  $^1H$  n.m.r. signals are shifted downfield in the case of steric hindrance the residual methyl signals have to be assigned to sterically hindered methyl groups. From these facts the following conclusions can be drawn regarding the signal intensities:

**Table 1.** Yields and analytical data for (1) and (2)

(1) or (2)	Yield (%)	Found (%) (Required)				$\lambda/\text{nm}^a$ ( $\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$ )
		C	H	N	M	
(1; M = H)	34	58.3 (58.7)	3.1 (3.5)	28.7 (29.3) <sup>c</sup>		643 (65 600), 613 (15 300), 584 (11 600), 380 (22 000), 32 (28 200) 666, <sup>f</sup> 633, <sup>f</sup> 608, <sup>f</sup> 576 <sup>f</sup>
(1; M = Mg)	63	62.5 (62.2)	2.5 (2.2)	30.9 (31.1)		643 (86 200), 616 (11 900), 582 (11 400), 366 (22 800), 329 (28 000)
(1; M = Cd)	45	53.2 (53.5)	2.1 (1.9)	26.4 (26.7)		648 (83 800), 618 (12 900), 586 (11 500), 380 (19 400), 328 (26 400)
[1; M = Al(OH)] <sup>b</sup>	17	60.4 (60.0)	2.6 (2.3)	30.3 (30.0)		642, 616, 580, 436, 427
(1; M = Cu)	65	54.8 (54.6)	2.6 (2.6)	27.5 (27.3)	10.4 (10.3) <sup>d</sup>	649, <sup>f</sup> 622, <sup>f</sup> 586, <sup>f</sup> 342 <sup>f</sup>
(1; M = Zn)	74	54.5 (54.4)	2.8 (2.6)	27.0 (27.2)	10.6 (10.6) <sup>d</sup>	642 (59 100), 613 (7 500), 582 (8 000), 390 (13 000), 329 (20 000)
(2; M = 2 H)	37	41.3 (40.8)	3.6 (4.0)	15.1 (15.9) <sup>d</sup>		642 (98 000), 583 (22 000), 396 (42 800), 318 (38 000), 300 (42 500) 652, <sup>g</sup> 621, <sup>g</sup> 594, <sup>g</sup> 572, <sup>g</sup> 337 <sup>g</sup>
[2; M = Al(OH)]	27	41.2 (40.6)	3.3 (3.5)	16.1 (15.8)		636 (29 300), 627 (28 800), 570 (6 700), 425 (11 400), 390 (18 500), 366 (18 600), 324 (20 200)
(2a; M = Cu)	11	35.9 (36.8)	3.5 (3.9)	14.2 (14.3)	5.4 (5.4) <sup>e</sup>	638 (104 800), 618 (91 300), 581 (25 900), 568 (24 800), 359 (47 900), 324 (47 300)
(2b; M = Cu)	24	35.8 (36.8)	3.7 (3.9)	14.7 (14.3)	5.1 (5.4) <sup>e</sup>	626 (86 200), 568 (16 300), 358 (33 700), 323 (33 600)
(2a; M = Zn)	8	38.4 (37.9)	3.5 (3.7)	14.5 (14.7)	5.7 (5.7) <sup>e</sup>	649 (99 900), 621 (69 800), 584 (29 600), 570 (21 100), 370 (46 200), 325 (38 600)
(2b; M = Zn)	22	37.7 (37.9)	3.8 (3.7)	14.9 (14.7)	5.6 (5.7) <sup>e</sup>	637 (86 100), 629 (85 000), 572 (15 700), 366 (35 200), 321 (29 800)

<sup>a</sup> (1) in DMF; (2) in H<sub>2</sub>O, pH 7. <sup>b</sup>  $\nu_{\text{max}}$  (KBr) 1 190, 1 130, 1 080 cm<sup>-1</sup> for Al-O-H; analogous for Al(OH)-phthalocyanine.<sup>19</sup> <sup>c</sup> Calc. with 3 × H<sub>2</sub>O. <sup>d</sup> Calc. with 2 × H<sub>2</sub>O. <sup>e</sup> Calc. with 5 × H<sub>2</sub>O. <sup>f</sup> In 1-chloronaphthalene. <sup>g</sup> In acidified H<sub>2</sub>O, pH 1.



**Figure 3.** Electronic absorption spectra of (2a) (—) and (2b) (---) (M = Zn) in H<sub>2</sub>O (see Table 1)

(1) (2a) consists of the isomers  $C_{4h}$  and  $D_{2h}$ ; (2) (2a) consists of  $C_{4h}$  and  $C_s$  or  $C_{4h}$  and  $C_{2v}$  or of a mixture of these three isomers; (3) (2b) consists of  $C_{4h}$ ,  $C_{2v}$ , and/or  $C_s$  and  $D_{2h}$ ; (4) (2b) consists of  $C_{4h}$ ,  $C_s$ , and  $C_{2v}$  or  $C_{4h}$ ,  $C_s$  (or  $C_{2v}$ ), and  $D_{2h}$ .

As a general conclusion it can be said that (2a) consists of at least two and (2b) of at least three isomers.

Visible spectra of (2a and b; M = Cu, Zn) show drastic differences in the long-wave region (Figure 3). U.v.-visible spectra of [2; M = 2 H, Al(OH)] match the spectra of (2b; M = Cu, Zn). U.v.-visible-spectra of (2) in aqueous solution show no aggregation of the macrocycles as in the case of tetrasulpho-

phthalocyanine, which forms dimers in aqueous solution.<sup>14,15</sup> Aggregation prevents photoredox activity since the dimers dissociate on excitation with visible light and so the excitation energy will be dissipated.<sup>28</sup>

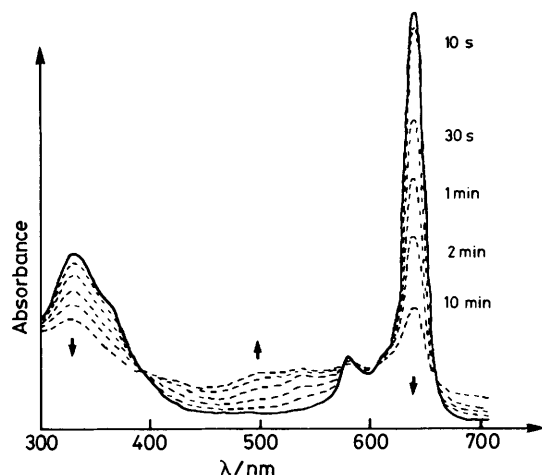
The absorption maximum of (2; M = 2 H) is pH-dependent. The strong electron-withdrawing effect of the annelated pyridine ring leads to enhanced N-H acidity compared with phthalocyanine. At pH 7 the porphyrine (2; M = 2 H) exists in the dicationic form ( $C_{4h}$  symmetry), which has the same symmetry as metal-containing compounds (2) and shows an analogous absorption spectrum (Table 1). At pH 1 the inner nitrogen atoms become protonated (2; M = 2 H), and the long-wave absorption splits into two peaks typical of metal-free porphyrines of  $C_{2v}$  symmetry.

Subsequent introduction of metal ions into the (2; M = 2 H) was attempted. With metal ions such as  $\text{Mg}^{2+}$  and  $\text{Cd}^{2+}$ , which are bound in porphyrin systems with a high degree of ionic bonding, no metal-containing (2) was obtained due to the decreased electron-density at the inner nitrogen-atoms. Only with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , which are bound more covalently in a porphyrin system, was metal introduction successful. Hence, Mg and Cd chelates of (2) cannot be obtained by alkylation of corresponding (1) nor by metal introduction into the macrocycle (2).

**Photoredox Behaviour of (1).**—The photoredox behaviour of the non-alkylated, water-insoluble chelates (1) upon irradiation with visible light has been investigated in DMF-H<sub>2</sub>O solution (9:1, v/v) in the presence of excess of EDTA as donor and methylviologen ( $\text{MV}^{2+}$ ) as acceptor.<sup>11</sup> Formation of methyl-

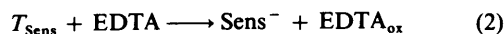
**Table 2.** Photoreduction of  $MV^{2+}$  through (1). Irradiated with visible light under argon at 24 °C. [(1)]  $10^{-5}M$ ; [ $MV^{2+}$ ]  $5 \times 10^{-4}M$ ; [EDTA]  $10^{-3}M$ ; DMF– $H_2O$  (9:1 v/v)

M in (1)	$10^5$ Initial rate of $MV^{2+}$ formation (mol l <sup>-1</sup> min <sup>-1</sup> )	$MV^{2+}$ after 5 min irradiation (%) (inserted $MV^{2+} = 100\%$ )
Al(OH)	10.0	19.6
Cd	4.9	13.8
Mg	1.9	6.6
Zn	1.4	7.0
2 H	0.5	3.2



**Figure 4.** Photoreduction of (1; M = Zn) ( $10^{-5}M$ ) with EDTA ( $10^{-3}M$ ) in DMF–water (9:1 v/v) with different irradiation times

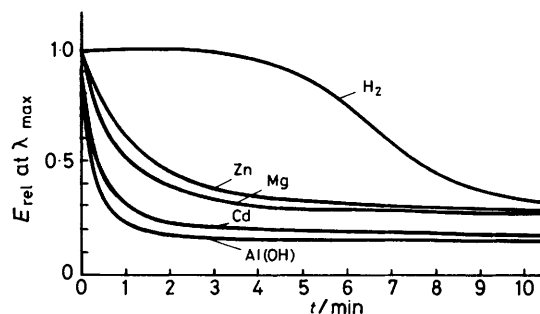
viologen cation radical ( $MV^{+•}$ ) occurred with velocities comparable to phthalocyanines (Table 2).<sup>11</sup> The lifetimes of the triplet state are only *ca.*  $10^{-7}$  s (Table 3) and are shorter compared with other water-insoluble phthalocyanines.<sup>1</sup> Photoredox activity of metal-free (1) may be due to the existence of the dianionic ligand in DMF solution with similar electron configuration as the metal-containing chelates (1). As expected, (1) with M = Cu does not exhibit considerable activity since phthalocyanines with paramagnetic transition metals have only extremely short triplet lifetimes.<sup>1</sup> Surprisingly, a photoredox reaction of the sensitizer with the donor occurred in the absence of the acceptor methylviologen (Figure 4), an observation not made when using phthalocyanines as sensitizers. Figure 5 shows that after an irradiation period of 1–5 min the reaction is terminated. Bubbling dioxygen through the solution leads to reoxidation of the reduced sensitizer. Since the sequence of activity of (1) does not depend on the presence of methylviologen [Al(OH) > Cd > Mg > Zn > H<sub>2</sub>], the mechanism of the photoredox reaction is assumed to proceed *via* reductive quenching [reactions (1)–(3)].



This means that equations (4) and (5) hold for the redox potentials.

**Table 3.** Triplet lifetimes of compounds (1)

M in (1)	$10^7$ Lifetime (s)
Mg	2.0
Zn	1.3
Cd	3.8
2H	2.8



**Figure 5.** Decrease in absorption of (1;  $10^{-5}M$ ) in the photoreduction with EDTA ( $10^{-3}M$ ) in DMF–water (9:1 v/v)

$$E^\circ (T_{\text{Sens}/\text{Sens}^-}) > E^\circ (\text{EDTA}_{\text{ox}}/\text{EDTA}) \sim +1.0 \text{ V (versus n.h.e.)} \quad (4)$$

$$E^\circ (\text{Sens}/\text{Sens}^-) < E^\circ (MV^{2+}/MV^{+•}) = -0.45 \text{ (versus n.h.e.)} \quad (5)$$

Phthalocyanines (Pc) with the same metals as in (1) have  $E^\circ$  values between +0.20 (CdPc) and +0.82 V (H<sub>2</sub>Pc) (versus n.h.e.) for  $E^\circ (T_{\text{Sens}/\text{Sens}^-})$ .<sup>1</sup> The electron-withdrawing effect of the annelated pyridine rings results in a distinct behaviour for reductive quenching of (1) compared with phthalocyanines. This is proved by the fact that phthalocyanines do not react with a donor (in the absence of  $MV^{2+}$ ) upon irradiation with visible light.

**Photoredox Behaviour of (2).**—The alkylated compounds (2) show a stronger tendency towards reductive quenching. Surprisingly, the mixtures of the constitutional isomers (2a and b) have very similar behaviour during photoredox reactions, although the long-wave band structures in the absorption spectra are different (Figure 3).

With (2) versenol, cysteine, triethanolamine, and ascorbic acid were used as donors in addition to EDTA. In the absence of  $MV^{2+}$  the following observation can be made when using (2). Irradiation of (2b; M = Zn) with visible light using EDTA and versenol as donors leads to a blue reduction product with  $\lambda_{\text{max}}$  570 nm in a very fast reaction (< 1 s) (Figure 6). Subsequently, a second reduction product with  $\lambda_{\text{max}}$  500 nm (fine purple precipitate) is formed in a slow reaction (*ca.* 10 min).

Irradiation of (2b; M = Zn) with cysteine as electron donor leads only to the reduction product with  $\lambda_{\text{max}}$  570 nm, whereby the reaction is much slower (*ca.* 10 min) compared with EDTA (Figure 7). With triethanolamine and ascorbic acid as donors, the first reduction product was formed in the dark. Irradiation did not change the absorption spectra further. The second reduction product ( $\lambda_{\text{max}}$  500 nm) was not formed. The photoredox products with  $\lambda_{\text{max}}$  570 and 500 nm are both formed in one-electron reductions. (a) The observed isobestic points (Figures 6,7) are hints of a two-step process. (b) Using equimolar amounts of cysteine and half-molar amounts of EDTA with reference to the sensitizers leads only to formation

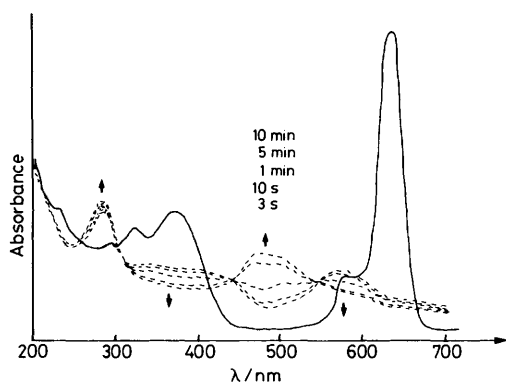


Figure 6. Photoreduction of (2b; M = Zn) ( $10^{-5}$  M) with EDTA ( $10^{-3}$  M) in water (— starting material; --- after different irradiation times)

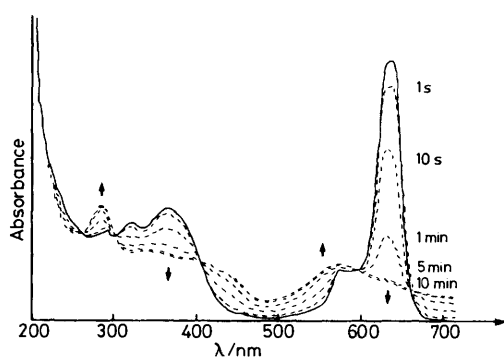


Figure 7. Photoreduction of (2b; M = Zn) ( $10^{-5}$  M) with cysteine ( $10^{-3}$  M) in water (— starting material; --- after different irradiation times)

of the first reduction product with  $\lambda_{\max}$  570 nm (Figure 7). Since cysteine is a one-electron-donating agent and EDTA a two-electron donating agent, a one-electron reduction as the first step (6) is proved. Absorption at 570 nm and other short-wave



absorptions are comparable with those of the monoanions of phthalocyanines.<sup>29,30</sup> As with phthalocyanines the LUMO of the ligand is filled up on reduction.<sup>31</sup> With cysteine as donor the velocity of the one-electron reduction is independent of the donor concentration within the chosen concentration range as can be seen from Figure 8. (c) Equimolar amounts of EDTA (referring to the sensitizer) lead to the observations depicted in Figure 6 with formation of the reduction product with  $\lambda_{\max}$  500 nm. Hence, for the step following the first reduction ( $\lambda_{\max}$  570 nm) a second one-electron process (7) has to be postulated.



Absorptions at 500 nm and short-wave absorptions are comparable with the dianions of phthalocyanine.<sup>29,30</sup>

This step is also nearly independent of the EDTA concentration within the chosen concentration range (Figure 8). Both photoredox products react in the dark with dioxygen back to the tetracation (2b) ( $\lambda_{\max}$  637 nm).

Using a mixture of EDTA-(2b; M = Zn) and  $MV^{2+}$ , no  $MV^{+}$  cation radical is obtained on irradiation with visible light. Instead the result is identical with that shown in Figure 6. Irradiation of a solution of sensitizer (2b) and methylviologen

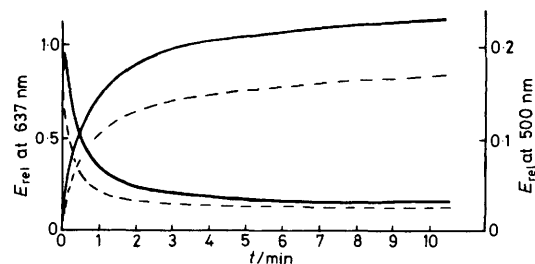


Figure 8. Photoreduction of (2b; M = Zn) ( $10^{-5}$  M) in water. Decrease in absorption at 637 nm using cysteine (—  $10^{-3}$  M, ---  $10^{-5}$  M). Increase in absorption at 500 nm using EDTA (—  $10^{-3}$  M, ---  $10^{-5}$  M)

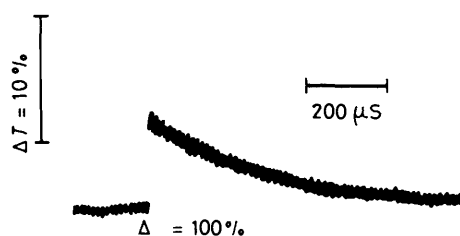


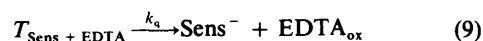
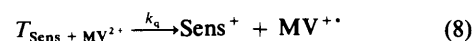
Figure 9. Oscilloscope trace of (2b; M = Zn) ( $10^{-5}$  M) aqueous solution monitored at 500 nm after a laser flash (532 nm, 20 ns)

Table 4. Triplet lifetimes of compounds (2)

M in (2b)	Lifetime (s)
Cu	$4.2 \times 10^{-8}$
Zn	$1.7 \times 10^{-4}$

without a donor leads to the photoredox product with  $\lambda_{\max}$  570 nm. No  $MV^{+}$  is observed. Since irradiation of an aqueous solution of (2b) with visible light under argon leads to no change in the u.v.-visible-spectra, it has to be assumed that  $MV^{2+}$  works in this case as electron donor and is oxidized. The result is identical to that when using cysteine as electron donor. This proves the strong oxidizing power of the sensitizers.

Figure 9 shows the oscilloscope trace of excited (2b) monitored at 500 nm after a laser flash. From Figure 9, the lifetime of the triplet state of (2b; M = Zn) was found to be 170  $\mu$ s (Table 4), which is comparable with some other phthalocyanines.<sup>1</sup> In the presence of methylviologen or EDTA, the decay rates of the transient spectrum with 500 nm increased. Typical decay curves in the presence of methylviologen or EDTA are shown in Figures 10 and 11. From the Stern-Volmer plots the quenching rate constants  $k_q$  of reactions (8) and (9) were determined as  $4.0 \times 10^7$  and  $1.4 \times 10^3$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>, respectively.

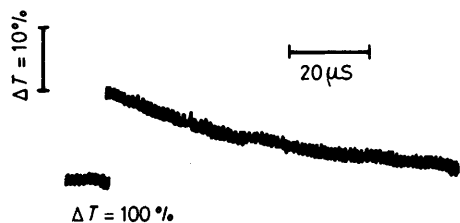


$T_{\text{Sens}}$  is quenched competitively by methylviologen and EDTA. From the result,  $T_{\text{Sens}}$  is more effectively quenched by methylviologen than by EDTA. However, as generally known,<sup>1-3</sup> the quenching reaction (8) is followed by a very fast back-reaction. Therefore no  $MV^{+}$  is detectable under continuous irradiation. The slower quenching reaction (9) is irreversible. Consequently, in the continuous-irradiation experiment, only the reductive quenching of  $T_{\text{Sens}}$  is observed.

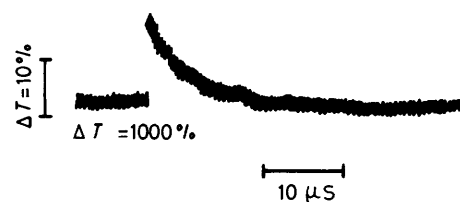
**Table 5.** Comparison of calculated  $E^\circ(T_{\text{Sens}/\text{Sens}^-})$  values for different phthalocyanine compounds

Phthalocyanine (Pc)	$\lambda_{\text{max.}}/\text{nm}$	Exen <sup>a</sup>	$E^\circ(\text{Sens}/\text{Sens}^-)/\text{V}$	$E^\circ(T_{\text{Sens}/\text{Sens}^-})/\text{V}^b$
ZnPc	642 <sup>c</sup>	1.31	-0.6 <sup>1</sup>	+0.71
ZnPc(CN) <sub>8</sub>	687 <sup>c</sup>	1.18	+1.0 <sup>32</sup>	+1.18
(2a; M = Zn)	649 <sup>d</sup>	1.29	~ -0.3 <sup>15</sup>	~ +1.0
(2b; M = Zn)	637 <sup>d</sup>	1.33	~ -0.3 <sup>15</sup>	~ +1.0

<sup>a</sup> Exen =  $(v_{\text{max.}} - 5000)/8065$  ( $v_{\text{max.}}$  in  $\text{cm}^{-1}$ ).<sup>10</sup> <sup>b</sup> Calculated from:  $E^\circ(T_{\text{Sens}/\text{Sens}^-}) = E^\circ(\text{Sens}/\text{Sens}^-) + \text{Exen}$ .<sup>10</sup> <sup>c</sup> In DMF. <sup>d</sup> In water.



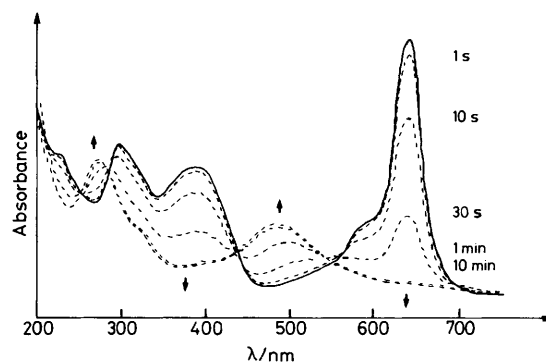
**Figure 10.** Oscilloscope trace of quenching of excited (2b; M = Zn) ( $10^{-5}\text{M}$ ) by  $\text{MV}^{2+}$  ( $5 \times 10^{-4}\text{M}$ ) in aqueous solution monitored at 500 nm after a laser flash (532 nm, 20 ns)



**Figure 11.** Oscilloscope trace of quenching of excited (2b; M = Zn) ( $10^{-5}\text{M}$ ) by EDTA ( $1.27 \times 10^{-4}\text{M}$ ) in aqueous solution monitored at 500 nm after a laser flash (532 nm, ns)

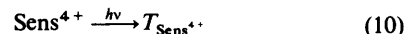
Other compounds [2; M = 2 H, Al(OH), Cu][isomer mixtures (2a and b)] display slightly different behaviour. Photoreduction in the presence of EDTA, in the absence or presence of methylviologen, leads to absorption at 500 nm directly without the intermediate absorption at 570 nm (Figure 12). The shape and position of the absorption at 500 nm is identical for all the sensitizers [2; M = 2 H, Al(OH), Cu] and the reduction product is also a fine purple precipitate as also with (2; M = Zn). With dioxygen, the reaction is reversible with the exception of (3; M = 2 H). As in the case of phthalocyanines<sup>1</sup> the excited states of [2; M = 2 H, Al(OH), Cu] are stronger oxidizing agents than (2; M = Zn).

Polarographic measurements show that (2; M = Co, Ni, Cu) has values of  $E_{\frac{1}{2}}$  of -0.3 V (*versus* n.h.e.) for the first reduction step.<sup>15</sup> From these and our cyclic voltammetric measurements the reductions are electrochemically less reversible due to precipitation of reduction products. With the aid of the lowest redox potential of -0.3 V, it is possible to calculate the redox energy of the lowest (spin forbidden) excited state, which is expected to be the photoactive level.<sup>10</sup> Furthermore, the triplet level of zinc phthalocyanine is not altered upon methylation.<sup>20</sup> The values in Table 5 show the strong oxidizing power of the redox couple  $\text{Sens}^{4+} - \text{Sens}^{3+}$  compared with phthalocyanines. The redox potentials of the first reduction step  $E^\circ(\text{Sens}/\text{Sens}^-)$  of phthalocyanines with M = Cu, Zn are *ca.* -0.6 V (*versus* n.h.e.),<sup>1</sup> whereas the value of zinc octacyanophthalocyanine [ZnPc(CN)<sub>8</sub>] is *ca.* +0.1 V (*versus* n.h.e.).<sup>32</sup> The  $E^\circ(\text{Sens}/\text{Sens}^-)$  potentials of porphyrazines with electron-withdrawing groups are shifted to more positive values.



**Figure 12.** Photoreduction of (2; M = 2H) ( $10^{-5}\text{M}$ ) with EDTA ( $10^{-3}\text{M}$ ) in water (— starting material; --- after different irradiation times)

Compared with unsubstituted phthalocyanines, the oxidizing power of the redox couple  $T_{\text{Sens}} - \text{Sens}^-$  for reductive quenching on irradiation with visible light is stronger in porphyrazines substituted with electron-withdrawing groups. In contrast, the reducing power of the couple  $\text{Sens} - \text{Sens}^-$  involved in a reaction in the dark is decreased. The chelates (2) are effective in double sensitization using EDTA as electron donor, whereby the two single steps are observable with (2; M = Zn).



For EDTA and cysteine as donors, redox potentials  $E^\circ(\text{Donor}_{\text{ox}}/\text{Donor})$  at pH 7 are cited as *ca.* +1.0 V (*versus* n.h.e.).<sup>33</sup> The calculated value  $E^\circ(T_{\text{Sens}/\text{Sens}^-}) \geq +1.0$  V (*versus* n.h.e.) (Table 5) indicates the possibility of a reductive quenching mechanism for the first step. The observed second reduction step with (2a,b; M = Zn) and the reduction of [2; M = 2 H, Al(OH), Cu] both show that the second reduction step must have a potential of  $E^\circ > +1.0$  V (*versus* n.h.e.). Thermodynamically, this may lead to  $\text{O}_2$  formation from  $\text{H}_2\text{O}$ . The different reactivity of EDTA and cysteine is not explained by the above mentioned facts. Using ascorbic acid as electron donor the first reduction product ( $\lambda_{\text{max.}}$  570 nm) is formed in a reaction in the dark. Data for the first reduction step in Table 5 show that reduction of methylviologen cannot be expected using sensitizers (2). Use of sensitizers (2) is limited to donors with  $E^\circ \geq +1.0$  V (*versus* n.h.e.) and acceptors with  $E^\circ \geq -0.3$  V (*versus* n.h.e.).

### Experimental

**Spectra.**—Electronic spectra were recorded on a Perkin-Elmer 554 instrument. <sup>1</sup>H N.m.r. spectra were measured with a Bruker WH 360 using tetramethylsilane as external standard.

Paper electrophoresis was carried out on Whatman 3 MM chroma paper at pH 1.5 using Phorograph Original Frankfurt, model 64. Cyclic voltammetry measurements were carried out with a Wenking ST 72 standard potentiostat, Wenking VSG 72 voltage scan generator using a PT-sheet (1 cm<sup>2</sup>) as working electrode, and an Ag-AgCl electrode [ $E^\circ(25\text{ }^\circ\text{C}) +0.222\text{ mV}$  versus n.h.e.] as reference electrode.

**Laser Flash Photolysis Measurements.**—Conventional laser photolysis was carried out by using an Nd-YAG laser, model HY-500 from JK Lasers Ltd., equipped with the second, third, and fourth harmonic generators. The second harmonic (532 nm), ca. 100 mJ cm<sup>-2</sup> and flash duration of 20 ns, was used for excitation of the sample solutions throughout this study. The light beam, after passage through a sample cell, came into the entrance slit of a monochromator (model MC-20 N from Ritsu Appl. Opt. Co.). The output from a Hamamatsu photomultiplier (R 758) attached to the slit of the monochromator was displayed on a Textronix oscilloscope, model 7904.

**Materials.**—All materials are of analytical grade or grade of highest available purity. Organic solvents were dried in the usual manner and distilled before use. Twice distilled water and argon of 99.998% purity were used if necessary.

**Photoredox Measurements.**—Measurements were carried out in a quartz cell (1 × 1 cm) at 24 °C under argon. Typically, a solution (3 ml) containing sensitizer (10<sup>-5</sup> M), donor (10<sup>-3</sup> M), and methylviologen (5 × 10<sup>-4</sup> M) with DMF-water (9:1 v/v) or water was used. The solutions were used without adding a buffer. The pH values of the solutions are ca. 9 working in DMF-water (9:1) and ca. 5.5 working in water. The quartz cell was placed into the light beam path of a u.v.-visible-spectrophotometer with DMF-water or water as reference. Perpendicular to the analytical light beam path the quartz cell was irradiated with visible light (400–700 nm) by opening a shutter. As light source a 12 V 100 W halogen lamp (power supply, Oriol 6329; lamp housing, Oriol 6385, condensing lamp assembly, f/0.75) with i.r.- and u.v.-cut-off filters (Oriol 5148 and 5740) was used. The light intensity was calibrated with a bolometer (Kipp and Zonen, CA1-754399) and adjusted to 150 mW cm<sup>-2</sup>. Irradiation and registration of the spectra were performed automatically through coupling to a computer. The concentration of MV<sup>•+</sup> was calculated from the increased absorption at 610 nm.  $\epsilon$  was assumed to be 13,700 l mol<sup>-1</sup> cm<sup>-1</sup>.<sup>34,35</sup>

**Tetrapyrido[2,3-b:2',3'-g:2'',3''-l:2''',3'''-q]porphyrazine Tetra-2,3-pyridinotetra-azaporphin (1; M = 2 H, Cd, Cu, Zn).**—2,3-Dicyanopyridine<sup>36–38</sup> (1.0 g, 7.7 mmol) and metal acetate (1.9 mmol) [for (1; M = 2 H) without addition of metal salt] were dissolved in dry *NN*-dimethylaminoethanol (100 ml) and then heated for 24 h at 130 °C under vigorous bubbling of dry ammonia through the solution. The dark blue product was filtered, washed with acetone, stirred for 1 h in DMF (20 ml) under reflux, filtered, treated 2 h with acetone in a Soxhlet-apparatus, and dried for 24 h at 200 °C in vacuum over P<sub>4</sub>O<sub>10</sub> (for further data, see Table 1).

**Tetra-2,3-pyridinotetra-azaporphin [1; M = Mg, Al(OH)].**—Mg or Al powder (4 mmol) was heated, after etching with iodine, with 2,3-dicyanopyridine (1.0 g, 7.7 mmol) in a sealed ampoule at 300 °C for 4 h. With M = Mg, the product was washed with DMF, treated with acetone in a Soxhlet apparatus, and dried for 24 h at 200 °C in a vacuum over P<sub>4</sub>O<sub>10</sub>. With M = Al(OH), the product was extracted into DMF from the reaction mixture and then treated with acetone in a Soxhlet

apparatus. The product was dried at 100 °C (for further data, see Table 1).

**Tetramethyltetrapyrido[2,3-b:2',3'-g:2'',3''-l:2''',3'''-q]porphyrazine Methyl Sulphate (1:4) (Quarternized Tetra-2,3-pyridinotetra-azaporphin) [2; M = 2 H, Al(OH), Cu, Zn].**—Compound (1) (0.2 mmol) was suspended in dry DMF (60 ml) and dimethyl sulphate (7.65 ml, 0.08 mol) was added. The mixture was heated to 120 °C with stirring under argon for 12 h. With M = 2 H or Al(OH), the cold, nearly clear solution was mixed with a ten-fold quantity of acetone to precipitate the reaction products. With M = Cu, Zn, the reaction products (2a) were directly isolated from the DMF solution. A ten-fold quantity of acetone was added resulting in the precipitation of (2b). All products were treated with dry acetone in a Soxhlet apparatus and dried in vacuum at 60 °C over CaCl<sub>2</sub> (for further data see Table 1).

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