

## Synthesis and Electrochemical Properties of some Metallated and Peripherally Substituted Porphyrin Co-Facial Dimers

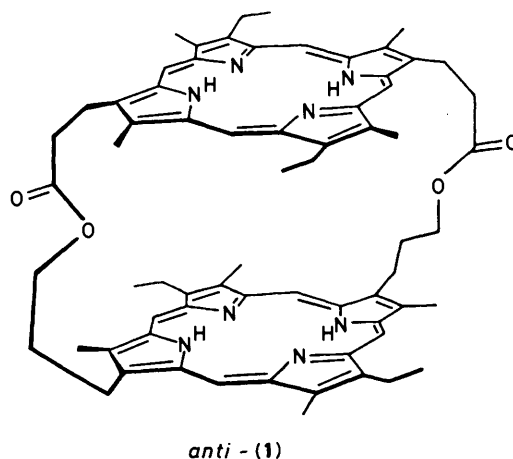
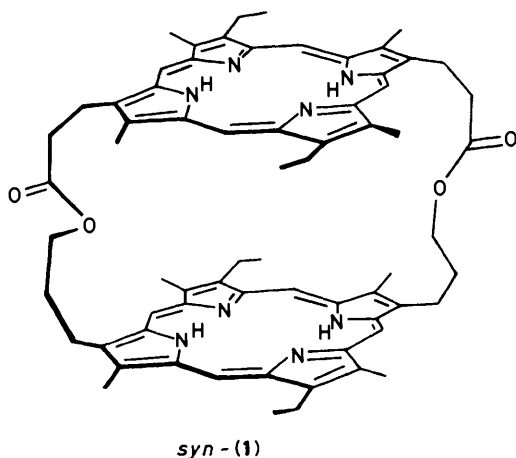
James A. Cowan and Jeremy K. M. Sanders\*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The high dilution coupling of mesoporphyrin-II bis(acid chloride) with a diol derived from mesoporphyrin-II bis(methyl ester) yields two diastereoisomers of a co-facial porphyrin dimer. The use of zinc as a removable protecting group for the diol face gives access to a wide range of mixed metal and mixed valence co-facial porphyrin dimers. Introduction of amino and nitro peripheral substituents provides another method for altering independently the properties of each of the porphyrin faces in a dimer.

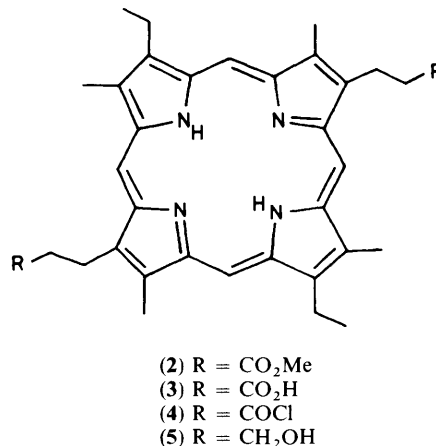
Dimeric porphyrins are the focus of much interest as model enzymes, model photosynthetic systems, and oxygen activators.<sup>1-7</sup> However, the repertoire of structural and electronic variation that has hitherto been built into these molecules has been rather limited. We now present details of two approaches that can be used, separately or together, to endow a basic porphyrin dimer framework with a wide range of molecular, electrochemical, and photochemical properties. In the first approach, different metal ions are inserted into each face of a porphyrin dimer, while in the other, amino or nitro peripheral substituents are introduced into one or both faces. In the present work, all the dimers described are based on (1), which is derived from mesoporphyrin-II bis(methyl ester) (2) by straightforward chemistry, but the ideas developed here should be applicable to porphyrins with other geometries and to other peripheral substituents. Some of the synthetic and electrochemical results presented here have been previously reported in preliminary form.<sup>8,9</sup>

The parent porphyrin co-facial dimer (1), and all its derivatives, have been synthesized as diastereoisomeric mixtures, e.g. *anti*-(1) and *syn*-(1), but for convenience only the *syn* form is shown in subsequent diagrams. Substitution of a divalent metal ion (M), into one face of (1) gives M(1) where the divalent state is implicit; insertion of a trivalent metal ion (M<sup>III</sup>), with its counterion, (X<sup>-</sup>), gives M<sup>III</sup>(1) X<sup>-</sup>. Metallation of both porphyrin faces of (1) is denoted by MM'(1), M and M' representing the metal ions. The same convention is used for metallated derivatives of peripherally substituted, bridged and other porphyrins throughout this and the accompanying paper.<sup>10</sup>



### Results and Discussion

Our general route to compound (1) and its derivatives begins with compound (2). This can readily be converted into the bis(acid chloride) (4) *via* (3),<sup>10</sup> or reduced to the diol (5). High dilution coupling of compounds (4) and (5) gives compound (1) in 57% yield. This is a remarkably good yield for closure of such a large ring, and may be ascribed to attractive interactions between the chromophores before cyclisation is complete.<sup>10</sup>



The <sup>1</sup>H n.m.r. spectrum of compound (1) in [<sup>2</sup>H<sub>2</sub>]tetrachloroethane solution at 390 K contains 8 resolved *meso* proton signals in the chemical-shift range 7.8–9.7 p.p.m. These shifts, which should be compared with the more usual value of *ca* 10.1

p.p.m. for *meso* protons, arise because the ring current from one porphyrin unit shields the protons of the other unit. Ring-current calculations demonstrate a strongly offset geometry for the two porphyrin units; the offset geometry is attributed to  $\pi$ - $\pi$  interactions.<sup>11</sup> The room-temperature n.m.r. spectrum is broadened by slow motions of one porphyrin face relative to the other face. Further evidence for  $\pi$ - $\pi$  interactions comes from the u.v./visible absorption spectrum of compound (1), which shows the characteristic broadening and shifting of bands by exciton coupling, and from a reduced fluorescence quantum yield.<sup>11,12</sup>

Metallation of compound (1) under standard conditions gave a variety of bis-metallated dimers such as Zn<sub>2</sub>(1), Co<sub>2</sub>(1), and Ag<sub>2</sub>(1), in good yield.

*Synthesis of Mixed Metal Dimers.*—We wished to develop a general synthesis of mixed metal dimers that avoided the coupling of two pre-metallated porphyrins.<sup>1,2</sup> This is perhaps the obvious route but it suffers certain drawbacks: (a) each compound requires a separate high dilution coupling reaction, which can be tedious when, as in our work, only milligram or sub-milligram quantities are needed for spectroscopic studies; (b) new macrocyclisation conditions must be developed for each new compound; the high dilution coupling is often low yielding since the solvents required to solubilise the relevant metalloporphyrins can often co-ordinate to one or both faces of the complex, introducing steric barriers<sup>1</sup> to the coupling reaction. An added possible complication is the co-ordination of the reactive hydroxy function to a metal centre.

An attractive alternative is to couple a free base monomer unit with one that contains a removable metal ion as protecting group. Collman *et al.* have described such a route<sup>1</sup> using silver as a protecting ion in one face; the silver is removed by borohydride reduction when required. This synthesis, however, required the high temperature reaction of a diaminoporphyrin with an activated bisester porphyrin in pyridine solution. Silver has the feature that, once incorporated into a porphyrin, it has virtually no affinity for additional ligands. However, it is only removable under reductive conditions, which makes it incompatible with the incorporation of high valent metals such as Co<sup>III</sup> or Mn<sup>III</sup>.

We sought, therefore, other metal ions which might be compatible with mild reaction conditions and be suitable for use as removable protecting groups. We found that copper was not removed from the monomeric porphyrin Cu(2) by BH<sub>4</sub><sup>-</sup> reduction, but that it was reductively eliminated by Cu<sup>2+</sup>/BH<sub>4</sub><sup>-</sup> in THF/MeOH.<sup>13</sup> We therefore coupled Cu(4) with (5) in dichloromethane at room temperature to give Cu(1) in 54% yield. Surprisingly, copper could not be reductively eliminated from this dimer under any conditions that we have tried, rendering it unsuitable for our synthetic purposes. The ease of silver's reductive removal from both monomeric and dimeric porphyrins contrasts with the selective removal of copper from monomeric porphyrins only. Further investigation revealed that the two reductions proceed by pathways with quite different geometric requirements.<sup>13</sup>

We then turned our attention to metal ions that can be removed by mild acid. Many metal ions in porphyrins are acid labile, the strength of the acid required for demetallation depending greatly on the metal ion involved. Although alkali and alkaline earth metalloporphyrins are extremely acid sensitive, most transition metal porphyrins are fairly robust toward dilute acid.<sup>14</sup> A suitable protecting metal would, therefore, be one which was acid labile under conditions which did not demetallate most other metal porphyrins. Although magnesium meets these conditions it is probably too acid sensitive to be convenient in general use. Zinc however, also satisfied the requirements and is stable in a mildly acidic

Table 1. Metallated porphyrin dimers prepared to date

M	Compound <sup>a</sup> M' X <sup>-</sup>	Molecular ion <sup>b</sup>	U.v. absorptions <sup>c</sup>
Zn	H <sub>2</sub>	1 130	390s, 500, 532, 568, 622
Zn	Ag	1 235	393s, 535, 564
Zn	Cu	1 191	390sh, 398s, 531, 567
Zn	Co	1 187	388s, 535, 571
Cu	Ag	1 234	390s, 533, 564
Cu	Co	1 186	384s, 527sh, 556
Zn	Zn	1 192	388s, 534, 577
Co	Co	1 182	384s, 526sh, 554
Ag	Ag	1 278	396s, 527, 561
Cu	Cu	1 190	390s, 526, 560
Zn	Co <sup>III</sup> Br	1 187	387s, 534, 560
Zn	Mn <sup>III</sup> Br	1 183	358s, 404s, 474m, 536, 572
Zn	Fe <sup>III</sup> Cl	1 184	378s, 537, 569, 634br
H <sub>2</sub>	Co <sup>III</sup> Br	1 125	382s, 504, 532, 558, 624
H <sub>2</sub>	Mn <sup>III</sup> Br	1 121	356s, 404s, 476m, 535, 570, 625
H <sub>2</sub>	Fe <sup>III</sup> Cl	1 122	378s, 500, 534, 568, 621
Co	Fe <sup>III</sup> Cl	1 179	390s, 530, 564
Co	Co <sup>III</sup> Br	1 182	384s, br, 520, 552
Co	Mn <sup>III</sup> Br	1 178	356s, 398s, sh, 473m, 560
Co <sup>III</sup>	Mn <sup>III</sup> 2Br	1 178 <sup>d</sup>	356s, 400s, 472m, 562br
Fe <sup>III</sup>	Fe <sup>III</sup> 2Cl	1 176	384s, 503, 536, 570, 624
Mn <sup>III</sup>	Mn <sup>III</sup> 2Cl	1 174 <sup>e</sup>	352s, 472m, br, 560br

<sup>a</sup> In mixed metal dimers, M denotes the first metal inserted, and M' the second. <sup>b</sup> Electron impact ionisation was used for porphyrins containing only divalent metal ions; positive ion f.a.b. ionisation was used where trivalent metal ions were present. <sup>c</sup> Absorption bands are labelled s, strong; m, moderate; sh, shoulder; and br, broad. <sup>d</sup> M<sup>2+</sup> 589. <sup>e</sup> M<sup>2+</sup>, 587.

medium, allowing flexibility in the preparation and purification of the resulting compounds.

The diol Zn(5) and acid chloride (4) were coupled under high dilution at room temperature in dichloromethane containing 4-(*N,N'*-dimethylamino)pyridine (DMAP) as catalyst and 0.5% pyridine to give Zn(1) in 40% yield. The trace of pyridine was crucial for the success of the reaction since intermolecular zinc-to-hydroxy bonding rendered the zinc diol Zn(5) virtually insoluble in non-basic solvents. Pyridine competes effectively for the zinc, thereby disaggregating and solubilising the compound. Alternatively, DMAP is effective in solubilising Zn(5) and may be used in place of pyridine.

A variety of metals could then be inserted into the free-base moiety of Zn(1) to give the mixed metal dimers ZnM(1) or ZnM<sup>III</sup>(1)X<sup>-</sup>. The synthesis of mixed metal dimers was completed by removal of the zinc protecting group and insertion of the second desired metal. Zinc was removed from ZnM(1) or ZnM<sup>III</sup>(1)X<sup>-</sup> by treatment with dilute acid (16% aq. HBr), and the resulting M'(1) or M<sup>III</sup>(1)X<sup>-</sup> was remetallated to give a wide range of mixed metal dimers in 77–86% overall yield from Zn(1). Table 1 lists compounds which have been made by this route thus far, together with the spectroscopic data used to characterise them; some of these compounds have to date been prepared only in milligram quantities sufficient for characterisation. Clearly this is not an exhaustive list and this approach would presumably also be applicable to porphyrin dimers of other geometries.

In general, this sequential insertion of metals caused no great problem, there being relatively little influence of one metal on the insertion procedure for another. However, there were a number of cases where care was necessary. Thus, relatively normal insertion procedures *via* divalent salts were used except that, to prevent loss of zinc, very acidic conditions were avoided. Also, in the preparation of cobalt/manganese dimers, cobalt was inserted first since it is known that cobalt<sup>15</sup> readily displaces

manganese from porphyrins. Such exchange was not found to occur with any other combination of metals used.

Manganese(III) halide porphyrins were best prepared *via*  $\text{Mn}(\text{OAc})_2$  with anion exchange at a later stage; direct use of the corresponding  $\text{MnX}_2$  salts resulted in demetallation of the zinc face due to the acidity of these inorganic compounds. Anion exchange was expected to be easy in the presence of an excess of  $\text{NEt}_4\text{X}$  since it is known that  $\text{Mn}^{3+}$  binds the counterion very weakly in polar solvents, but strongly in nonpolar solvents.<sup>16</sup> Stirring the manganese porphyrin acetate with an excess of  $\text{NEt}_4\text{X}$  in  $\text{DMF-MeOH-CH}_2\text{Cl}_2$ , and subsequent washing with aqueous  $\text{NaX}$ , gave the desired manganese halide. That anion exchange had actually occurred under these conditions was determined in a series of test experiments, both by studying the intensity of the charge-transfer band at *ca.* 470 nm in the electronic absorption spectra of  $\text{Mn}^{\text{III}}$  porphyrins, which is known<sup>17</sup> to vary with the identity of the counterion, and also by negative ion f.a.b. mass spectrometry (f.a.b.m.s.). Verification of the identity of the co-ordinating anions of  $\text{Co}^{\text{III}}$  porphyrins was also possible, since these molecules gave good results with negative ion f.a.b.m.s.; however, although ferric porphyrins behaved well in positive ion f.a.b.m.s., definite results could not be obtained from the reverse potential experiment for either monomers or dimers. Based on the established reaction for the monomer, the identity of the anion in the case of  $\text{Fe}^{\text{III}}$ -containing dimers was assumed.

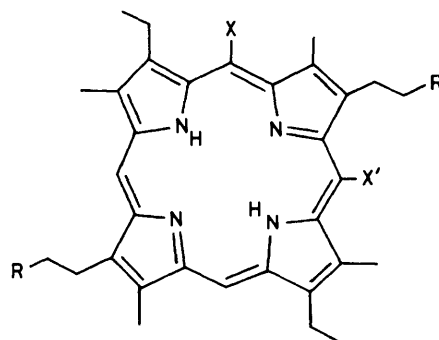
In the course of the metallation reactions, we observed that  $\text{FeCl}_3$  in  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  rapidly demetallated zinc porphyrins.  $\text{FeCl}_3$  does not metallate porphyrins under these conditions and therefore demetallation cannot be due to a transmetallation process. It is probable that zinc is removed by the acidity of  $\text{FeCl}_3$  in this solvent system, although a radical mechanism due to the oxidising action of  $\text{FeCl}_3$  cannot be ruled out.

Although the acid conditions employed may result in trace oxidation of  $\text{Co}^{2+}$  porphyrins in the presence of oxygen, this is easily rectified by subsequent dithionite reduction. Upon attempting to prepare the fully oxidised  $\text{Co}_2^{\text{III}}(1)2\text{Br}^-$  derivative by the normal acid-catalysed air oxidation method, we found that only one of the  $\text{Co}^{2+}$  ions had been oxidised. AC polarography revealed that the first oxidation potential of  $\text{Co}_2(1)$ , *i.e.* oxidation of a Co to  $\text{Co}^{\text{III}}$ , occurred at 0.71 V, while oxidation of the second metal did not occur until 0.94 V. This is presumably due to the electrostatic influence of the  $\text{Co}^{3+}$  ion in the opposite face. The second oxidation is outwith the normal oxidising range of molecular oxygen. The characterisation of this mixed valent cobalt complex was supported by e.s.r. spectroscopy, positive and negative ion f.a.b.m.s. and n.m.r. spectroscopy.<sup>12</sup>

The spectroscopic, magnetic and electronic properties of these mixed metal porphyrin dimers reveal a good deal about porphyrin-porphyrin and metal-metal interactions; these are discussed in separate papers.<sup>11,12</sup>

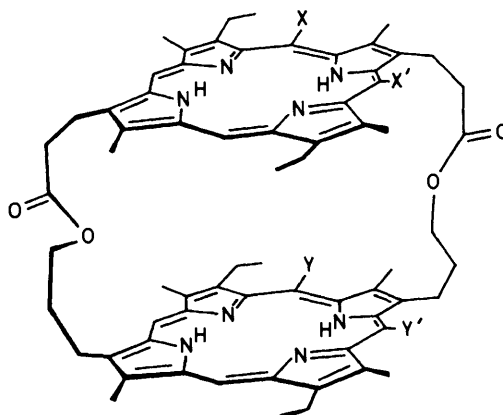
*Synthesis and Electrochemistry of Peripherally Substituted Dimers.*—As noted previously, an important element in any porphyrin dimer molecule designed to model successfully a biological photosystem would lie in the ability to control both the relative and absolute redox properties of each porphyrin face. One such approach, by selective metallation, was discussed above. Another possibility however, lies in the use of electron donating or withdrawing substituents on the periphery of the porphyrin rings.

Nitro and amino mesoporphyrin-II diesters (6) and (7) were synthesized in a relatively straightforward manner. Nitration was achieved with fuming nitric acid/glacial acetic acid.<sup>18</sup> Reduction to the amine was more readily carried out by proton transfer hydrogenation using  $\text{Pd}(\text{charcoal})/\text{cyclohexene}$  rather than the  $\text{Pd}(\text{charcoal})/\text{BH}_4^-$  method described elsewhere.<sup>19</sup> As



- (6)  $\text{X}, \text{X}' = \text{H}, \text{NO}_2$ ;  $\text{R} = \text{CO}_2\text{Me}$   
 (7)  $\text{X}, \text{X}' = \text{H}, \text{NH}_2$ ;  $\text{R} = \text{CO}_2\text{Me}$   
 (8)  $\text{X}, \text{X}' = \text{H}, \text{NO}_2$ ;  $\text{R} = \text{COCl}$   
 (9)  $\text{X}, \text{X}' = \text{H}, \text{NH}_2$ ;  $\text{R} = \text{CH}_2\text{OH}$

a result of donation into the  $\pi$ -system of the porphyrin, the amine was found to be remarkably non-basic, reacting neither intramolecularly with the adjacent ester group in (7), nor to any extent with added activated acyl derivatives. As indicated in (6) and (7), all the peripherally substituted compounds are actually mixtures because nitration takes place with equal facility at either of the two non-equivalent meso positions. No attempt was made to separate the nitro and amino regioisomers other than in the case described below. Conversion of compound (6) into the acid chloride (8), and of (7) into the diol (9) allowed the synthesis of substituted dimers (10)–(12). Zinc was incorporated into compound (9), and hence into one face of the dimers, to allow the future possibility of selective mixed metallation. The presence of many regio- and stereo-isomers in each substituted porphyrin dimer precluded any detailed analysis of n.m.r. spectra.



- (10)  $\text{X}, \text{X}' = \text{H}, \text{NO}_2$ ;  $\text{Y} = \text{Y}' = \text{H}$   
 (11)  $\text{X} = \text{X}' = \text{H}$ ;  $\text{Y}, \text{Y}' = \text{H}, \text{NH}_2$   
 (12)  $\text{X}, \text{X}' = \text{H}, \text{NO}_2$ ;  $\text{Y}, \text{Y}' = \text{H}, \text{NH}_2$

The electrochemical properties of the porphyrin dimers are summarised in Table 2. Note that for substituted dimeric porphyrins the first oxidation and reduction potentials will normally refer to different faces of the molecule. This spatial redox control is explained in Figure 1. Figure 1(a) shows the normal effect on the HOMO/LUMO energy levels in a porphyrin molecule, following the introduction of metal or peripheral substituents into the porphyrin ring. Functions enhancing the electron donor properties of the system raise the energies of both HOMO and LUMO, resulting in easier electron loss and more difficult electron gain. Conversely, electron-withdrawing functions lower both orbital energies,

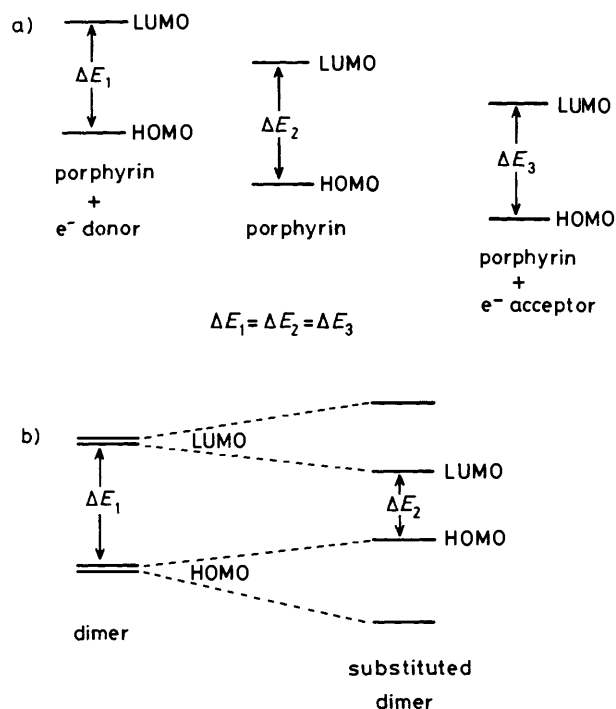


Figure 1. The influence of peripheral substitution on HOMO and LUMO levels: (a) in a monomeric porphyrin and (b) in a dimeric porphyrin

leading to more difficult loss but easier addition of electrons. This is the basic reason for the general uniformity of  $E_{\text{ox}} - E_{\text{red}} = 2.2$  V found in most metalloporphyrins. The introduction of electron donating or accepting peripheral substituents has a similar effect, although some slight variation is observed (Table 2) due to the effects of conjugation on the MO energies by such functions. However, in dimers, two sets of HOMOs and LUMOs are now available; it is, therefore, possible to lower selectively the energy of one HOMO/LUMO pair while simultaneously raising the energy of the other pair. This, in effect, allows the value of  $E_{\text{ox}} - E_{\text{red}}$  to be freely varied, as shown in Figure 1(b). Oxidation and reduction will now occur from a HOMO or LUMO from different porphyrin faces.

In general, the dimeric porphyrins appear to be slightly more readily oxidised but more difficult to reduce than the corresponding monomers, although the difference in potential is not normally more than 0.03–0.04 V. This is particularly noticeable in those cases involving primary oxidation of the porphyrin ring, rather than a central metal ion, and can be attributed to the known ability<sup>20,21</sup> of such dimers to delocalise the resulting charge, to varying degrees, over the dimer as a whole. This charge delocalisation, with resultant stabilisation, has been postulated<sup>22,23</sup> as one of the fundamental reasons for the presence of dimers in reaction centres, since in most other respects monomers perform similar tasks equally well.

The amino porphyrins were of particular interest since they exhibited an additional oxidation wave at low potential. The similarity in values for the first oxidation potential in a variety of aminoporphyrins strongly suggested that, in each case, initial oxidation occurred at the amino group. Interestingly this  $E_0$  value lay very close to 0.53 V, the value we found for aniline. The extra oxidation wave is not due to the presence of regioisomers: the isomers of (7) were separated and gave identical redox and fluorescence properties. The second oxidation of aminoporphyrins varied with metal substitution in the normal way, indicating that it occurs at the porphyrin

Table 2. Oxidation and reduction potentials for peripherally substituted porphyrin dimers

Compd.	$E_{\text{ox}}^a$	$E_{\text{red}}^a$	$E_{\text{ox}} - E_{\text{red}}$
(2)	1.00	1.26	2.26
(6)	1.23	0.78	2.01
(7)	0.50	1.37	1.87
Zn(2)	0.80	1.43	2.23
Zn(6)	1.01	0.96	1.97
Zn(7)	0.50	1.57	2.07
Cu(2)	0.88	1.39	2.27
Cu(7)	0.53		
(1)	0.92	1.24	2.16
(10)	0.95	0.86	1.81
(11)	0.52	1.30	1.82
(12)	0.51	0.86	1.37
Zn(1)	0.76	1.28	2.04
Zn(10)	0.78	0.87	1.65
Zn(12)	0.49	0.87	1.36

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub> solution, 0.2M TBABF<sub>4</sub> electrolyte,  $E$ (V) vs. Ag/AgCl.

Table 3. Second oxidation potentials for aminoporphyrins<sup>a</sup>

Compound	$E_{\text{ox}}$
(7)	1.2
Zn(7)	0.9
Cu(7)	0.95
(11)	1.1
Zn(12)	0.8

<sup>a</sup>  $\pm 0.1$  V as a result of poorly resolved waves. The second oxidation of (12) was not resolved at all.

system (Table 3). The first oxidation potential of nitroporphyrins also varied in the usual way with metal ion (Table 2). E.s.r. spectra of the monocation radical of (7) and Zn(7), generated both by bromine oxidation and preparative cyclic voltammetry, did not show hyperfine coupling to the amine nitrogen but were typical of porphyrin radical cation spectra.<sup>24</sup> Following oxidation, the sample was left standing until the radical had reverted back to unoxidised material, when absorption spectroscopy verified that the amino function remained attached to the porphyrin ring. In view of these results it is likely that initial electron loss from the amine is followed by an intramolecular redox change, with the electron localised, as for other octa-alkyl porphyrins, at the  $\alpha$ -pyrrole positions of the porphyrin ring.

Although the first oxidation and reduction potentials for each molecule were readily resolvable it was found that the resolution of subsequent waves decreased with increasing molecular complexity, with greater amounts of material required, possibly reflecting the manner in which the porphyrin interacts with the electrode. This precluded a more detailed analysis of the results, although in general the zinc derivatives gave stronger waves than the free base compounds. It was found that the subsequent oxidation waves for the aminomesoporphyrin (7) and its copper derivative were close to the solvent breakdown region in dichloromethane, slightly better resolution being obtained in acetonitrile using AC polarography.

Illustrative cyclic voltammograms are shown in Figure 2. Figure 2(a) shows the three consecutive oxidation waves for Zn(7) whilst the first reduction is irreversible. Such irreversible reduction waves for unstable porphyrin anions are not uncommon,<sup>25</sup> and in this case is possibly due to loss of hydride from the amine function. The cyclic voltammogram for Zn(10) in Figure 2(b) shows a two electron reduction followed by two one-electron reductions. The initial two-electron reductive step was also seen for Zn(6). The reduction waves can be assigned to

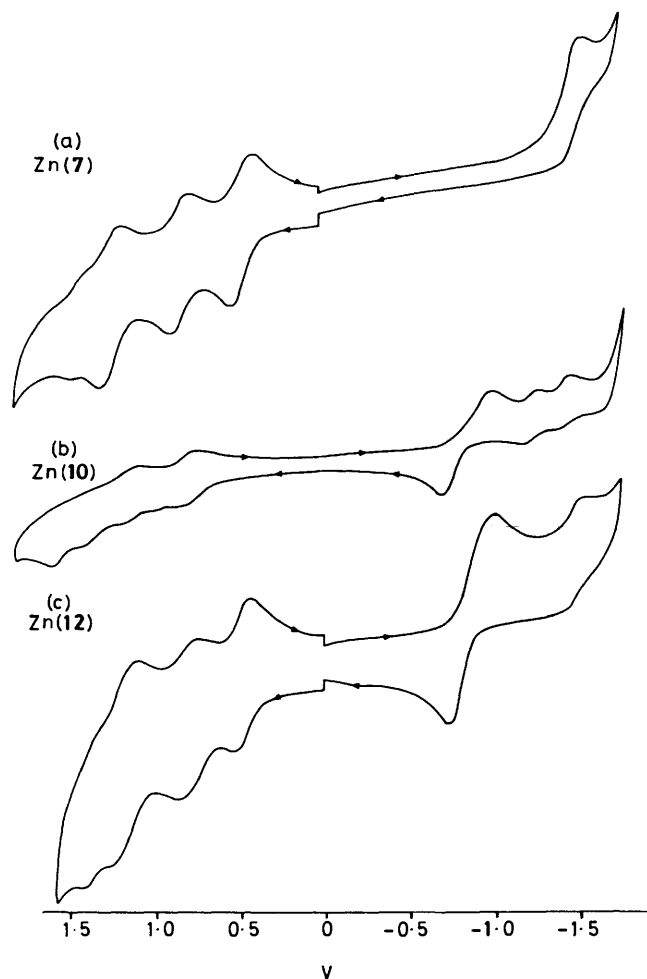


Figure 2. Cyclic voltammograms for three substituted porphyrin cofacial dimers

the nitro face, zinc face and nitro face respectively, as supported by comparison with Zn(12) in Figure 2(c) which shows similar behaviour, although the middle reduction wave in 2(b) has now moved to a higher potential [*cf.* Figure 2(a)] and has not been resolved. With Zn(1) the reduction potentials for each face of the dimer were poorly resolved. The partially overlapping reduction waves for the free base and metallated faces in this compound hindered the accurate assignment of the potential for the initial reduction of the freebase half of the molecule. The signals were resolved by the addition of a trace of pyridine which, by co-ordinating to the zinc ion, shifted the reduction potential of this face to more negative values, whilst that of the free base was unaffected.<sup>25</sup>

The  $E_0$  values in Table 2 clearly illustrate the effect of incorporating electron donating ( $\text{NH}_2$ ), or electron withdrawing ( $\text{NO}_2$ ) groups, into the porphyrin ring. The redox changes are greater than many of the effects produced by metallation and so the possibility exists, particularly in the case of porphyrin dimers, of using nitro and amino functionality 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 changes in the primary redox potentials of monomeric porphyrins in a dimer (unless there is an  $\text{M}^{3+}$  ion in the opposite face exerting an electrostatic influence), the results in Table 2 imply that a suitable combination of functionality can be chosen, prior to synthesis, to give a dimer with the required redox properties. Conversely, comparison of redox potentials

offers a powerful method for aiding in the characterisation of such dimers.

The  $E_0$  value of 0.5 V for the first oxidation potential of aminoporphyrins corresponds very closely to the value found<sup>26,27</sup> in many natural reaction centres, and so ought to allow the synthesis of dimers which accurately model reaction centre redox properties. Our present synthetic approach, which leads to difficult mixtures of regioisomers, is clearly not suitable in the long term: routes to peripherally substituted porphyrins that are isomerically pure will have to be developed if this approach is to be viable.

### Experimental

N.m.r. spectra were recorded on Bruker WH-400 or WM-250 operated in a Fourier transform mode, and the chemical shift scale of spectra was referenced to the residual proton signals of the solvent. Data were accumulated over 16 K data points with a spectral width of 12 or 20 p.p.m. Spectra were normally obtained in deuteriochloroform solutions. P designates the porphyrin aromatic ring in spectral assignments.

E.p.r. spectra were recorded on a Varian E-line spectrometer with a Varian E102 microwave bridge, in the X-band range. Fixed frequencies were measured from a Hewlett-Packard 5342A microwave frequency counter. Spectra were normally obtained in dichloromethane frozen matrices at 77 K.

High-resolution mass spectra were obtained on a Kratos MS-50 or MS-30 instrument. Low-resolution mass spectra were recorded on an MS-12 or MS-30 spectrometer, and fast atom bombardment (f.a.b.) mass spectra were obtained on an MS-902 instrument. For the latter experiments porphyrin samples were dissolved in a thioglycerol-diglycerol matrix. Mass spectra of compounds containing zinc or copper are quoted for the  $^{64}\text{Zn}$  or  $^{63}\text{Cu}$  isotopomer.

U.v./visible electronic absorption spectra were recorded on a Pye Unicam PU 8800 spectrometer in 1 cm  $\times$  1 cm cuvettes. Unless otherwise stated, all measurements were obtained from dichloromethane solutions. The following abbreviations were used: br broad; sh shoulder; s, strong; m, medium.

Electrochemical measurements were recorded by cyclic voltammetry or AC polarography on a linear chart recorder or Metrohm VA-Scanner E612 respectively. Measurements were made in dichloromethane or acetonitrile, employing platinum working and counter electrodes against an Ag/AgCl reference. Tetrabutylammonium tetrafluoroborate was used as supporting electrolyte.

Preparative thin layer chromatography was carried out on plates coated with 2 mm thickness Whatman 513F 230–400 mesh silica gel. The plates used for porphyrin purification were prepared without ZnS indicator. Column chromatography was carried out using Merck Art 7734 Kieselgel 60 (0.063–0.200 mm) or Merck Art 9385 Kieselgel 60 (0.040–0.063 mm) (flash silica). Metalloporphyrins were purified, where indicated, by passage through a column of neutral UG1 alumina.

Dichloromethane was distilled from phosphorus pentoxide, tetrahydrofuran (THF) from lithium aluminium hydride, and dimethylformamide (DMF) and dimethyl sulphoxide (DMSO) from calcium hydride prior to use. All porphyrin dimers described in this paper were diastereoisomeric mixtures lacking sharp or characteristic melting points.

Porphyrin bis(acid chlorides) were prepared from the corresponding bis(acids) as described in the accompanying paper,<sup>10</sup> and were used without isolation, purification or characterization.

**Copper Mesoporphyrin-II Bisacid Cu(3).**—Mesoporphyrin-II bisacid (200 mg) and  $\text{Cu}(\text{OAc})_2$  (72 mg) were refluxed in pyridine (10 ml) for 45 min. The resulting solution was

transferred to a conical flask and Et<sub>2</sub>O (70 ml) added. After several hours the product was filtered off, washed with Et<sub>2</sub>O, and dried *in vacuo* to give the title compound (210 mg, 97%);  $\lambda_{\max}$ . 401, 513, and 560 nm.

**Mesoporphyrin-II-diol (5).**—Lithium aluminium hydride (300 mg) was added in portions to mesoporphyrin-II bis(methyl ester) (1 g) in dry dimethoxyethane (200 ml). The mixture was stirred under nitrogen at room temperature for 3 h after which unchanged LAH was destroyed by the careful addition of aqueous Rochelle salt. Water (200 ml) was added and the aqueous phase extracted with CH<sub>2</sub>Cl<sub>2</sub> until the organic layer was pale purple. The CH<sub>2</sub>Cl<sub>2</sub> extracts were washed with water until the aqueous layer was clear, and then isolated, and reduced to dryness, finally under high vacuum. The product was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–hexane to yield the title compound (854 mg, 94%);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 10.14 and 10.09 (4 H, meso), 4.18 (4 H, t, PCH<sub>2</sub>CH<sub>2</sub>), 4.11 (4 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 3.97 (4 H, t, OCH<sub>2</sub>), 3.64 (12 H, br, PCH<sub>3</sub>), 2.55 (4 H, br, PCH<sub>2</sub>CH<sub>2</sub>), and 1.87 (6 H, t, PCH<sub>2</sub>CH<sub>3</sub>) (Found:  $M^+ - 2\text{H}$ , 536.3151. C<sub>34</sub>H<sub>40</sub>N<sub>4</sub>O<sub>2</sub> - 2 H, requires 536.3151);  $\lambda_{\max}$ . 397 ( $\epsilon$  125 × 10<sup>3</sup>), 497 (12), 532 (8.3), 566 (5.4), and 620 nm (3.7).

**Copper Co-facial Dimer Cu(1).**—Solutions of compound (5) and Cu(4) in CH<sub>2</sub>Cl<sub>2</sub> (2 × 500 ml) were added, dropwise over a period of 8 h, to a 3-neck flask containing DMAP (0.5 g) in CH<sub>2</sub>Cl<sub>2</sub> (300 ml). The mixture was stirred overnight and then evaporated and the residue chromatographed through a column of 0.063–0.200 mm silica. CH<sub>2</sub>Cl<sub>2</sub> removed some minor impurities and CHCl<sub>3</sub> eluted the major component. The title compound was isolated as the fastest running band from preparative t.l.c. plates [eluant CH<sub>2</sub>Cl<sub>2</sub>–MeOH, 95:5] and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–MeOH (201 mg, 54%);  $\lambda_{\max}$ . 388, 502, 532, 567, and 624 nm (Found:  $M^+$ , 1 129.5133. C<sub>68</sub>H<sub>74</sub>–CuN<sub>8</sub>O<sub>4</sub> required  $M$ , 1 129.5128).

**Zinc Co-facial Dimer Zn(1).**—Mesoporphyrin-II-diol (5) (207 mg) and Zn(OAc)<sub>2</sub> (70 mg) were refluxed in CH<sub>2</sub>Cl<sub>2</sub>–MeOH (100 ml) for 30 min to give zinc mesoporphyrindiol Zn(5). Solvent was removed, finally under high vacuum, and the zinc diol was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 ml) containing pyridine (3 ml). The acid chloride (4), prepared from compound (3) (220 mg), was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 ml). The reactants were added dropwise over a period of 8 h to a 3-neck flask containing DMAP (0.5 g) in CH<sub>2</sub>Cl<sub>2</sub> (300 ml), and the mixture was then stirred overnight. Solvent was removed, finally under high vacuum, and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed through a column of 0.063–0.200 mm silica. CH<sub>2</sub>Cl<sub>2</sub> removed some minor components and the desired product was included in the first major band following elution with CHCl<sub>3</sub>. The title compound was isolated as the fastest running band from preparative t.l.c. plates [eluant CH<sub>2</sub>Cl<sub>2</sub>–MeOH, 95:5] and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>–MeOH (175 mg, 41%);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 9.65–9.32 and 8.18–8.02 (meso), 3.33 and 3.20 (PCH<sub>3</sub>), 1.95 and 1.79 (m, PCH<sub>2</sub>CH<sub>3</sub>) and –5.09 (br, NH);  $\lambda_{\max}$ . 390 ( $\epsilon$  159 × 10<sup>3</sup>), 500 (11), 534 (13.7), 570 (16.8) and 622 nm. (3.1) (Found:  $M^+$ , 1 130.5124. C<sub>68</sub>H<sub>74</sub>N<sub>8</sub>O<sub>4</sub>Zn requires  $M$ , 1 130.5124).

**Co-facial Dimer (1).**—Mesoporphyrin-II bisacid (212 mg) and the diol (5) (174 mg) were allowed to react according to the procedure described for the synthesis of Cu(1). An identical work-up procedure gave the title compound (222 mg, 57%);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 9.71–9.52 and 8.31–7.92 (meso), 3.1 (major), 3.21 (major), 3.22 (minor), 3.34 (minor) (PCH<sub>3</sub>), 1.99 and 1.83 (m, PCH<sub>2</sub>CH<sub>3</sub>), and –5.08 and –5.38 (br, NH) (Found:  $M^+$ , 1 068.5989. C<sub>68</sub>H<sub>76</sub>N<sub>8</sub>O<sub>4</sub> requires  $M$ , 1 068.5987);  $\lambda_{\max}$ . 382 ( $\epsilon$  192 × 10<sup>3</sup>), 500 (18), 532 (12), 568 (9.6), and 622 nm (6.2).

**Nitromesoporphyrin-II Bis(methyl ester) (6).**—Mesoporphyrin-II bis(methyl ester) (500 mg) was added to fuming nitric acid–AcOH (1:1) (80 ml) at 4 °C, and the mixture was stirred vigorously for 90 s before being poured onto ice–water (800 ml). The product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and washed with aqueous NaHCO<sub>3</sub> and water before removal of the organic solvent under reduced pressure. Flash chromatography [eluant CH<sub>2</sub>Cl<sub>2</sub>] gave a small amount of unchanged starting material, whilst CHCl<sub>3</sub> eluted the title compound (491 mg, 91%);  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 10.23–10.06 (4 H, meso), 4.37–4.00 (4 H, m, PCH<sub>2</sub>CH<sub>2</sub>), 4.10 and 3.78 (4 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 3.65 (12 H, br, PCH<sub>3</sub>), 3.29–3.02 (4 H, m, PCH<sub>2</sub>CH<sub>2</sub>), 1.90–1.69 (6 H, m, PCH<sub>2</sub>CH<sub>3</sub>), and –5.1 (br, NH) (Found:  $M^+$ , 639.3057. C<sub>36</sub>H<sub>41</sub>N<sub>5</sub>O<sub>6</sub> requires 639.3036.  $\lambda_{\max}$ . 396 ( $\epsilon$  90 × 10<sup>3</sup>), 500 (9.9), 534 (6.9), 568 (5.2), and 622 nm (3.8).

**Aminomesoporphyrin-II Bis(methyl ester) (7).**—Nitromesoporphyrin-II bis(methyl ester) (520 mg) was dissolved in EtOH (30 ml)–THF (10 ml) containing Pd/C catalyst (600 mg) and cyclohexene (2 ml), and the reaction mixture was stirred under reflux for 10 h. After cooling, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 ml), filtered, and evaporated to provide a residue which was taken up in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed through a column of 0.063–0.200 mm silica. CHCl<sub>3</sub> eluted some starting material and CH<sub>2</sub>Cl<sub>2</sub>–MeOH (9:1) gave the title compound, which was further purified by preparative t.l.c. (eluant CH<sub>2</sub>Cl<sub>2</sub>–MeOH, 95:5). The top two bands were collected (381 mg, 77%);  $\delta_{\text{H}}$  (250 MHz, CDCl<sub>3</sub>) 9.48, 9.12, 9.08, (meso), 6.69 (NH<sub>2</sub>), 4.09–3.83 (8 H, br m, PCH<sub>2</sub>), 3.68–3.37 (12 H, br, PCH<sub>3</sub>), 3.19–3.04 (4 H, m, PCH<sub>2</sub>CH<sub>2</sub>), 2.73 (6 H, br m, PCH<sub>2</sub>CH<sub>3</sub>) (Found:  $M^+$ , 609.3315. C<sub>36</sub>H<sub>43</sub>N<sub>5</sub>O<sub>4</sub> requires  $M$ , 609.3315);  $\lambda_{\max}$ . 413 ( $\epsilon$  63.4 × 10<sup>3</sup>), 514 (4.7), 552 (2.6), 586 (2.3), and 644 nm (3.2).

**Aminomesoporphyrin-II-diol (9).**—Lithium aluminium hydride (200 mg) was added to the amino diester (7) (370 mg) dissolved in dry dimethoxyethane (80 ml) and the solution stirred under nitrogen for 2 h. Following the work-up procedure described earlier for compound (5), chromatography on silica plates (eluant CH<sub>2</sub>Cl<sub>2</sub>–MeOH, 93:7) gave the title compound (285 mg, 86%) (Found:  $M^+ - \text{NH}_3$ , 536.3168. C<sub>34</sub>H<sub>43</sub>N<sub>5</sub>O<sub>2</sub>–NH<sub>3</sub> requires  $M$ , 536.3151);  $\lambda_{\max}$ . 414 ( $\epsilon$  51 × 10<sup>3</sup>), 514 (3.8), 554 (2.2), 586 (1.5), and 644 nm (1.9).

**Zinc Amino(nitro)co-facial Dimer Zn(12).**—Aminomesoporphyrin-II-diol (9) (185 mg) and Zn(OAc)<sub>2</sub> (65 mg) were refluxed in CH<sub>2</sub>Cl<sub>2</sub>–MeOH (9:1) (100 ml) for 30 min. Solvent was removed, finally under high vacuum, and the zinc amino diol Zn(9) was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 ml), containing a trace of pyridine, if required, to give complete dissolution.

Nitromesoporphyrin-II bis(acid chloride) (8) was prepared from compound (6) (205 mg), in the standard manner. The acid chloride (210 mg) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 ml) and high dilution conditions followed. Solvent was removed and the residue eluted through a 0.063–0.200 mm silica column. CHCl<sub>3</sub> eluted a fast running minor component and CH<sub>2</sub>Cl<sub>2</sub>–MeOH (9:1) gave a major band containing product. Following chromatography over preparative silica plates [eluant CH<sub>2</sub>Cl<sub>2</sub>–MeOH, 96:4], the top band was isolated to give the title compound (76 mg, 19%) (Found:  $M^+ - \text{NH}_2$ , 1 174.4870. C<sub>68</sub>H<sub>74</sub>N<sub>10</sub>O<sub>6</sub>Zn - NH<sub>2</sub> requires  $M$ , 1 174.4897);  $\lambda_{\max}$ . 400 ( $\epsilon$  156 × 10<sup>3</sup>), 413 (116), 506 (15.3), 540 (11.7), 566 (9.1), and 600 nm (6.9).

**Amino(nitro)co-facial Dimer (12).**—Zinc was removed from Zn(12) by the method described below to give the free-base compound virtually quantitatively;  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 10.22–8.95 and 8.7–7.6 (meso), 7.0–5.0 (br, NH<sub>2</sub>), and –5.09

and  $-3.91$  (br, NH) (Found:  $M^+ - NH_2$ , 1 112.5762.  $C_{68}H_{76}N_{10}O_6 - NH_2$  requires  $M$ , 1 112.5767).

**Zinc Nitroco-facial Dimer Zn(10).**—Nitromesoporphyrin-II bis(acid chloride) was prepared from the bisester (6) (230 mg) as described earlier. The synthesis of the zinc diol Zn(5) (207 mg) has also been described above and, following identical reaction and work-up procedures, the title compound (189 mg, 47%) was obtained;  $\delta_H$  (400 MHz,  $CDCl_3$ ) 10.17–9.31, 8.92, 8.74 and 8.37 (meso), and  $-4.96$  (br, NH) (Found:  $M^+$ , 1 175.4899.  $C_{68}H_{73}N_9O_6Zn$  requires  $M$ , 1 175.4975);  $\lambda_{max}$ . 386s, 398 ( $\epsilon$   $175 \times 10^3$ ), 500 (10.1), 530 (13.0), 568 (14.7), and 624 nm (2.6).

**Nitroco-facial Dimer (10).**—Nitromesoporphyrin-II bis(acid chloride), prepared from the bisester (6) (210 mg), was treated with the diol (5) (174 mg) as described in the synthesis above. An identical work-up procedure gave the desired product (174 mg, 51%).  $\delta_H$  (400 MHz,  $CDCl_3$ ) 10.19–8.89 (meso),  $-5.2$  (br, NH) (Found:  $M^+$ , 1 113.5840.  $C_{68}H_{75}N_9O_6$  requires  $M$ , 1 113.5869);  $\lambda_{max}$ . 390 ( $\epsilon$   $92.7 \times 10^3$ ), 500 (89), 532 (6.0), 568 (4.6), and 622 nm (2.7).

**Aminoco-facial Dimer (11).**—The nitroco-facial dimer (10) (5 mg) was dissolved in EtOH (1 ml)–THF (2 ml), containing 10% Pd/C (20 mg) and cyclohexene (0.5 ml). The mixture was stirred under reflux for 8 h and then cooled, diluted with  $CH_2Cl_2$  (2 ml), and the catalyst filtered off. Following work-up and chromatography on preparative silica plates (eluant  $CH_2Cl_2$ –MeOH, 9:1), compound (11) (3.8 mg, 78%) was obtained from the bands below the faster running unchanged (10);  $\delta_H$  (400 MHz,  $CDCl_3$ ) 9.73–8.73 and 8.05–7.85 (br, meso), 6.2–4.7 (br,  $NH_2$ ), and  $-3.9$  and  $-5.1$  (br, NH);  $\lambda_{max}$ . 393 ( $\epsilon$   $105 \times 10^3$ ), 503 (6.5), 528 (5.9), 569 (4.2), 623 (2.9), and 652 nm (2.5).

**General Metallation Procedures.**—The following conditions were used in the metallation reactions of porphyrin samples. In each case, reaction was followed using electronic absorption spectroscopy.

**Magnesium.** The porphyrin (10 mg) and anhydrous  $Mg(ClO_4)_2$  (20 mg) were stirred in refluxing pyridine (3 ml) until the reaction had gone to completion. The reaction mixture was poured onto water (50 ml) and the porphyrin extracted with  $CH_2Cl_2$ . The extracts were washed with water, dried ( $Na_2SO_4$ ), and evaporated. The residue was taken up in  $CH_2Cl_2$  (which had been previously de-acidified by standing over neutral alumina), eluted through a column of neutral alumina with  $CH_2Cl_2$ –MeOH (95:5), and recrystallised from  $CH_2Cl_2$ –pentane by vapour diffusion.

**Zinc.** The porphyrin (10 mg) and  $Zn(OAc)_2$  (5 mg) were dissolved in  $CH_2Cl_2$  (3 ml)/MeOH (1 ml) and warmed gently for 15 min.  $CH_2Cl_2$  (10 ml) was added and the organic layer washed with water, dried ( $Na_2SO_4$ ), and solvent removed. The residue was taken up in  $CH_2Cl_2$ , eluted through a column of alumina with  $CH_2Cl_2$ –MeOH (99:1), and recrystallised from  $CH_2Cl_2$ –pentane by vapour diffusion.

**Silver.** The porphyrin (10 mg) and  $Ag(OAc)$  (8 mg) were dissolved in  $CH_2Cl_2$  (3 ml)–MeOH (1 ml) and stirred under reflux for 30 min. Work-up proceeded as for zinc.

**Copper.** The porphyrin (10 mg) and  $Cu(OAc)_2$  (8 mg) were dissolved in  $CH_2Cl_2$  (3 ml)–MeOH (1 ml) and stirred under reflux for 20 min. Work-up proceeded as for zinc.

**Cobalt.** The porphyrin (10 mg) and  $Co(OAc)_2$  (8 mg) were dissolved in  $CH_2Cl_2$  (3 ml)–MeOH (1 ml) and stirred under reflux for 30 min. Work-up proceeded as for zinc.

**Cobalt(III)X** ( $X = Cl^-$  or  $Br^-$ ). The corresponding cobalt(II) porphyrin (5 mg) was dissolved in  $CH_2Cl_2$  (20 ml)–MeOH (10 ml) and 1 drop of conc. HX was added. After aerobic stirring for

6 h at room temperature,  $CH_2Cl_2$  (10 ml) was added and the reaction mixture washed with aqueous NaX. The organic layer was dried ( $Na_2SO_4$ ) and evaporated and the residue recrystallised from  $CH_2Cl_2$ –pentane by vapour diffusion.

**Manganese(III)X** ( $X = Cl^-$ ,  $Br^-$ , or  $I^-$ ). The porphyrin (5 mg) and  $Mn(OAc)_2$  (10 mg) were added to DMF (3 ml) and the mixture stirred aerobically at  $120^\circ C$  for 6 h. After the mixture had cooled, a solution of  $NEt_4X$  (1 g) in  $CH_2Cl_2$  (3 ml)–MeOH (2 ml) was added and stirring continued for 15 min at room temperature.  $CH_2Cl_2$  (10 ml) was added and the reaction mixture washed with aqueous NaX. The organic layer was dried ( $Na_2SO_4$ ), evaporated, and the residue recrystallised from  $CH_2Cl_2$ –pentane by vapour diffusion.

**Iron(III)Cl<sup>-</sup>.** The porphyrin (5 mg) and  $FeCl_2$  (10 mg) were added to a solution of  $NEt_4Cl$  (0.4 g) in  $CH_2Cl_2$  (4 ml)–MeOH (0.5 ml). After the mixture had been warmed gently for 10 min it was diluted with  $CH_2Cl_2$  (10 ml) and washed with brine. The organic layer was dried ( $Na_2SO_4$ ) and evaporated, and the residue recrystallised from  $CH_2Cl_2$ –pentane by vapour diffusion.

**Synthesis of Mixed Metal Dimers.**—In those dimers containing one  $M^{3+}$  ion, it was convenient to introduce this particular ion last in the metallation sequence. Zn(1) was metallated by the previously described procedures to give ZnM(1).

**Removal of Zinc from a Dimer.**—The porphyrin (10 mg) was dissolved in  $CH_2Cl_2$  (15 ml) and the solution shaken vigorously for 90 s with 16% HBr (20 ml). The organic layer was washed with water, dried ( $Na_2SO_4$ ), and evaporated under reduced pressure.

The synthesis of MM'(1) was then completed by the procedures described above. Note that, in the synthesis of Co/Mn mixed metal porphyrins, cobalt was introduced first to avoid transmetallation of the manganese porphyrin. In addition, after the removal of zinc from ZnCo(1) by acid, the  $CH_2Cl_2$  solution of the porphyrin was washed with aqueous dithionite in order to reduce any cobalt oxidised as a result of the acidic conditions. In general this was not found to be a serious problem.

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