Quinone-Capped Metalloporphyrins: Synthesis and Co-ordination Chemistry

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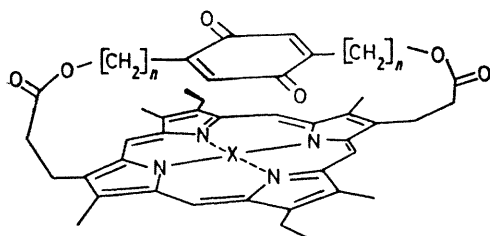
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Summary Compounds in the title series have been synthesised by capping mesoporphyrin-II with protected hydroquinone derivatives, deprotection, and oxidation, followed by magnesium insertion; ^{1}H n.m.r. spectroscopy demonstrate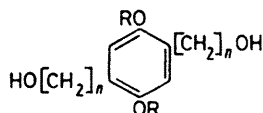s that the metal ion is 5-co-ordinate, bound intramolecularly to a quinone carbonyl oxygen, and can accept a sixth ligand from the unhindered side.

PHOTOSYNTHESIS is, in essence, a light-induced electron transfer from a donor (D) to an acceptor (A) resulting in the
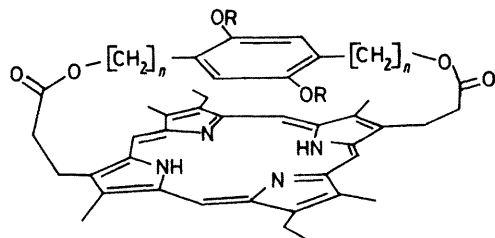
generation of chemical oxidising and reducing power (D+ and A−). Numerous laboratory approaches to synthetic photosynthesis are being investigated at present, including those based on both catalytic[1] and modified[2] chlorophylls, porphyrins,[3] and on other chromophores, some inorganic.[4] We report here the synthesis of the quinone-capped porphyrins (1) and (2) and the metallated derivatives (3) and (4). This type of system is attractive because the relative oxidation–reduction potentials, chromophore orientation, absorption maxima, and co-ordination chemistry can all be rationally controlled by synthesis.† In addition these molecules should be useful in connection with studies of the thermal electron transfer[5,6] and co-ordination chemistry[5,7] of chlorophylls and porphyrins; finally they have promise in the area of radical-induced pseudocontact n.m.r. shifts.[5,8]

suitable for model compounds in the presence of porphyrins. The methoxymethyl compounds (6) and (7) condensed with mesoporphyrin-II bisacid chloride to give the desired (9) and (10) in 5 and 15% yield, respectively These were then deprotected (BCl₃, 90%) and oxidised (PbO₂, 85%) to quinones (1) and (2). Magnesium was inserted by Eschenmoser's method[10] to give (3) and (4) in 85% yield.

(1) n = 2, X = H₂
(2) n = 3, X = H₂
(3) n = 2, X = Mg
(4) n = 3, X = Mg

(5) R = Me, n = 2
(6) R = CH₂OMe, n = 2
(7) R = CH₂OMe, n = 3

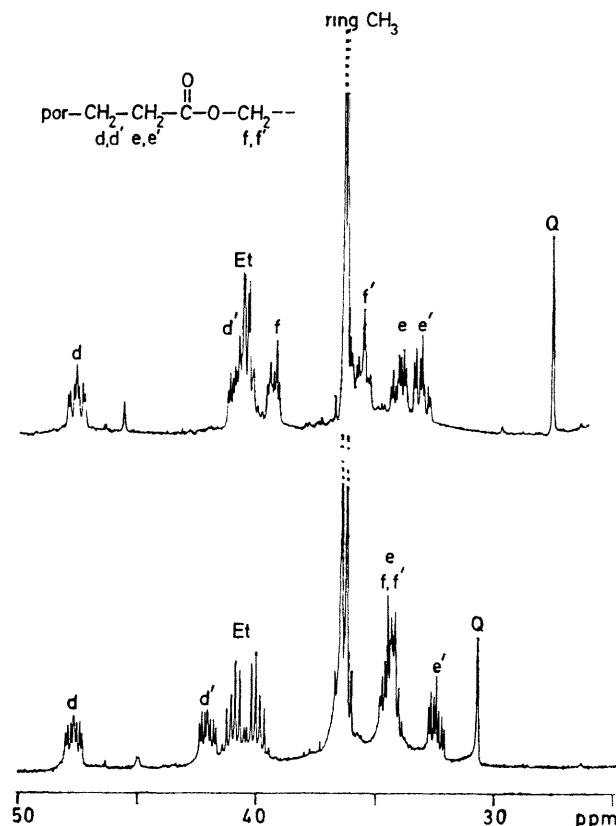(8) R = Me, n = 2
(9) R = CH₂OMe, n = 2
(10) R = CH₂OMe, n = 3

FIGURE. Lower trace: partial 400 MHz ^{1}H n.m.r. spectrum of (4) (1 mg/0·4 ml CDCl₃), resolution enhanced. Upper trace: the same after addition of C₅D₅N. Q is the proton directly attached to quinone ring, por denotes the porphyrin nucleus.

Mesoporphyrin-II bisacid chloride was allowed to react with the protected hydroquinone (5) under high dilution in dichloromethane[9] but the resulting capped product (8) could not be converted into (1) using a variety of conditions

N.m.r. spectra of capped porphyrins are highly characteristic. The molecules are chiral, so the protons within each methylene group, including ethyl, are diastereotopic (see the Figure). The protons of the cap are shifted upfield by up to 4 p.p.m. by the porphyrin ring current (Table); proton relaxation rates ($R_1 = 1/T_1$) at ambient temperature are ca. twice as large as in simple porphyrins but are much more temperature dependent.‡ In addition, the chemical shifts of the cap protons in (4) are dependent on the presence of external ligands in a way which allows elucidation of some details of both intra- and inter-molecular co-ordination chemistry [(3) behaves similarly].

† The development of more sophisticated model systems is being carried out in collaboration with Prof. A. R. Battersby's group.

‡ We believe this is because the motion causing relaxation is a spinning around the fourfold axis like a disk: in capped porphyrins the same motion is severely hindered (as the cap must displace solvent, rather like a propeller) but more sensitive to solvent viscosity.

TABLE. Some chemical shifts of quinone-capped porphyrins.[a]

Proton	(2)	(4)	(4) + pyridine
Q	2·57	3·07	2·76
d	4·61	4·76	4·76
d′	3·91	4·20	4·10
e	3·3[b]	3·4[b]	3·41
e′	3·3[b]	3·24	3·31

[a] In p.p.m. ($\pm$ 0·01) for ca. 3 mM solutions in $CDCl_3$. All assignments have been confirmed by n.O.e. difference spectroscopy or spin decoupling. Only a few representative protons are shown here. [b] $\pm$ 0·1 p.p.m. owing to overlap.

The Figure shows a portion of the 400 MHz proton n.m.r. spectrum of (4) in the presence and absence of pyridine; analysis of the proton shift titration curves of both the porphyrin and added pyridine gives a binding constant of only ca. 10^2 l mol^{-1}, indicating that pyridine is a *sixth* ligand. The central magnesium ion is therefore bound to a quinone carbonyl oxygen as fifth ligand. The relative simplicity of these spectra demonstrates that exchange of quinone carbonyls as the ligand is rapid on the n.m.r. time-scale. Neither shifts nor relaxation rates are concentration dependent, ruling out intermolecular quinone–metal interactions.

Upfield shifts induced in the pyridine protons on binding to (4) are essentially identical to those induced by model porphyrins, confirming that the mode of binding is, as expected, from the unhindered side The proton attached directly to the quinone moiety in (4) is shifted 4·0 p.p.m. upfield in the absence of pyridine and a further 0·3 p.p.m. on addition of pyridine, consistent with but not proving, a 5-co-ordinate out-of-plane metal ion being pulled into the plane when a sixth ligand is added from the unhindered side. Further evidence for the maintenance of metal–quinone binding comes from detailed analysis of coupling constants which change only slightly on pyridine binding, but which are quite different from those in (1) and (2).

U.v./visible spectra of (3) and (4) show only slight differences from model compounds; however, both the nanosecond photochemistry[11] and the electrochemistry of these compounds demonstrate substantial deviations from normality.

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