PHOTOCHEMISTRY OF FREE-BASE PORPHYRIN LINKED TO METHYL VIOLOGEN

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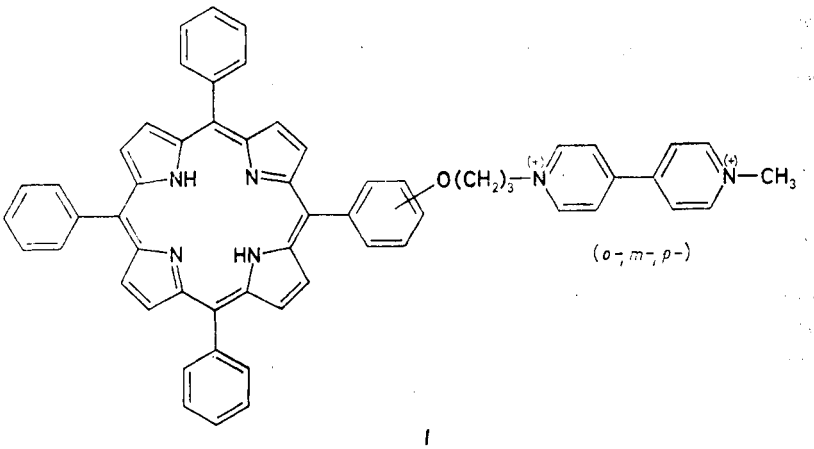
The photochemistry of free-base *meso*-tetraphenylporphyrin linked to methyl viologen via an alkoxy chain ($n = 3$) at the *ortho*, *meta* or *para*-position of one *meso*-phenyl group, in Triton X-100 micellar aqueous solutions is reported. The appended viologen does not quench the porphyrin fluorescence nor its triplet excited state due to the different solubilization of both parts of the molecule in the medium where the porphyrin ring resides in the hydrophobic phase and the alkoxy linker protrudes into the rather diffuse outer phase of detergent oxyethylene units, while the viologen moiety penetrates into the aqueous layer. However, laser flash photolysis measurements show that in the presence of nicotinamide dinucleutide, NADH, the porphyrin ring is reduced to phlorin due to the penetration of NADH into the organic phase. For porphyrin–tetraviologen in which a viologen molecule is linked to each of the porphyrin *meso*-position via alkoxy chain, fluorescence quenching could be achieved. The values of the quenching efficiency are high (94% in acetonitrile) compared to intramolecular quenching and are dependent upon the solvent viscosity.

In reaction centres of photosynthetic bacteria, nature makes extensive use of membranes and proteins to hold the reactants at optimum geometries so that electron transfer can proceed efficiently and rapidly. Among the systems studied which mimic the natural reaction-centre complexes is porphyrin and methyl viologen. It is well known that methyl viologen quenches the excited states of metalloporphyrins in fluid solutions[1-3]. Redox ion intermediates have been shown to arise from both excited singlet[4,5] and triplet[6] although the efficiency of the singlet state processes is very low. In part, this low efficiency is due to the short lifetimes of porphyrin singlet states (typically in the nanosecond region)[7] which require very high quencher concentrations for biomolecular diffusion to compete with non-radiative deactivation of the excited state. On the other hand, the redox ion products are rarely seen from metalloporphyrin singlet excited state reactions due to the favoured back-electron transfer in the intermediate ion pair[8,9].

To overcome the problems of relatively slow mass diffusion, the viologen moiety has been brought into close proximity with the porphyrin ring by electrostatic binding[10] and covalent bonding[10-13]. The latter approach offers a good means

of quenching the excited singlet state at low quencher concentration although the site of attachment requires careful design. Also, among the factors affecting the quenching efficiency are the chain length and the solvent.

The present study is devoted to the photochemistry of free-base *meso*-tetraphenylporphyrin covalently linked to methyl viologen *I* in micellar aqueous solutions owing to their importance as model systems mimicing natural photosynthesis.



I

EXPERIMENTAL

Materials

Monomethyl viologen covalently linked to free-base porphyrin in the *ortho*-, *meta*- and *para*-positions of one of the *meso*-aryl groups of tetraphenyl porphyrin, ($H_2P \sim MV^{2+}$) and tetramethyl viologen covalently linked to free-base porphyrin in *para*-positions of the *meso*-aryl groups of tetraphenylporphyrin were kindly provided by Dr A. Harrimann, Davy Faraday Research Laboratory, Royal Institution, London.

Triton X-100 (polyethylene glycol tert-octylphenylether) and methyl viologen were supplied from B.D.H. Reduced nicotinamide dinucleotide (NADH) was obtained from Sigma. The solvents, ethyl alcohol, acetonitrile, dimethylformamide and dimethyl sulfoxide were from Aldrich and were of spectroscopic grade.

Spectroscopic Measurements

Absorption spectra were recorded with Perkin–Elmer 554 spectrophotometer in cells of path length 1 cm. Fluorescence spectra were measured with a Perkin–Elmer MPF4 fluorescence spectrophotometer. Fluorescence quantum yields were calculated relative to zinc porphyrin by weighing the area under fluorescence emission curve, where $\Phi_F \approx$ area under the curve.

Flash Photolysis

Measurements were made using nanosecond flash photolysis system. A helical flash lamp pumped

a neodymium laser, which was passively Q-switched with vanadyl phthalocyanine in nitrobenzene. Absorption changes were followed using a high radiance monochromator and a Hamatsu R 928 photomultiplier tube. These changes were displayed on a Tektronix 5974 fast storage oscilloscope. The monitoring source was a 250 W xenon arc lamp. Measurements were made in a 1 cm quartz cell. Optical densities at the excitation wavelength (530 nm) were 0·2. The oscilloscope traces were photographed and digitized manually.

Steady State Irradiations

Samples were irradiated using an Applied Photophysics 950 W Xenon lamp and the light was filtered to remove $\lambda < 350$ nm. For anaerobic experiments, micellar aqueous solutions were flushed with oxygen-free nitrogen for 30 min. The rate of bubbling was very slow in order to minimize foaming.

RESULTS AND DISCUSSION

Spectroscopic Properties

Porphyrin covalently linked via a flexible chain in *ortho*-, *meta*- or *para*-positions to methyl viologen ($H_2P{\sim}MV^{2+}$) in aqueous solution of Triton X-100 (5 vol.%) exhibits the typical porphyrin absorption and emission spectra[14], assigned to (π, π^*) transition with no evidence for any perturbation due to linking methyl viologen to the free-base porphyrin (Fig. 1).

The value of the fluorescence quantum yield of $H_2P{\sim}MV^{2+}$ in Triton X-100 micellar aqueous solution is identical with that of the free-base porphyrin indicating the absence of intramolecular interaction between singlet excited porphyrin and methyl viologen. Such a result is believed to be due to the solubilization effect of the micellar medium. The solubilization of $H_2P{\sim}MV^{2+}$ in a Triton X-100 micelle is presumably visualized in a configuration in which the porphyrin ring resides in the inner hydrophobic core and the alkoxy chain protrudes into the rather diffuse outer core of detergent (oxyethylene oxide) units, while the viologen moiety penetrates into the aqueous phase. This finding is in contrast to the studies of zinc porphyrins bound with methyl viologen in alcoholic solutions, which showed intramolecular electron transfer between their singlet excited states and methyl viologen[10]. To prove the effect of the medium on the quenching process, the study was carried out in fluid solutions involving the tetraviologen complex where efficient fluorescence quenching of the singlet excited state of porphyrin was observed. The solubilization of the porphyrin tetraviologen in water can be explained as being due to the strong packing of the four hydrophilic methyl viologen moieties upon the hydrophobic porphyrin ring adapting a cofacial arrangement leading to an effective (π–π^*) overlap for intramolecular electron transfer[15].

The quenching of the signlet excited state of porphyrin linked to four viologens was also studied in various solvents (Table I). Data obtained indicate that the quenching efficiency decreases with increasing viscosity of the solvent.

Relative fluorescence quantum yield for porphyrin–tetraviologen compound in ethanol solution ($\phi_F = 5{\cdot}5$) when compared to that of the free base porphyrin ($\phi_F^0 = 43$) under the same experimental conditions gives a value of $\phi_F^0/\phi_F = 7{\cdot}8$. This value when compared to the Stern–Volmer plot (Fig. 2, intermolecular quenching of free-base porphyrin by methyl viologen) indicates that for reduction of ϕ_F of free-base porphyrin by intermolecular quenching to the level observed for the intramolecular quenching of porphyrin–tetraviologen, concentration of methyl viologen must reach in the solution 0·11 mol dm^{-3}. This shows the tremendous quenching efficiency of the intramolecularly bound viologen in fluid solutions.

TABLE I

Fluorescence quenching of porphyrin–tetraviologen compound in different solvents

Solvent	Viscosity cp	Quenching %
Acetonitrile	0·352	94
Dimethylformamide	0·802	85
Dimethyl sulphoxide	1·996	81

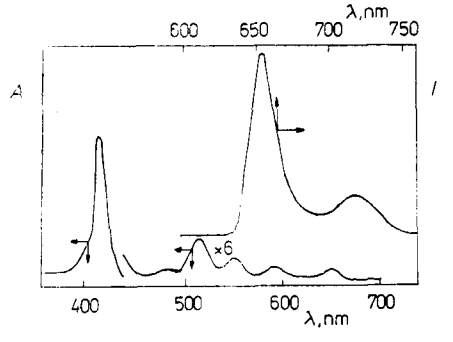


FIG. 1

Absorption and fluorescence spectra of *ortho*-$H_2P \sim MV^{2+}$ in Triton X-100 micellar aqueous solution (5 vol. %)

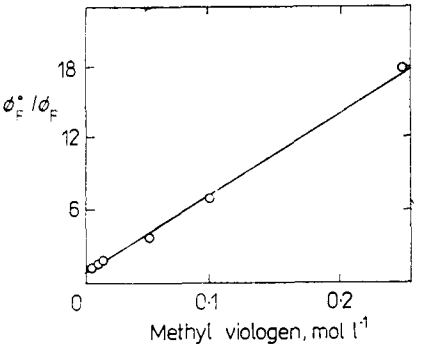


FIG. 2

Stern–Volmer plot for quenching of free-base tetraphenyl porphyrin by methylviologen (MV^{2+}) in methanol solution

Flash Photolysis

$H_2P\sim MV^{2+}$. Flash photolysis study of the triplet absorption spectrum of *ortho*-$H_2P\sim MV^{2+}$ in air equilibrated Triton X-100 micellar aqueous solution showed a maximum absorption at λ 800 nm, characteristic of the triplet spectrum of the free-base porphyrin in organic solvents. From the triplet decay curves for *o*-, *m*-, and *p*-$H_2P\sim MV^{2+}$, a value of 1 μs was obtained for the triplet lifetime irrespective of the position of methyl viologen. This value is identical with that of the free base porphyrin under the same experimental conditions indicating that, similar to the singlet excited, the triplet excited state of the porphyrin was not quenched by methyl viologen. This is believed to be due to particular orientation of the compounds in the medium. Consequently, the geometry possessed by $H_2P\sim MV^{2+}$ due to solubilization in micellar system reflects the spatial separation of the porphyrin moiety which could explain the efficiency of the intramolecular electron transfer.

$H_2P\sim MV^{2+}$ and NADH. Micellar aqueous solutions of $H_2P\sim MV^{2+}$ containing various concentrations of NADH ($10^{-5}-10^{-2}$ mol l^{-1}) were studied by laser flash photolysis in aerated solutions. Figure 3 shows that at low concentrations of NADH ($10^{-5}-10^{-4}$ mol l^{-1}), the triplet decay of $H_2P\sim MV^{2+}$ was unchanged where a max-

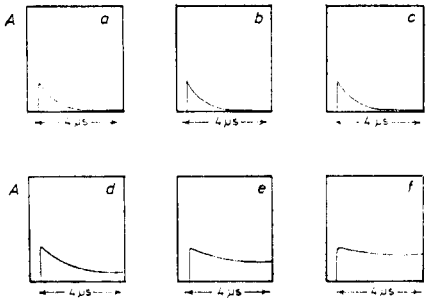


FIG. 3

Typical flash photolysis oscillograms showing triplet decay of Triton X-100 micellar aqueous solutions of $H_2P\sim MV^{2+}$ in presence of different NADH concentrations (mol l^{-1}). *a* 0; *b* 10^{-5}; *c* 10^{-4}; *d* 10^{-3}; *e* 5.10^{-3}; *f* 5.10^{-2}

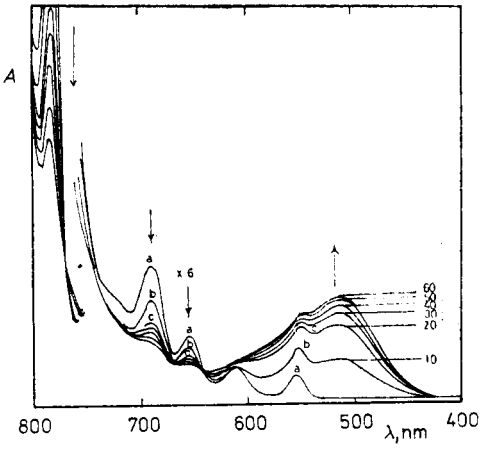


FIG. 4

Photolysis of degassed Triton X-100 micellar aqueous solution containing $H_2P\sim MV^{2+}$ (10^{-5} mol l^{-1}) in presence of NADH (3.10^{-2} mol l^{-1}). Absorption spectra taken after different irradiation time intervals (min). a 0; b 10; c 20

imum transmittance of the monitoring light was obtained after triplet decay is complete. Also the calculated value of the triplet decay rate constant of $H_2P \sim MV^{2+}$ ($k = 0{\cdot}99\,\mu s^{-1}$) is similar to that in absence of NADH (Fig. 3,*a*–*c*). This indicates that NADH, similar to MV^{2+}, is mainly residing in the aqueous phase of the micellar system and thus it is far away from the porphyrin ring. However, at high concentrations of NADH ($10^{-3}-5 \cdot 10^{-2}$ mol l^{-1}), a remarkable decrease in transmittance of the monitoring light in the triplet decay curve of $H_2P \sim MV^{2+}$ was observed due to product formation (Fig. 3, *d*–*f*). As NADH concentration increases, it approaches the excited porphyrin to form the encounter complex required for electron transfer reaction between an excited acceptor (A*) and donor (D). It is believed that this can take place if NADH enters through water channels created by the introduction of the porphyrin ring moiety[16,17] or by partitioning of the NADH between the aqueous and micellar phases with a certain distribution coefficient and thus by increasing the total NADH concentration the probability of its presence in the organic phase is increased as well.

Steady State Photolysis

Micellar Triton X-100 solution of *ortho*-, *meta*- and *para*-$H_2P \sim MV^{2+}$ were stable upon prolonged irradiation with visible light ($\lambda > 500$ nm) up to four hours in degassed solutions. However, in the presence of NADH ($3 \cdot 10^{-3}$ to $3 \cdot 10^{-2}$ mol l^{-1}), photolysis leads to the formation of a new broad band around 680 nm, Fig. 4. The photolysis product was identified as phlorin via a comparison with the spectra of an authentic sample. The phlorin formation was confirmed by aeration of the final solution which caused the oxidation of phlorin to the parent porphyrin.

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