Chemical modelling of photosynthesis: Intramolecular quinone-porphyrin complexes

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Abstract. The strategies for the synthesis of covalently linked, flexible and rigid quinone-porphyrin complexes are described. Several anomalous chemical reactivities were observed in the quinone-capped porphyrins which may be attributed to the proximity of quinone and porphyrin moieties. Previous investigations by ^{1}H NMR spectroscopy have demonstrated that the metal ion in capped metalloporphyrins is 5 co-ordinate, bound intramolecularly to quinone carbonyls and can accept a sixth ligand from the unhindered side. Here, additional evidence from ^{13}C NMR spectroscopy is presented to support the intramolecular co-ordination of the quinone and establish the cooperativity in binding of an external ligand; this process involves the movement of the metal ion into the porphyrin plane, pulling the quinone chromophore closer to the porphyrin. Electrochemical results reveal that the quinone in capped metalloporphyrins are better electron acceptors than simple quinones. The intramolecular quinone-porphyrin complexes promise to be potential model compounds to demonstrate the primary photosynthetic event *in vitro*.

Keywords. Photosynthetic modelling; quinone-porphyrin complexes.

1. Introduction

The primary photochemical process in algal and green plant photosynthesis is known to involve a one-electron transfer reaction from a chlorophyll donor species to an electron-acceptor molecule, the electron transfer taking place across the thylakoid membrane within a special reaction centre. There have been numerous laboratory approaches to mimic this reaction *in vitro*, the objective being to achieve a stable charge separation after the electron transfer from the excited donor (D) to the acceptor (A).

$$A + D \xrightarrow{h\nu} [AD]^* \rightarrow A^- + D^+.$$

A special arrangement of the donor-acceptor molecules *in vivo* permits efficient electron transfer and to achieve this *in vitro*, experimental attempts have centred around studies on catalytic and modified chlorophylls, porphyrins and other chromophores. Among the various factors responsible for an efficient electron transfer are the relative oxidation-reduction potential of donor-acceptor system, chromophore separation, relative orientations and absorption characteristics. Since all these factors are amenable to a rational control by chemical synthesis, a new class of molecules, "quinone-porphyrins", have emerged in which the two chromophores are covalently linked. This article is intended to highlight the various synthetic approaches, interesting photo-chemical and spectroscopic properties of these intramolecular complexes, which promise to be potential non-biological models for the primary photosynthetic event.

One of the prime motivating factors for studying the covalently linked quinone-porphyrins arises from the fact that simple irradiation of porphyrins or metallo-porphyrin complexes in the presence of quinone does not lead to an effective separation

of the oxidizing species (porphyrin radical cation) and the reducing species (quinone radical anion). At low concentrations of the electron acceptor, the large separation between the donor and acceptor molecules may result in an inefficient electron transfer, whereas at high concentrations the two species may be too close resulting in a fast recombination of charges. In frozen or aggregated states, the structural features are not well defined to systematically probe the structure-function relationships. In view of these facts, quinones which are covalently bonded to porphyrin framework are of interest in evaluating the structure and photochemical properties and as aid in the molecular engineering of a synthetic photosystem.

Structurally, two classes of quinone-porphyrins can be recognised: (i) quinone-tailed porphyrins in which a quinone moiety is linked through spacer groups to a porphyrin at the meso position either directly such as (1) and (2) or through a phenyl substituent at meso position, e.g. (3) and (4) and (ii) quinone-capped porphyrins (5–8) in which the diagonal pyrroles are connected by a bridge which spans across one face of the porphyrin and contains a quinone function. The following sections discuss separately these two classes of molecules.

2. Quinone tailed porphyrins

2.1 General synthetic approach

The general synthetic approach to this class of porphyrins involves an initial preparation of unsymmetrically substituted porphyrins. This is achieved by a slight modification of the general procedure (Adler et al 1967) which involves condensation of equimolar amounts of pyrrole and an aldehyde. For unsymmetrically substituted prophyrins, a second aldehydic component is added in stoichiometric amounts to the reaction mixture (Kong and Loach 1980). This leads to a mixture of products in which either some or all phenyl rings at the meso positions carry substituents. The ratio of products can be controlled by the stoichiometry of the starting aldehydes and the separation of products effected by chromatography. The functional group on the phenyl rings are then used as anchor points to append the benzoquinone through a spacer chain. The quinone functions are masked either as dimethyl ethers or as diacetates at the stage of condensation with the porphyrin. On deprotection under mild conditions (e.g. BBr_3 in CH_2Cl_2), one obtains the hydroquinone-porphyrins which are converted into quinone-porphyrins with oxidizing agents such as 2,3-dichloro-5,6-dicynanobenzoquinone (DDQ) or lead dioxide in benzene. By varying the length of the spacer chain, the distance between the two chromophores can be controlled and the point of anchor on the porphyrin can be o-, m- or p-position on the phenyl ring. These possibilities allow a subtle control over the orientation of the two chromophores in the final product. When the starting porphyrin has no aromatic substituents at meso position such as that required for (1), Vilsimier reaction introduces an aldehyde group at the meso position; this after reduction to a hydroxymethyl group serves as an extension point to add the quinone chain (Nishitani et al 1981).

2.2 Spectral characterisation

The UV-visible absorption spectrum of the quinone-linked porphyrins exhibit no major changes compared to unlinked entities except in case of (2). They are almost identical to
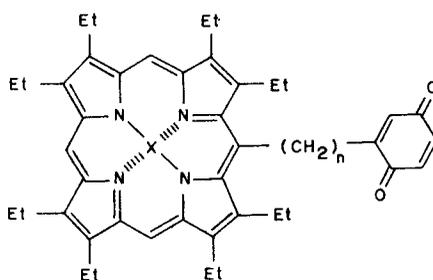
(1) $n = 2, 4$ and 6, $X = H_2$ and Zn
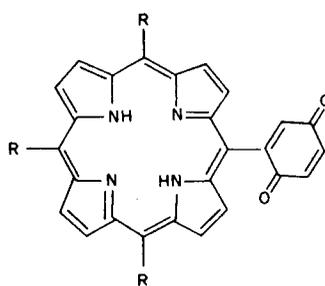
(2)

a 1:1 addition spectrum of the two components and hence indicate no appreciable interaction between the two chromophores in ground state. In case of (2) the uniform symmetrical broadening of the Soret (B band) and visible (Q bands) regions becomes more pronounced on addition of acid (Dalton and Milogram, 1982). It has been suggested that the broadenings may be either due to a vibrational modulation of the porphyrin excited state by quinone or due to charge transfer interactions between the two chromophores (Bergkamp *et al* 1982).

One of the characteristic features of ^1H NMR of porphyrins is the upfield shifts of certain resonances located above the plane of the porphyrin. This is due to the large ring current generated by the 18π electron system and the magnitude of such shifts can be correlated with the spatial proximity of the protons to the porphyrin plane. Specifically, the protons of the hydroquinone and quinone moieties in the linked quinone-porphyrin complexes exhibit large upfield shifts compared to their corresponding positions in unlinked species, for *e.g.* in the hydroquinone form of (4), the H_1, H_2 and H_3 protons are upfield shifted by 2·9, 1·4 and 1·6 ppm, but on oxidation to the quinone (4), the ring current induced shifts change to 0·1, 2 and 3 ppm respectively (Tabushi *et al* 1979). This suggests that both quinone and hydroquinone moieties are located in close proximity to the porphyrin plane in both these molecules but are in quite different orientations. Similar effects are noticed in other quinone-porphyrins (Kong and Loach 1980). Significantly, on metallation of the complexes the upfield shifts are increased, indicating a much more favourable interaction between the two chromophores. This may be due to an intramolecular co-ordination of the quinone to the central metal atom of metalloporphyrins and the detailed aspects of such co-ordination effects are discussed in §3.2.

(3)

(4)
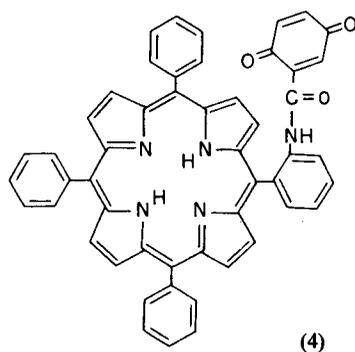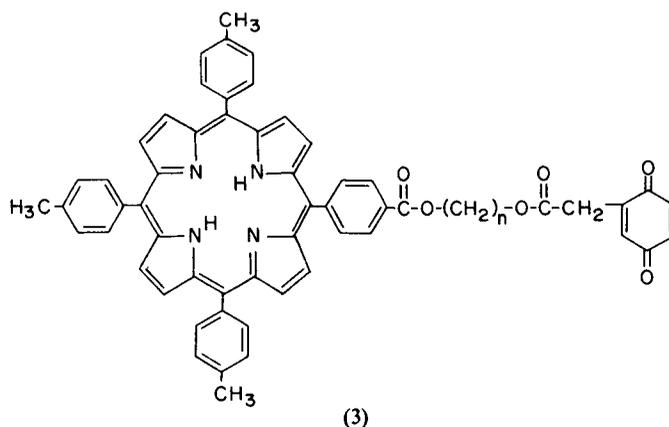
2.3 Fluorescence and electron transfer studies

Quinones are known to quench porphyrin excited states in a bimolecular reaction and the extent of quenching depends on the concentration and the reduction potentials of the quinones. All quinone-porphyrins exhibit very low fluorescence spectrum and by intropolating the benzoquinone concentration-dependent fluorescence data of tetraphenylporphyrin, the effective concentration of quinone to quench TPP fluorescence intramolecularly is estimated in (4) to be 4.2×10^{-2} M (Tabushi *et al* 1979). This indicates a more favourable interaction of the two chromophores in the linked molecules compared to the free intermolecular reaction. In a similar study by Nishitani *et al* (1981), the relative quenching efficiency in different intramolecular complexes (1) over the free component mixtures was in the range 700 to 5000; the shortening of polymethylene chain ($n = 2$) and coordination with the metal resulted in larger quenching efficiencies. Though these results indicate an effective donor-acceptor combination in these systems they alone do not prove that photochemical electron-transfer has taken place. The direct evidence for this comes from the steady state and transient EPR measurements in the linked molecules (3) (Ho *et al* 1980). When the unlinked components of (3) are photolysed in methanol at low temperatures (160 K) an irreversible intermolecular electron transfer is observed when the concentration of quinone is about 1000 times that of porphyrin, as indicated by the formation of

quinone radical anion. On the other hand the electron transfer in the linked molecules (3) was found to be reversible at 160 K but irreversible at lower temperatures (140 K). The quantum efficiency of the production of EPR signal by photolysis in unlinked molecules was much less than that of linked species at equivalent concentrations. The electron transfer kinetics in the linked molecules was similar to that in the natural system and suggested a range of activation energies for the electron to return to the primary donor. This may be due to the relative motions of the donor-acceptor ends of the tailed molecules caused by the various conformations of the intervening hydrocarbon chain. In order to circumvent this type of diffusional and configurational uncertainties prevailing in the quinone-tailed porphyrins, the more rigid quinone-capped porphyrins have been synthesised by us (Ganesh and Sanders 1980) and their properties are discussed in the following section.

3. Quinone-capped porphyrins

These systems are attractive for various reasons. The distance between the quinone and porphyrin can be carefully controlled by merely varying the size of the bridge. This would enable and study of the effect of distance and molecular structure on the kinetics and mechanisms of the intramolecular electron transfer processes. The bridge can be designed either to facilitate or to prevent intramolecular binding between the quinone and central metal ion. This allows a rational control of the co-ordination chemistry which may be usefully employed to influence the chromophore orientation and hence the electron transfer characteristics. In addition, these systems would be ideal to investigate radical induced NMR effects since both porphyrin radical cations and quinone radical anions can be generated selectively by chemical means. These studies may eventually be valuable in the study of chlorophyll-protein complexes. The capped porphyrins have received wide attention recently (Bogatskii and Zhilana 1982) in studies related to oxygen binding properties and synthetic systems related to haem proteins.

3.1 *Synthesis*

There are two approaches to the synthesis of capped porphyrins. One approach involves a direct condensation of a bifunctional porphyrin such as (9) with the capping constituents which are also bifunctional. In the second approach, the bridge is preformed with the porphyrin precursors built on the two ends and cyclised
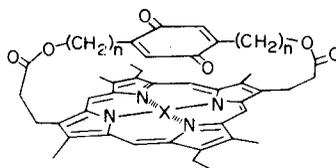
(5) n = 2; X = H$_2$
(6) n = 2; X = Mg
(7) n = 3; X = H$_2$
(8) n = 3; X = Mg

subsequently by an intramolecular condensation. An excellent review by Bogatskii and Zhilana (1982) describes the various synthetic approaches to the bridged porphyrins. The details of the synthetic route to the quinone-capped porphyrins are described elsewhere (Ganesh and Sanders 1982) and here we mention only three interesting chemical properties observed during the chemical synthesis, which arise as a consequence of bringing the two chromophores close in space.

(i) The quinone function was protected as the diacetal (methoxy methyl) during the condensation with the porphyrins. All attempts to deprotect this group with aqueous dilute mineral acids failed, though under similar conditions the porphyrin free components reacted smoothly. In all cases, the formation of porphyrin dications could be inferred on the basis of uv-visible spectra. The proximity of the porphyrin dications presumably inhibits the acetal protonation and deprotection to the hydroquinone was eventually achieved with BCl_3.

(ii) The oxidation of the hydroquinone-capped porphyrins to the quinone-porphyrins with lead dioxide was at least five times rapid compared to normal hydroquinones. The capped hydroquinones were unstable and produced free radicals on standing at room temperature (presumably semiquinone radical ion) as detected by broadened NMR signals. This modified red-ox behaviour of hydroquinones when in close proximity to the porphyrin is corroborated by electrochemical results described in §3.4.

(iii) One expects the capped porphyrins to be difficult to metallate because of the steric constraints to the axial approach of the metal. On the contrary, the bridged porphyrins could be metallated at least 3 times faster than simple porphyrins. Such rapid metallations seems to be a general feature of capped porphyrins irrespective of whether the cap is functionalised with a co-ordinating group or not. The source of this reactivity may reflect either the higher oxidation potential of the free-base porphyrin or the greater accessibility of the central N–H protons in a nonplanar macrocycle severely distorted by the bridge.

3.2 *Spectral characterisation*

The main characteristic features of ^1H NMR of capped porphyrins centre around the large ring current induced upfield shifts observed for the cap protons. A detailed analysis of the ^1H NMR spectra in these and related systems to elucidate the molecular shape, motions and flexibility has been presented earlier (Ganesh *et al* 1982) and the following picture emerges as a consequence.

(i) The bridged porphyrins are chiral on the NMR time scale *i.e.* racemisation by flipping the cap from above to below the macrocycle takes seconds at least. This causes the non-equivalence of geminal protons on the proponate side chain, which occur as complex multiplets (figure 1). The analysis of vicinal and geminal coupling constants together with nuclear Overhauser enhancements(nOe) for the propionate side chain protons favours a *trans* relationship between the porphyrin and the carbonyl group of the propionate ester. It may be pointed out that the crystal structure of two other related compounds by Cruse *et al* (1980) indicates a *qauche* relationship between these groups.

(ii) The broader intrinsic linewidths (2 Hz) in capped porphyrins compared to simpler porphyrins (0·5 Hz) indicate considerable slow molecular tumbling in the former. This is reflected in a greater viscosity dependence of spin-lattice relaxation
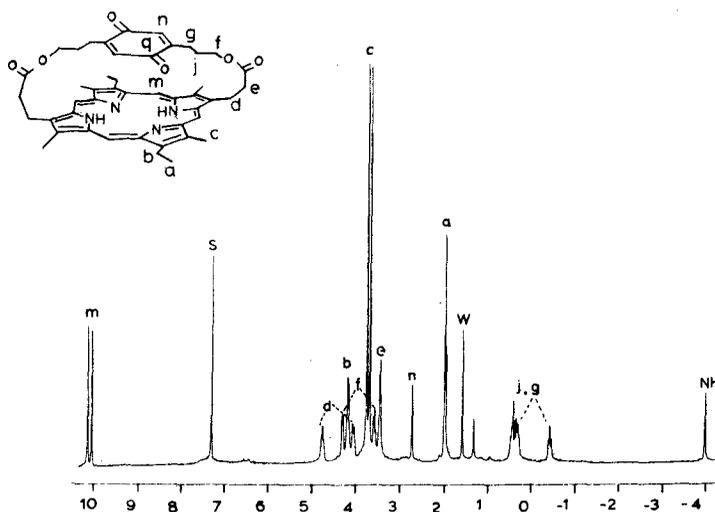
Figure 1. 400 MHz ^{1}H NMR spectrum of (7) in CDCl$_3$. The chemical shifts are in ppm on scale. S = Solvent, W = Water.

times in the capped porphyrins than for simple porphyrins. The slower motions are due to the "cap" which severely hinders the motion causing relaxation *i.e.* spinning around the four fold axis.

(iii) The lone signal observed for the quinone proton (*n*) arises by a fast exchange process which averages the different conformations possible for the cap. This averaging can occur with the quinone ring being either parallel or perpendicular to the porphyrin plane. The cap fragment C–C–quinone–C–C– is essentially planar though rotational averaging around C–C bond is permissible. The closer proximity of the quinone cap to the porphyrin indicated by ^{1}H NMR in compounds with flexible bridges (8, 9) compared to rigid ones (6, 7) seems to be a general feature of bridged porphyrins since similar results have been noticed in other cases (Baldwin *et al* 1981). The remarkable temperature dependent chemical shifts observed for the quinone and protected hydroquinone precursors of these porphyrin derivatives agrees with a picture in which the interchromophore distance increases with temperature and decreases on cooling.

(iv) UV visible absorption spectra of the capped porphyrins show only small differences from simple porphyrins indicating little optical interaction between the two chromophores. This lack of substantial interchromophore interaction may partly be explained by the orientational dynamics of the quinone cap as revealed by ^{1}H NMR results.

3.3 *Intramolecular co-ordination chemistry*

The addition of molar equivalents of pyridine to solutions of the capped metalloporphyrins (6) and (8) in CDCl$_3$ results in large upfield shifts for the pyridine and cap protons. This is due to the porphyrin ring current and for pyridine the effect is largest on the α-protons and progressively decreases with β- and γ-protons. The pyridine shift ratios β/α and γ/α (table 1) are therefore sensitive to the co-ordinate distance between
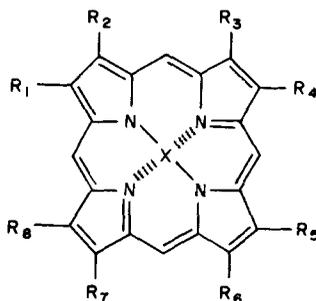
(9) $R_1 = R_3 = R_5 = R_7 = Me$, $R_4 = R_8 = Et$, $R_2 = R_6 = CH_2CH_2COOMe$, $X = H_2$.
(10) $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = R_7 = R_8 = Et$, $X = Mg$
(11) $R_1 = R_4 = R_5 = R_8 = Me$, $R_2 = R_3 = R_6 = R_7 = Et$, $X = Mg$
(13) $R_1 = R_3 = R_5 = R_8 = Me$, $R_2 = R_4 = Et$, $R_6 = R_7 = CH_2CH_2COOMe$, $X = H_2$
(14) (13) with $X = Mg$.
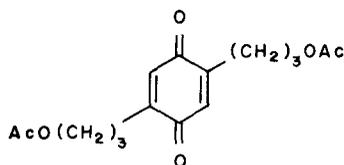
(12)

Table 1. Pyridine shift ratios* and binding constants (K).

Compound	β/α	γ/α	K	Co-ordination
(11)·Py†	0·315	0·263	—	5
(11)·2 Py†	0·309	0·264	—	6
Mg·TPP·Py†	0·275	0·241	—	5
Mg·TPP·2 Py†	0·269	0·206	—	6
(10)·2 Py	0·317	0·250	$4·25 \times 10^5$ mol^{-2}	6
(8)·Py	0·312	0·260	25·2 mol^{-1}	6

* Limits of error: $\beta/\alpha \pm 0·005$, $\gamma/\alpha \pm 0·01$.
† Values quoted from Storm and Corwin (1964); TPP = tetraphenyl porphyrin.

the metalloporphyrin and pyridine. For example the smaller β/α ratio for tetraphenyl-porphyrins may result from the phenyl substituents which sterically prevent the closer approach of the ligand to the metal. The evidence for pyridine binding on the unhindered face of the capped porphyrins comes from the fact that shift ratios observed with these molecules are similar to those observed with simple porphyrins. The binding constants for pyridine with capped porphyrins are many orders of magnitude weaker than the usual first ligand binding to a magnesium porphyrin and are rather similar to a second binding. These facts together with the pattern of shifts observed for the cap protons point towards a picture (Ganesh et al 1982) in which the central magnesium ion

in the absence of added external ligand binds a quinone carbonyl as fifth ligand and is displaced out of the porphyrin plane towards the cap (figure 2). Addition of an external ligand such as pyridine which binds on the unhindered side, pulls the metal into the plane; the metal in turn pulls the cap closer to the porphyrins. This cooperative intramolecular binding of quinone to the central metal atom should perturb the electron densities at the skeletal carbons of the porphyrin and quinone chromophores. Since the carbon nucleii in unsaturated systems are more sensitive than protons to long range electron donating and withdrawing substituents, we have studied the ^{13}C NMR of capped porphyrins (table 2). Several interesting conclusions follow from these results.

The chemical shifts of carbons from the cap of the molecule (q, n, y, g, j and f) are all upfield compared to their shifts in simple quinones, due to the ring current of the porphyrin. The absolute magnitude of such induced shifts is the same for both ^{1}H and ^{13}C but seems less prominent for ^{13}C whose intrinsic chemical shifts are spread over 200 ppm. Any intramolecular binding of quinone is expected to decrease the electron density from the quinone, leading to a downfield shift of the quinone carbon resonances. Consistent with this, the metallation of the capped porphyrins induces a downfield shift on all the carbons of the cap and especially on the quinone carbonyls (q). The observation of a single carbonyl resonance indicates that the quinone carbonyls are in fast exchange for the co-ordination site on the metal and so are indistinguishable. Addition of pyridine to the metalloporphyrin (8) shows increased upfield shifts of the cap resonances, particularly the carbonyls and this may be explained as due to the pulling of the cap closer to the porphyrin by the metal when it becomes 6 coordinate species.

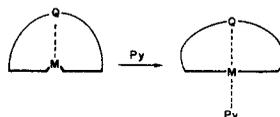The slight downfield shifts observed for the meso carbons (m, m') and ring methyls

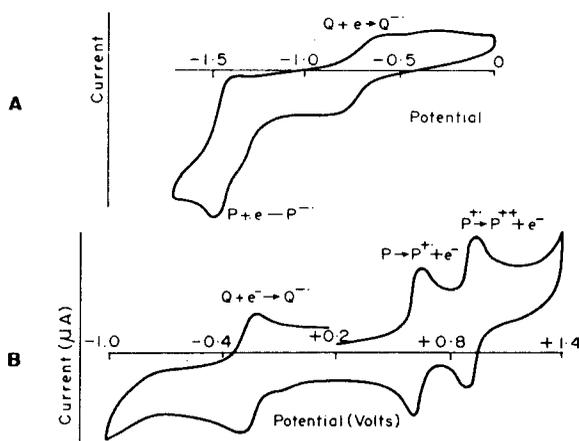**Figure 2.** 5 and 6 co-ordinate complexes of quinone capped metalloporphyrins.

Figure 3. **A** and **B** are cyclic voltammograms of (7) and (8) respectively.

Table 2. ^{13}C Chemical shifts*.

Compound	a	b	c,c'	d	e	f	g,j	n	m,m'	y	s	q	β	α
(9)	17·5	19·5	10·7 11·1	21·8	37·3	52·0	—	—	96·1 96·3	—	173·4	—	133·7 136·9	140·5 (br)
(12)	—	—	—	—	20·6	63·5	25·0 26·6	133·3	—	148·4	171·0	186·0	—	—
(7)	17·5	19·7	11·3 11·8	24·8	36·8	63·3	22·2 22·6	127·0	96·4 96·9	144·0	174·3	183·4	127·4 128·3 140·8 143·7	138·3 141·4
(8)	17·5	19·6	11·3 11·5	24·7	37·6	61·7	22·5 22·8	130·5	97·7 98·2	146·8	174·0	185·6	136·2 137·5 138·0 143·2	147·1 147·4 147·8 147·4
(8)+ pyridine	17·6	19·9	11·2 11·6	25·5	37·2	61·7	22·6 22·7	128·5	97·7 98·0	144·8	174·2	183·8	137·6 143·2	147·1 147·8 147·4 148·4

* All samples were run in $CDCl_3$, on Varian XL-100-12A at 25·2 MHz for ^{13}C. The values are in δ units, concentration 30 mM and temperature 26°C.

(c, c') in capped porphyrins compared to simple porphyrins may suggest a weaker ring current in the capped molecules. Such decreases in the ring current could arise in porphyrins which are non-planar due to the strain induced by the bridge. This may also suggest an explanation for the greater ease of metallation of these molecules where the non-planar structure results in greater accessibility of the central N–H protons by the metal ion. The metallation also causes an upfield shift of the f carbons which may presumably result from a simple movement of this carbon into the ring current area as a result of the conformational changes induced in the bridge. Not much significant influences are noticed on the chemical shifts of the quarternary carbons (α, β), of the porphyrin ring. The origin of the observed changes in ^{13}C shifts though partly is due to steric factors (such as conformational changes) in addition to the electronic effects, the shifts yet qualitatively confirm the coordination picture derived from ^{1}H NMR.

3.4 *Electrochemistry*

It was pointed out earlier that some unusual red-ox properties were noticed during the chemical synthesis of the quinone-capped porphyrins. Because of the obvious importance of the radicals from these compounds, we have done preliminary electrochemical experiments to establish the red-ox states (table 3) by using cyclic voltametry. The capped metalloporphyrin (8) shows two one-electron oxidations in the potential range scanned $(-1\cdot7\text{ V} + 1\cdot4\text{ V})$ (figure 3) whereas its free base porphyrin (7) exhibits single one-electron oxidation, all processes being electrochemically reversible. This behaviour is similar to those observed with simpler porphyrins but the measured half wave potentials $(E^0_{1/2})$ reveal interesting information. The $E^0_{1/2}$ for the first oxidation of porphyrin in (7) is more positive by $0\cdot14$ V compared to simpler porphyrins meaning that the former are more difficult to oxidise than the latter; metallation decreases this margin to $0\cdot07$ V. For free base porphyrin (7) $E^0_{1/2}$ for quinone reduction is more negative by $0\cdot25$ V indicating that this process is more difficult than in simple quinones. However, the situation is reversed on metallation; the quinone reduction in capped metalloporphyrin (8) is now easier by $0\cdot3$ V compared to free quinones. This is a very encouraging result from the point of photochemical electron transfer reactions and also explains the facile oxidations observed during the chemical synthesis. The addition of pyridine does not show significant deviations in the $E^0_{1/2}$ values but the electrode processes seemed more irreversible. From the shape of the

Table 3. Half-wave potentials*.

Compound	$P \rightarrow P^{\dot{+}} + e^-$	$P^+ \rightarrow P^{++} + e^-$	$Q + e^- \rightarrow Q^{\dot{-}}$	$P + e^- \rightarrow P^{\dot{-}}$
(12)	—	—	$-0\cdot5$	—
(13)†	$0\cdot78$	—	—	$-1\cdot34$
(14)†	$0\cdot54$	$0\cdot94$	—	—
(7)	$0\cdot92$	—	$-0\cdot75$	$-1\cdot4$
(8)	$0\cdot61$	$0\cdot89$	$-0\cdot2$	—
(8)† pyridine	$0\cdot61$	$0\cdot85$	$-0\cdot23$	—

* Reference electrode = Ag/AgCl, Working electrode: platinum, electrolyte $0\cdot1$ M Tetrabutyl ammonium perchlorate, solvent: dichloromethane, Temp: 25°C, All values are in volts.
† From Buchler (1975).

voltammo grams, the formation of anions of porphyrin and quinones can be observed as separate processes, but the possibility of intramolecular electron exchange between them cannot be ruled out.

The nanosecond photochemistry of the capped porphyrins shows substantial but undramatic deviations from the unlinked molecules; the fluorescence lifetime of the capped molecules are only 3 times shorter than simple porphyrins. More detailed investigations are needed on this aspect before meaningful conclusions are drawn about the photochemical properties of these compounds. One common feature in all the above systems is that the porphyrin and quinone components are present in a stoichiometric ratio of one. Since the energy transfer also depends on the relative concentrations of the donor and acceptor molecules, we have synthesised molecules in which two quinones are attached to a single porphyrin (porphodiquinones*) and the spectroscopic results on these molecules will be reported shortly.

3.5 Conclusions

The synthetic routes to covalently linked quinone-porphyrins are now established and meets many of the prerequisites demanded for a synthetic photosystem such as easy variation of interchromophoric distances and relative red-ox potentials. In capped porphyrins the quinone ring is mobile on NMR time scale to average the chemical shifts, though CPK models indicate considerable hindrance to such motions. The quinone binds intramolecularly to the central metal atom as shown by ^{1}H and ^{13}C NMR spectra; in spite of such a binding, the two carbonyls cannot be distinguished since they are in fast exchange process for ligation site on the metal. The metal atom is 5- coordinate in capped porphyrins but accepts a sixth ligand to become 6 coordinated, the latter being a weaker process. The introduction of bulky substituents into the cap may prevent intramolecular binding and such control over the coordination chemistry may eventually be useful to orient the two chromophores for a favourable photochemical interaction. Electrochemical results reveal that the quinone in capped metallo-porphyrins is a better electron acceptor (easy reduction) compared to simple quinones. These facts together with remarkable photochemical behaviour of one of the quinone-tailed porphyrins (3) suggest these intramolecular complexes to be potential non-biological models for a synthetic approach to photosynthesis.

Acknowledgements

References

Adler A D, Longo F R, Finarelli J D, Goldmacher J, Assaur J and Kosakoff L 1967 *J. Org. Chem.* **32** 476
Baldwin J E, Crossley M J, Debernaids J F, Dyer R L, Huff J R and Peters M K 1981 *Tetrahedron* **37** 3589
Bergkamp M A, Dalton J and Netzel T L 1982 *J. Am. Chem. Soc.* **104** 253

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* Ganesh K N and Rao B N (unpublished results).

Bogatskii A V and Zhilana Z I 1982 *Russ. Chem. Rev.* **51** 592
Buchler J H 1975 in *Porphyrins and metalloporphyrins* (ed.) K M Smith (Amsterdam: Elsevier)
Cruse W B, Kennard O, Sheldrick G M, Hamilton A D, Hartley S G and Battersby A R 1980 *J. Chem. Soc. Chem. Commun.* 700
Dalton J and Milogram L R 1979 *J. Chem. Soc. Chem. Commun.* 609
Ganesh K N and Sanders J K M 1980 *J. Chem. Soc. Chem. Commun.* 1129
Ganesh K N and Sanders J K M 1982 *J. Chem. Soc. Perkin Trans. I* 1611
Ganesh K N, Sanders J K M and Waterton J C 1982 *J. Chem. Soc. Perkin Trans I* 1617
Ho T, McIntosh A R and Bolton J R 1980 *Nature (London)* **286** 254
Kong JLY and Loach P A 1980 *J. Heterocyclic Chem.* **17** 737
Nishitani E, Kurato N, Sakata Y, Misumi S, Migita M, Okada T and Mataga N 1981 *Tet. Lett.* 2099
Storm C B and Corwin A H 1964 *J. Org. Chem.* **29** 3700
Tabushi I, Koga N and Yanagita M 1979 *Tet. Lett.* 257

Note added in proof

Since the submission of this manuscript, reports have appeared about a quinone-tailed porphyrin in which two types of quinones are linked to an etioporphyrin (Nishitani *et al* 1983) and a tetraphenyl porphyrin covalently linked to both a carotenoid and a quinone (Moore *et al* 1984). In the latter molecule excitation of the porphyrin moiety by visible light results in rapid formation of Carotene$^{+\cdot}$—porphyrin-quinone$^{-\cdot}$ as transient species with unfavourable recombination of charges similar to *in vivo* photosynthesis. A cofacial porphyrin-quinone molecule of a tetraphenyl type has also been reported (Lindsey and Mauzerall, 1982).

Nishitani S, Kurata N, Sakata Y and Misumi S 1983 *J. Am. Chem. Soc.* **105** 7771
Moore T A *et al* 1984 *Nature (London)* **307** 630
Lindsey J S and Mauzerall D C 1982 *J. Am. Chem. Soc.* **104** 4498