Viologen-capped Porphyrins as Model Photosynthetic Systems: Intra- and Intermolecular π–π Interactions

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The title compounds exhibit extremely efficient fluorescence quenching, remarkable solution aggregation, and unusual oxidation potentials; these effects are attributed to strong intramolecular π–π interactions which themselves give rise to intermolecular attraction.

Photosynthesis is, in essence, a light-induced electron transfer from a donor (D) to an acceptor (A); this process results in the generation of chemical oxidising (D^+) and reducing (A^-) power. The search for model photosynthetic systems is centred around the synthesis of molecules which contain electron donating and accepting groups suitably arranged so that $k_1 > k_{-1}$, equation (1).[1—3] We report here that the methylviologen-capped porphyrins (**1**) and (**2**) show very promising π–π interactions as detected by fluorescence quenching, electrochemistry, and n.m.r. spectroscopy.

The synthesis of the bipyridyl-capped compounds (**3**) and (**4**) was described in the preceding communication.[4] Treatment of (**3**) and (**4**) with methyl iodide in CH_2Cl_2 gave the viologens (**1**) and (**2**) in good yield as the di-iodide salts. Anion exchange on IR45 gave the di-chloride salts.†

$$A + D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + D^+ \qquad (1)$$

^1H N.m.r. spectra of (**1**) and (**2**) showed the characteristic non-selective broadening of aggregated porphyrins; the effect

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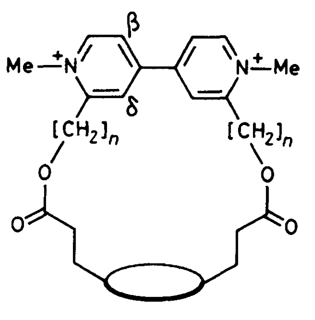
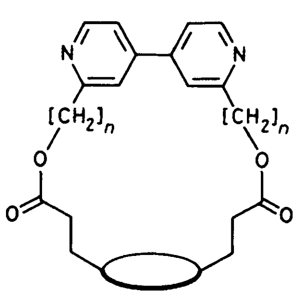
† All new compounds gave satisfactory u.v., n.m.r., and fast atom bombardment-mass spectra.



(1) n = 3
(2) n = 4



(3) n = 3
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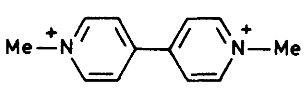
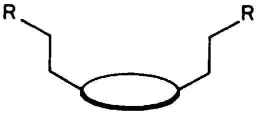


(5)



(6) $R = CH_2OH$
(7) $R = CO_2Me$

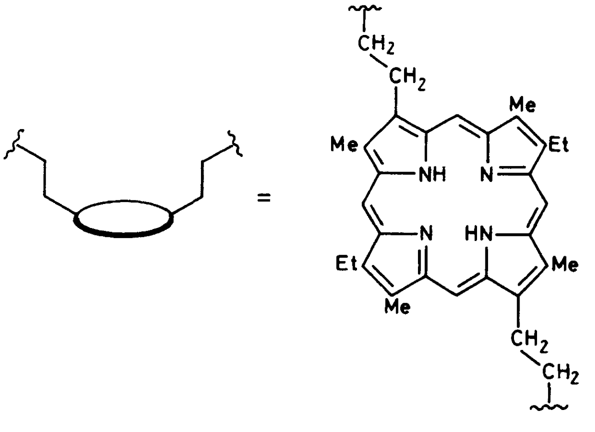


Table 1. Fluorescence quenching in capped porphyrins.[a]

Compound	Relative fluorescence (620 nm)
(7)	1.0
(5) $2Cl^-$ + (7) (1 : 1)	0.92
(1) $2Cl^-$	0.0048
(3)	0.92
(2) $2Cl^-$	0.0056
(4)	0.88

[a] MeCN solutions ($<10^{-5}$ M) with absorbance = 1.28 at 395 nm. Excitation at 395 nm.

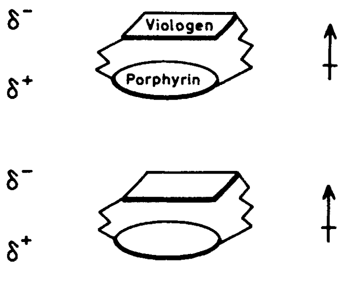


Figure 1

was stronger for the chlorides than the iodides, and more marked in polar (D_2O, CD_3OD) than in non polar (CD_2Cl_2) solvents. Only in CD_3CN was it possible to obtain spectra of the chloride salts with relatively 'normal' linewidths. H_β and H_δ on the viologen cap are each shifted 1.8 p.p.m. upfield (relative to uncapped viologen) by the porphyrin ring current. This result shows that the effective planarity of methyl viologen (**5**) is retained in these capped compounds.

U.v.-visible spectroscopy confirms the presence of the strong aggregation. Solutions of (**1**) di-iodide in water do not obey Beer's law even at 10^{-6} M. However, in agreement with the n.m.r. observations, (**1**) dichloride did appear to be monomeric and obey Beer's law at 10^{-4} M in acetonitrile. The Soret band (with extinction coefficient) for mesoporphyrin-II-dimethyl ester, for (**3**), and for (**1**) occurs at 398 nm (ε 1.7 × 10^5 $dm^3 mol^{-1} cm^{-1}$), 400 (1.5 × 10^5), and 400 nm (1.1 × 10^5) respectively.

No combination of solvent, methylviologen (**5**) itself, and meso-II-porphyrin diol (**6**) gave any evidence, either by n.m.r. or u.v. spectroscopy, of substantial interactions. The strong intermolecular aggregation of (**1**) and (**2**) must therefore result from the influence of intramolecular effects. The oxidation potentials for (**1**) and (**3**) (relative to standard hydrogen electrode) are +0.93 and +0.78 V respectively. The 150 mV shift implies that the porphyrin moiety in (**1**) is electron deficient. We suggest, therefore, that there is polarisation of electron density from porphyrin to viologen, giving rise to strong aggregation (Figure 1).

Further evidence for π–π interaction comes from fluorescence quenching measurements on non-aggregated (**1**)—(**4**) in acetonitrile (Table 1). Following excitation of the Soret band, the fluorescence emissions of (**1**) and (**2**) are reduced by *ca.* 260 and 180 fold respectively, relative to the unquaternised (**3**) and (**4**). The iodide salts of (**1**) and (**2**) show a further 2—3 fold quenching.

These appear to be the most efficient fluorescent quenching results reported to date, and presumably indicate very efficient trapping of the excited electron by the viologen, to give the radical cation of both chromophores. Preliminary e.s.r. experiments show that visible light irradiation of (**1**) and (**2**) dichlorides (10^{-4} M in frozen acetonitrile glass matrix) indeed generates radicals.

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