Photoreduction of Methyl Viologen in Micellar Solutions Sensitized by Zinc Phthalocyanine

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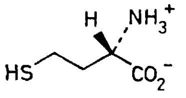
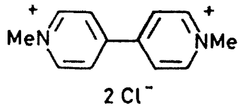
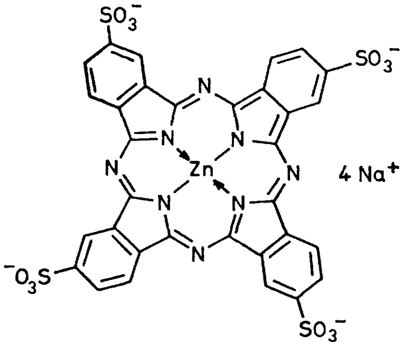
Summary Incorporating zinc(II) tetrasulphophthalocyanine in cationic micelles prevents dimerisation and inhibits the formation of photoinactive complexes with Methyl Viologen, and illumination of such solutions in the presence of cysteine leads to irreversible reduction of viologen; nonsulphonated zinc(II) phthalocyanine can also be solubilized in surfactant solutions and is a more efficient photosensitizer for this reaction.



(1) cysSH



(2) MV^{2+}



(3) Zn(pcts)

Photoproduction of H_2 from water is an expanding area of research, stimulated by the quest for an efficient method to convert sunlight into chemical potential. Recent work[1–4] has shown that three component systems, consisting of an electron donor [*e.g.*, cysteine (cysSH) (**1**)], an electron acceptor [Methyl Viologen (MV^{2+}) (**2**)], and a photosensitizer, can be used to evolve H_2 when a suitable catalyst (either hydrogenase or platinum) is present.

A large fraction of the solar spectrum could be harvested if the photosensitizer absorbs strongly in the near i.r. For this reason phthalocyanines are attractive chromophores, since they absorb very strongly in the region 660—700 nm

($\epsilon > 10^5$ mol l^{-1} cm^{-1}) Furthermore, they can be synthesized at low cost in a one-step process and the various known metallo-phthalocyanines offer a wide range of potentially useful redox states [5]

Recent work in our laboratory has shown that zinc(II) 4,4′,4″,4‴-tetrasulphophthalocyanine [Zn(pcts)] (**3**) is an inefficient photosensitizer in homogeneous aqueous solutions, since dimers are formed and aggregation occurs with MV^{2+} [6] We here report that this complexation can be prevented by incorporating Zn(pcts) into cationic micelles so that the photosensitized reduction of MV^{2+} can occur Nonsulphonated zinc(II) phthalocyanine [Zn(pc)] can also be solubilized in surfactant solutions and is a more efficient sensitizer than the sulphonated derivative

A μs flash photolysis system (Applied Photophysics KR 1) was used for time-resolved studies as described previously [4b] Steady-state illuminations used a 100-W quartz-iodide lamp with a filter to restrict light to $\lambda > 600$ nm Solutions were out-gassed by repeated freeze–thaw cycles

In a solution containing hexadecyltrimethylammonium chloride (CTAC) (10^{-2} mol l^{-1}), Zn(pcts) shows no deviation from Beers Law for the concentration range 10^{-7}—2 × 10^{-5} mol l^{-1} and no dimers could be detected A similar effect is observed with a neutral surfactant [Igepal CO-630 (A)], but anionic micelles (sodium decyl sulphate) were ineffective High surface charge on cationic micelles additionally prevents complexation between MV^{2+} and Zn(pcts) Concentrations of MV^{2+} up to 10^{-1} mol l^{-1} lead to only 15% fluorescence quenching In contrast, low concentrations of MV^{2+} were found to quench efficiently this fluorescence in homogeneous solution and non-fluorescent ion-pairs were formed [6]

Nonsulphonated Zn(pc) can also be solubilized in cationic (CTAC) and neutral micelles (A) Such solutions are strongly fluorescent and their visible spectra show that no dimers or oligomers are present

The metallo phthalocyanines Zn(pc) and Zn(pcts) can both act as photosensitizers for the reduction of MV^{2+} in aqueous micellar solutions When a sample containing MV^{2+}, cysSH, and photosensitizer is illuminated ($\lambda > 600$ nm), the spectrum of $MV^{\cdot+}$ (ϵ_{395} 3 8 × 10^4 and ϵ_{605} 1 1 × 10^4 mol l^{-1} cm^{-1}) develops with time, as shown in the Figure As with similar systems,[2–4] the rate of reduction decreases with time and the concentration of $MV^{\cdot+}$ reaches a constant value This is not due to destruction of the sensitizer which is very stable, but presumably results from competitive reactions of $MV^{\cdot+}$ The Table summarises the initial rate of $MV^{\cdot+}$ formation observed under various reaction conditions, the rate of reduction is strongly dependent on pH and cysSH concentration In neutral micelles, Zn(pcts) is a particularly poor photosensitizer for this reaction since nonproductive ion pairs can still be formed with MV^{2+} Nonsulphonated Zn(pc) is a more efficient photosensitizer in both neutral and cationic micelles In the absence of either cysteine or sensitizer no reduced viologen is observed

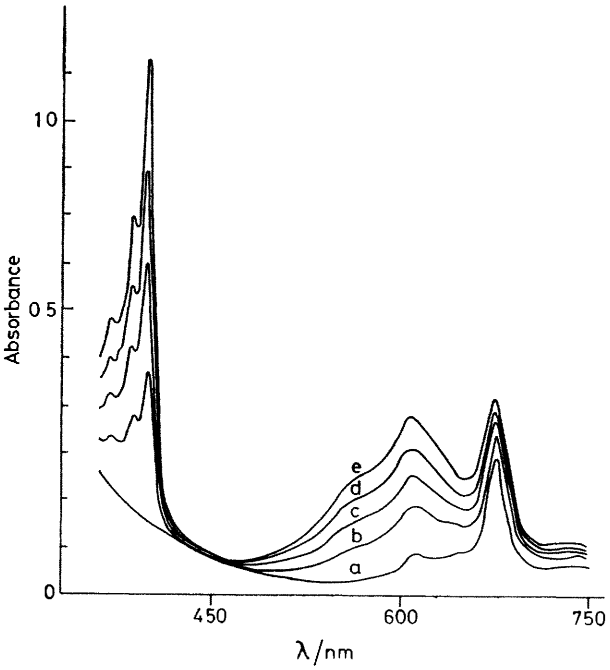


FIGURE Absorption spectrum of the three component system Zn(pc) (2 × 10^{-6} mol l^{-1}) MV^{2+} (10^{-2} mol l^{-1}) and cysteine (10^{-1} mol l^{-1}) in neutral micellar solutions of Igepal (5 × 10^{-3} mol l^{-1}) before (a) and after 5 min (b) 15 min (c) 30 min (d), and 60 min (e) illumination with red light

Flash photolysis and fluorescent studies have been used to investigate the mechanism of these processes The triplet state of Zn(pcts) was observed in cationic micelles (CTAC, 10^{-2} mol l^{-1}) and its spectrum was similar to that reported previously[7] for Zn(pc) in propanol Ground state recovery (677 nm) and decay of the triplet–triplet absorption (λ 480 nm) followed first-order kinetics (k 5 6 × 10^3 s^{-1}), a decay which was unaffected by concentrations of MV^{2+} up to 10^{-1} mol l^{-1} Also, fluorescence-quenching of the excited singlet state by MV^{2+} produced no charge-transfer products detectable on the μs timescale In contrast, cysSH was found to quench the singlet and

TABLE Variation in the initial rate of $MV^{\cdot+}$ formation

Sensitizer[a]	Surfactant[b]	Donor concentration/ mol l^{-1}	MV^{2+} concentration/ mol l^{-1}	pH	Initial rate 10^9 mol l^{-1} s^{-1}
Zn(pcts)	CTAC	10^{-1}	10^{-2}	6 5	2 2
Zn(pcts)	CTAC	10^{-2}	10^{-2}	6 5	1 0
Zn(pcts)	CTAC	10^{-1}	10^{-1}	6 5	2 5
Zn(pcts)	CTAC	10^{-1}	10^{-2}	8 0	4 7
Zn(pcts)	CTAC	10^{-1}	10^{-2}	4 6	0
Zn(pcts)	Igepal	10^{-1}	10^{-2}	6 5	1 0
Zn(pc)	Igepal	10^{-1}	10^{-2}	6 5	17
Zn(pc)	CTAC	10^{-1}[c]	10^{-1}	6 5	20

[a] 2 × 10^{-6} mol l^{-1} [b] [CTAC] = 10^{-2} mol l^{-1} and [Igepal] = 5 × 10^{-3} mol l^{-1} [c] Ethylenediaminetetra-acetic acid replaced cysSH as the electron donor

triplet states (k 1·4 × 10^5 mol l^{-1} s^{-1}) of Zn(pcts). These observations and those summarized in the Table are consistent with a mechanism involving reductive quenching of cysSH to give $Zn(pcts)^{\bullet -}$ and $cysSH^{\bullet +}$ as in reaction (1).

$$\mathrm{Zn(pcts)} \overset{h\nu}{\rightleftharpoons} {}^{*}\mathrm{Zn(pcts)}$$

$$^{*}\mathrm{Zn(pcts)} + \mathrm{cysSH} \rightarrow {}^{*}[\mathrm{Zn(pcts)}^{-} - - - \mathrm{cys}\overset{+}{\mathrm{S}}\mathrm{H}]$$

$$^{*}[\mathrm{Zn(pcts)}^{-} - - - \mathrm{cys}\overset{+}{\mathrm{S}}\mathrm{H}] \rightarrow \mathrm{Zn(pcts)}^{\bullet -} + \mathrm{cysSH}^{\bullet +} \qquad (1)$$

$$\mathrm{Zn(pcts)}^{\bullet -} + \mathrm{cysSH}^{\bullet +} \rightarrow \mathrm{Zn(pcts)} + \mathrm{cysSH} \qquad (2)$$

$$\mathrm{cysSH}^{\bullet +} \rightarrow \mathrm{cysS}^{\bullet} + \mathrm{H}^{+} \qquad (3)$$

$$2\mathrm{cysS}^{\bullet} \rightarrow \mathrm{cysSScys} \qquad (4)$$

$$\mathrm{Zn(pcts)}^{\bullet -} + \mathrm{MV}^{2+} \rightarrow \mathrm{Zn(pcts)} + \mathrm{MV}^{\bullet +} \qquad (5)$$

A large fraction of these radicals back-react in a non-productive cycle, but a significant fraction of the $Zn(pcts)^{\bullet -}$ radicals escape recombination owing to the formation of cystine in reactions (3) and (4).[4b] The radical anion $Zn(pcts)^{\bullet -}$ is a powerful reducing agent [E_0 −0·65 V[8] for Zn(pc)] and can reduce MV^{2+} (E_0 −0·45 V) in a slow, dark reaction (5), which is impeded by the high positive charge on the surface of the CTAC micelles so that high concentrations of MV^{2+} are required.

Alternative phthalocyanines and electron donors may be used to improve the efficiency of this system by increasing the charge separation achieved in reaction (1) and by impeding reaction (2) relative to reaction (5). The long wavelength absorption and low cost of phthalocyanines make further work in this area attractive.

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