

Independent Control of Oxidation and Reduction Potentials in Porphyrin Dimers by Peripheral Substitution

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Peripheral substitution of a single face of porphyrin cofacial dimer gives independent control of the oxidation and reduction potentials; use of NH_2 as a substituent in one face, and NO_2 in the other reduces $E'_{\text{ox.}} - E'_{\text{red.}}$ by almost 0.8 V.

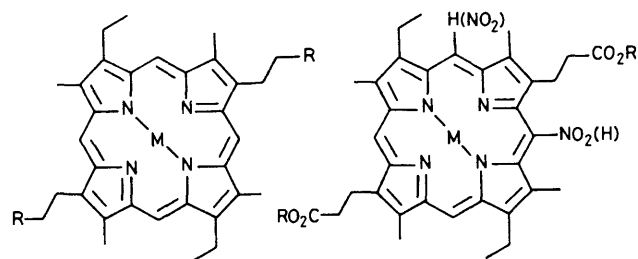
Many biological photosystems involve light-induced electron transfer from a chlorophyll dimer reaction centre to an electron accepting unit.^{1,2} In our laboratory we have been aiming to synthesise such a model porphyrin complex with the hope that we might, by careful control of the porphyrin dimer redox chemistry, be able to mimic more closely certain features of the natural system, *viz.*, the relative redox potentials and forward and reverse electron transfer rates. A key element in such a molecule would be the ability to control both the relative and absolute redox properties of each face of the porphyrin dimer. One approach is selective metallation.³ However another possibility lies in the use of peripheral substituents on the porphyrin rings. We report here the use of nitro and amino functionalities for such a purpose and describe some of the physical and chemical properties of such systems.

The monomeric porphyrin derivatives shown were synthesised by the route outlined in Scheme 1, and the cofacial

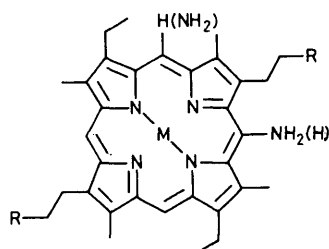
porphyrin dimers (CFD) as in Scheme 2.† Nitration was achieved by a standard method.⁴ However we found reduction to the amine to be more convenient *via* proton transfer hydrogenation using Pd-charcoal-cyclohexene rather than the Pd-charcoal-borohydride method reported elsewhere.⁵ The NH_2 group is remarkably non basic, reacting neither intramolecularly with the adjacent ester group in (9), nor to any great extent with added activated acyl derivatives. This is a result of donation into the π -system of the porphyrin.⁶ No attempt was made to separate the nitro- and amino-regioisomers formed except in the case described below. Zinc was incorporated into one face of the dimer to allow the future possibility of selective mixed metallation.

The results from several electrochemical experiments are shown in Table 1. It should be noted that in the case of

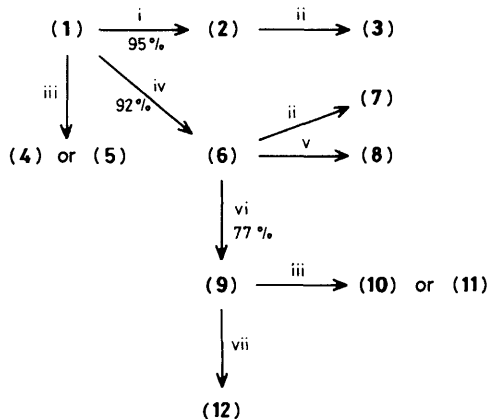
† All new compounds gave satisfactory analyses or high resolution mass spectra.



- (1) R = CO₂Me; M = H₂
 (2) R = CH₂OH; M = H₂
 (3) R = CH₂OH; M = Zn
 (4) R = CO₂Me; M = Zn
 (5) R = CO₂Me; M = Cu
 (6) R = Me; M = H₂
 (7) R = Me; M = Zn
 (8) R = H; M = H₂



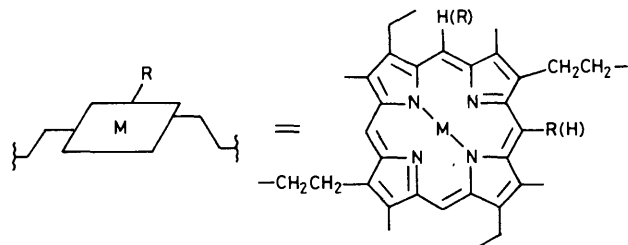
- (9) R = CO₂Me; M = H₂
 (10) R = CO₂Me; M = Zn
 (11) R = CO₂Me; M = Cu
 (12) R = CH₂OH; M = Zn



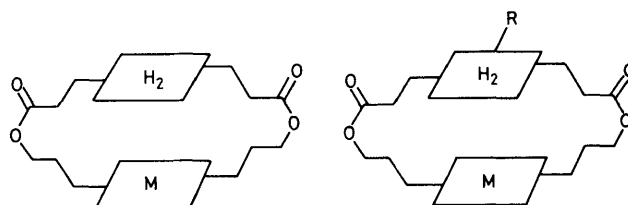
Scheme 1. Reagents: i, LiAlH₄; ii, Zn²⁺; iii, Zn²⁺ or Cu²⁺; iv, fuming HNO₃, HOAc; v, aqueous KOH; vi, Pd-C, cyclohexene; vii, LiAlH₄, then Zn²⁺.

substituted dimeric porphyrins, the first oxidation and reduction potentials will refer to different faces. In general the dimeric porphyrins appear to be slightly more readily oxidised but more difficult to reduce than the corresponding monomers, although in most cases the difference in potential is not more than 0.03–0.04 V. The amino porphyrins can be singled out since they exhibit an additional oxidation wave.† The similarity in the first oxidation potentials for the various amino porphyrins detailed in Table 1 [compounds (9)–(11)] strongly

† The extra oxidation wave is not due to the presence of regioisomers since the amino meso isomers of (9) were separated and gave identical redox and fluorescence properties.

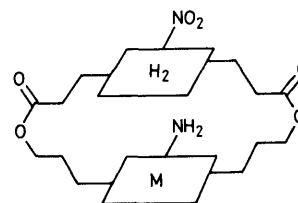


(mixture of regioisomers)

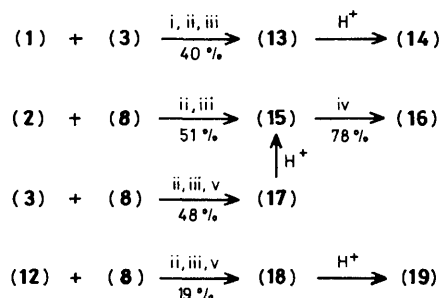


- (13) M = Zn
 (14) M = H₂

- (15) R = NO₂; M = H₂
 (16) R = NH₂; M = H₂
 (17) R = NO₂; M = Zn



- (18) M = Zn
 (19) M = H₂



Scheme 2. Reagents and conditions: i, KOH hydrolysis of ester; ii, (COCl)₂; iii, high dilution coupling in CH₂Cl₂ using *N,N*-dimethylaminopyridine; iv, Pd-C, cyclohexene; v, 0.5% pyridine to solubilise the Zn component.

suggests that initial oxidation occurs at the NH₂ group.‡ It is of interest that the *E*_o value lies very close to that found for aniline (Table 1). This, as expected, does not hold for nitro porphyrins where the oxidation potential varies as usual with the nature of the metal. E.s.r. spectra of the monocation radicals of (9) and (10), generated by preparative cyclic voltammetry and by Br₂ oxidation, did not show hyperfine coupling to the amine but were very typical of porphyrin radical cation spectra.⁷ It is likely therefore, that initial loss from the amine is followed by an intramolecular redox change with the electron density localised, as for other octa-alkyl porphyrins, at the α-pyrrole positions of the porphyrin ring.

‡ The second oxidation potential of amino porphyrins is metal dependent in the usual way.

Table 1.^a

Compound ^b	$E'_{ox.}$	$E'_{red.}$	$(E'_{ox.} - E'_{red.})'$
(1) P	1.00	1.26	2.26
(6) NO ₂ P	1.23	0.78	2.01
(9) NH ₂ P	0.50	1.37	1.87
(4) ZnP	0.80	1.43	2.23
(7) ZnNO ₂ P	1.01	0.96	1.97
(10) ZnNH ₂ P	0.50	1.57	2.07
(5) CuP	0.88	1.39	2.27
(11) CuNH ₂ P	0.53	—	—
(14) CFD	0.92	1.24	2.16
(15) NO ₂ CFD	0.95	0.86	1.81
(16) NH ₂ CFD	0.52	1.30	1.82
(19) NH ₂ NO ₂ CFD	0.51	0.86	1.37
(13) ZnCFD	0.76	1.28	2.04
(17) ZnNO ₂ CFD	0.78	0.87	1.65
(18) ZnNH ₂ NO ₂ CFD	0.49	0.87	1.36
Aniline	0.53	—	—

^a CH₂Cl₂ solution 0.2 M NBu₄BF₄ electrolyte, E_o vs. Ag/AgCl. ^b P = meso-II-porphyrin bis(methyl ester); CFD = cofacial porphyrin dimer.

The effect of incorporating electron donating NH₂ or electron withdrawing NO₂ groups into the porphyrin ring is striking, the redox changes being greater than most results of metallation. Therefore we can use, particularly in porphyrin

dimers, nitro and amino groups as coarse controls and metallation as a fine control for the tuning of relative porphyrin redox potentials. In addition, since there are generally only small differences between the redox potentials of porphyrins as monomers or in a dimer, the results in Table 1 imply that a suitable combination of functionality can be chosen to give the required redox properties before embarking on the synthesis. Conversely, comparison of redox potentials offers a powerful method for aiding the characterisation of such dimers.

It should be noted that the E_o value of ca. 0.5 V for the first oxidation potentials of amino porphyrins corresponds very closely to the value found in many natural reaction centres¹ and so allows the formation of porphyrin dimers which accurately model reaction centre redox properties.

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References

- 1 K. Sauer, *Ann. Rev. Phys. Chem.*, 1979, **30**, 155.
- 2 M. G. Goldfield and L. A. Blumenfield, *Bull. Magn. Reson.*, 1979, **1**, 66.
- 3 J. A. Cowan and J. K. M. Sanders, preceding communication.
- 4 R. Bonnett and G. F. Stephenson, *J. Org. Chem.*, 1975, **30**, 2791.
- 5 M. F. Billing and E. W. Baker, *Chem. Ind. (London)*, 1969, 654.
- 6 R. J. Abraham, K. M. Smith, F. W. Bobe, and O. M. Minnetian, *Org. Magn. Reson.*, 1984, **22**, 771.
- 7 J. Fajer and M. S. Davis, in 'The Porphyrins,' ed. D. Dolphin, vol. IV, Academic Press, 1979.