

Quinone-capped Porphyrins as Model Photosynthetic Systems: Use of Metal Co-ordination to Control Chromophore Orientation and Interaction

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Extremely efficient fluorescence quenching occurs when the quinone and porphyrin chromophores of the title compounds are effectively parallel; intramolecular metal co-ordination forces the quinone to be perpendicular, and reduces the fluorescence quenching.

Previous reports from this laboratory have described the synthesis of the quinone-capped porphyrins (1)–(4),¹ and the co-ordination properties of (3) and (4).² It appeared² that the perpendicular relationship between porphyrin and quinone, which results from intramolecular binding of quinone to magnesium, led to 'relatively unremarkable photochemical properties.' We now report striking confirmation of that hypothesis, and show that judicious choice of central metal ion, or the absence of metal ion, leads to very strong chromophore interactions and extremely efficient fluorescence quenching.

Zinc was chosen as a central ion for the following reasons: (i) it is more readily inserted than magnesium, and once inserted is more resistant to demetallation; (ii) zinc porphyrins have similar spectroscopic and electrochemical properties to magnesium porphyrins but they have lower affinity for oxygen ligands; (iii) zinc is exclusively five-co-ordinate in porphyrins.³ It was therefore expected that there would be less cap–porphyrin interaction and that the interaction would be controllable. Zinc insertion into (1) and (2), to give (5) and (6), was readily achieved with $Zn(OAc)_2$ in $CHCl_3$ –MeOH.[†]

Figure 1 summarises some of the n.m.r. evidence on which we base our conclusions concerning the geometry and co-ordination properties of these materials. The shifts of the quinone proton [Figure 1(a)] are essentially sensitive only to the quinone–porphyrin distance,[‡] whereas the methylene proton H^* [Figure 1(b)] is also sensitive to its orientation with respect to the quinone. § The shifts in the free bases (1) and (2)

are characteristic of the geometry where there is no co-ordination between cap and porphyrin. A larger upfield shift demonstrates that on average, the quinone proton is closer to the porphyrin in the longer chain compound (2).

The shifts in the Mg complexes (3) and (4) *in the absence of the ligand* are characteristic of the geometry where the quinone is intramolecularly bound through a carbonyl group to the central metal ion. This intramolecular binding is demonstrated by the very low affinity of (3) and (4) for added ligand; the binding constant K for 3,5-lutidine is 150 l mol^{-1} for (3), and 30 l mol^{-1} for (4), as against 10^4 for normal porphyrins. Note that (3) and (4) have essentially identical geometries. Addition of ligand changes the geometries but does not yield 'free-base' geometry; six co-ordination occurs, at least in part.^{2,3}

By contrast, the zinc complexes in the presence of added ligand have very similar geometries to the free base compounds. This is to be expected from the five co-ordination limit of zinc, and the likelihood that intramolecular binding is strained.^{3,4}

The intramolecularly bound zinc complexes are either intermediate in geometry between free base and the Mg complexes, or are in equilibrium between free and bound forms. We favour the latter explanation because (a) evidence from related molecules shows virtually identical binding geometries for Zn and Mg porphyrins,⁴ and (b) the binding constant for added 3,5-lutidine is much higher for the short-chain compound [300 for (5)] than the long-chain compound [60 for (6)]. This implies more co-ordinative unsaturation in the short chain compounds.

The absorption spectra of all the capped porphyrins are very similar to those of their uncapped analogues, indicating the lack of a strong ground-state cap–porphyrin interaction. The zinc complexes have Soret absorptions at 405 nm, which is intermediate between the positions which are characteristic of four- and five-co-ordinate ions.³

† Both new compounds gave satisfactory u.v., n.m.r., and mass spectra.

‡ The observed shift is the average of two non-equivalent positions. Rapid spinning of the quinone ring interconverts these protons, so the average orientation is of no consequence.

§ Other protons behave similarly, but the shifts are smaller.

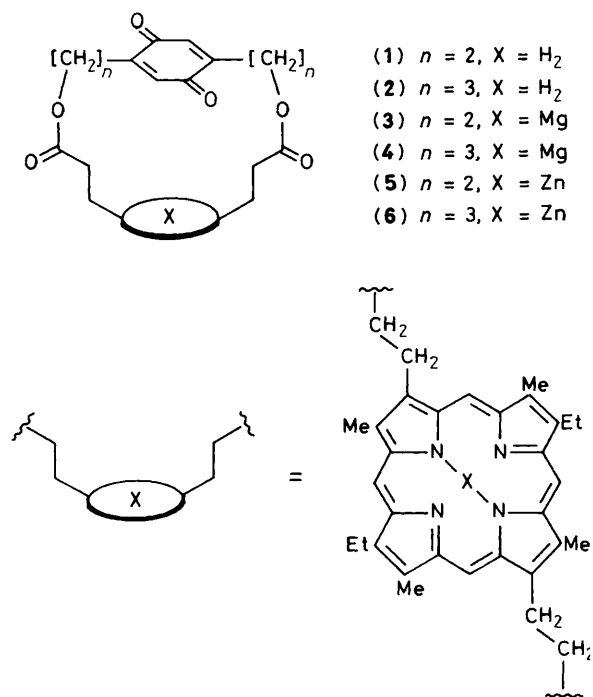


Table 1. Fluorescence properties of quinone-capped porphyrins (1)–(6).

Central ion	Relative fluorescence intensity ^a	
	$n = 2$	$n = 3$
H_2	$10 (\times 10^{-3})$	$1.1 (\times 10^{-3})$
Zn^b	33	2.9
Mg^b	100	50

^a Relative to uncapped porphyrin; for excitation of the Soret band; solutions were $< 10^{-5}$ M in MeCN, with absorbance at the Soret band = 1.28. Fluorescence intensities were similar in dichloromethane solutions. ^b Relative fluorescence intensities were virtually identical in the presence or absence of added ligand.

The geometrical differences revealed by n.m.r. spectroscopy are strongly reflected in the fluorescence properties of these compounds (Table 1). All the quinone-capped porphyrins show efficient fluorescence quenching, relative to the corresponding H_2 , Zn, or Mg *meso*-porphyrin II dimethyl ester. The free base and Zn porphyrins are much more efficient than the Mg derivatives and the long-chain free base and Zn porphyrins are an order of magnitude more efficient than their shorter chain analogues. In contrast, both Mg porphyrins are very similar, reflecting the n.m.r. conclusions. Reference mixtures of *meso*-porphyrin II ester and quinones showed no significant effect, and observations on other capped porphyrins show no intrinsic differences in the fluorescence of Mg and Zn porphyrins.⁵

It appears, therefore, that the close approach of the chromophores (as detected by n.m.r.) leads to more efficient quenching, presumably *via* intramolecular electron transfer.⁶ It also appears that this quenching is more efficient with the chromophores effectively parallel than perpendicular. For the zinc porphyrins, we presume that quenching occurs in the 'unbound' conformation; this is likely to have a lifetime of only a millisecond or less, but this is orders of magnitude more

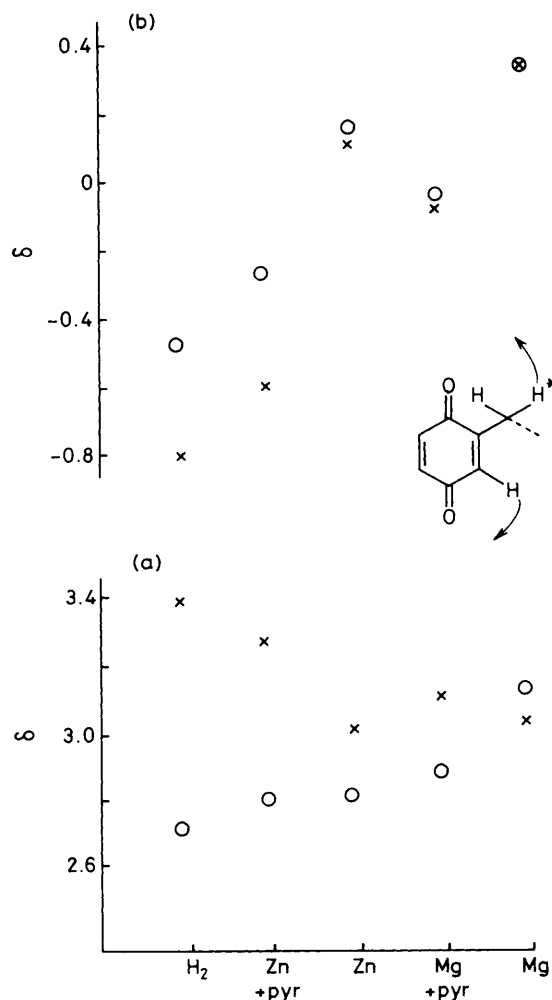


Figure 1. 1H Chemical shifts in CD_2Cl_2 solutions of quinone-capped porphyrins \times : $n = 2$; \circ : $n = 3$. In the corresponding non-capped quinones, the quinone proton and H^* resonate at δ ca. 6.7 and 2.7 respectively.

than is required for electron transfer.⁷ Therefore further increasing the unbound population by adding ligand has little effect.

We are grateful to Dr. D. East for use of his fluorescence spectrometer and to the S.E.R.C. for financial support. The quinone-capped porphyrin samples were synthesised by Dr. K. N. Ganesh.

Received, 18th July 1984; Com. 1043

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