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A new and general synthesis of porphyrin dimers is described. The synthesis involves the reaction of dibromoalkanes with phenolic porphyrins, such as 5(4-hydroxyphenyl)-10,15,20-triarylporphyrin, to form ω -bromoalkyl porphyrin ethers. The latter compounds are then reacted with a second phenolic porphyrin to give porphyrin dimers. A mixed metalloporphyrin dimer has been prepared which contains both V(IV) and Cu(II). The compounds have been examined spectroscopically. The free-base porphyrin dimers show a splitting of the intense Soret band. This is interpreted as indicative of weak singlet energy transfer between the covalently linked porphyrins.

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Introduction.

Porphyrin aggregates play an important role in both photosynthetic and metabolic processes (1,2). The study of electron transfer within these aggregates is difficult because of the complexity of the naturally occurring systems and would be greatly aided if simple dimeric and polymeric porphyrin molecules were available.

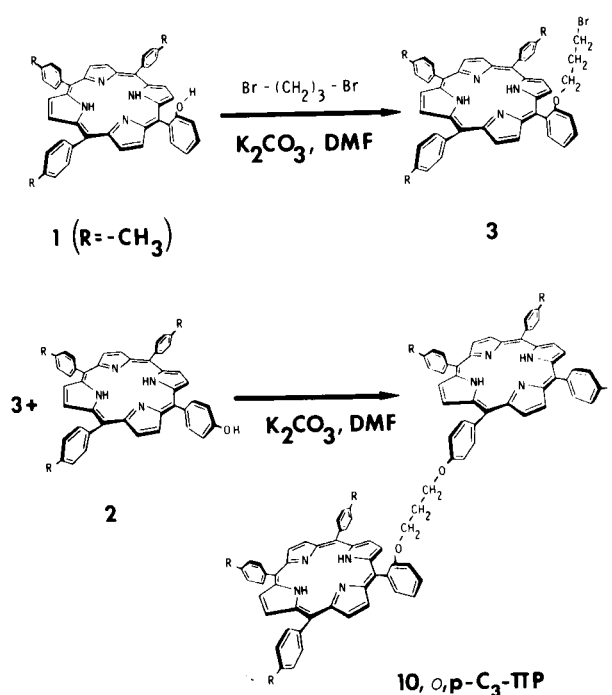
Because of their ease of preparation the tetraarylporphyrins have been widely used as models for the naturally occurring porphyrins (3). The utility of the tetraarylporphyrins has been limited by the fact that these porphyrins are difficult to functionalize. Recently we reported the first synthesis of a series of monosubstituted tetraarylporphyrins (4). We have subsequently shown that these porphyrins can be easily functionalized and we have used them as models for the active sites in hemoglobin (5). In this paper we further demonstrate the synthetic utility of these compounds by presenting a simple two-step synthesis of porphyrin dimers with yields as high as 76%. This report details the synthesis of a series of dimeric porphyrins in which there is a systematic variation in the geometrical relationship of the two halves of the dimer. Dolphin, *et al.*, (6) have previously reported the synthesis of some covalently linked octaalkylporphyrins. The procedure reported here for tetraarylporphyrins should be of considerably greater utility in view of its simplicity.

In more recent work Ogoshi, *et al.*, (7), Collman, *et al.*, (8), and Arnold, *et al.*, (9) have reported the synthesis of some 'cyclophane porphyrins' and porphyrin dimers in which the porphyrins are held together by a double linkage. The difference between the properties of these cyclophane porphyrins and the singly linked porphyrins reported here are discussed.

Results and Discussion.

The synthetic route used in this paper is illustrated in Scheme I where the synthesis of the mixed porphyrin dimer, *o,p*-C₃-TTP (10) is shown. The reaction of an excess of dibromopropane with the *o*-hydroxyporphyrin, 1, gives the 3-bromopropoxy derivative, 3, in 96% yield.

Scheme I

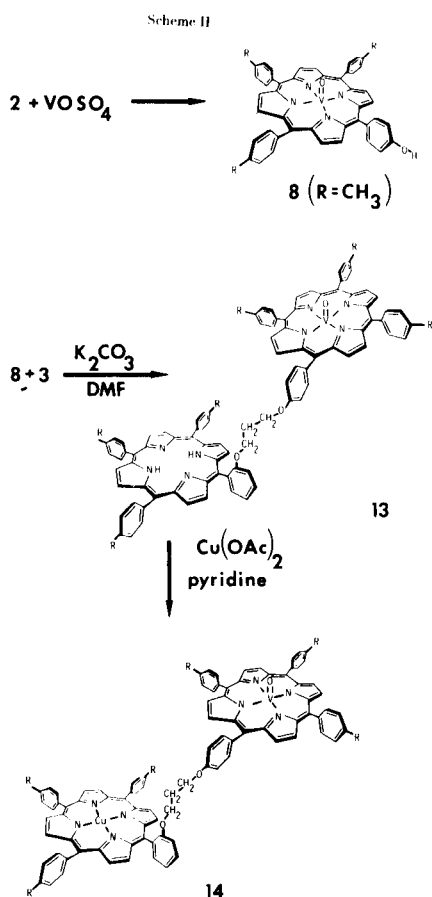


The latter compound is easily separated from the starting materials by chromatography since it is relatively nonpolar.

The porphyrin dimer is formed by the reaction of 3 with one mole of the *p*-hydroxyporphyrin, 2. The reaction proceeds in high yield, but reactants must be separated by gel permeation chromatography since both compound 3 and the dimer 10 are nonpolar.

Metals may be inserted into the free base porphyrin dimers by standard procedures (11,12). Mixed metalloporphyrin dimers may be synthesized by inserting a metal into either of the porphyrin monomers. This is illustrated in Scheme II by the synthesis of the mixed vanadium, copper dimer, 14.

The *p*-hydroxyvanadylporphyrin, 8, reacted without difficulty with the *o*-bromopropoxy porphyrin, 3, to give the vanadyl dimer, 13, from which the mixed copper,



vanadium complex, **14**, could readily be prepared. Interestingly, the vanadyl complex, **7**, of *o*-hydroxytritolyl-

porphyrin reacted extremely slowly, if at all, with alkyl bromides. This may indicate a significant amount of interaction between the *o*-hydroxy group and the vanadyl moiety. Hydrogen bonding may be important, but purely steric factors cannot be ruled out. It does not seem likely that the decreased reactivity of **7** is due to the electron withdrawing ability of the vanadyl ion, since the vanadyl complex of the *p*-hydroxyprophyrin **2** reacts readily with alkyl bromides.

The dimeric tritolylporphyrins prepared in this study are stable, purple, micro-crystalline solids which have essentially the same physical properties as TPP. The more symmetric dimers such as *p,p*- C_6 -TTP are much less soluble than their asymmetric analogues, probably because of increased intermolecular interactions.

Singlet energy transfer is known to occur between chlorophyll, Chl, molecules (**13,14**). Presumably the Chl molecules are arranged in planar, parallel arrays in the chloroplasts (**15**) in order to facilitate energy transfer. It was therefore of interest to examine the absorption spectra of the porphyrin and metalloporphyrin dimers prepared in this study. The data in Table I show that the visible absorption bands have positions which are essentially identical to those of the corresponding porphyrin monomers.

The intensities are, except in the Soret region, those that would be expected for a molecule containing two non-interacting chromophores. In the Soret region the intensities of the free-base dimers are about 70% of that expected. This appears to be the result of a splitting of the 420 nm bands into two or more components. This is

Table I
Absorption Band Maxima (a)

Compound	λ max (ϵ) (b)					
TTP	648 (5.1)	590 (5.3)	550 (7.5)	515 (17.9)	484 (3.1) (c)	418 (416)
TTP	648 (5.0)	592 (5.8)	553 (9.4)	516 (17.4)	486 (4.0) (c)	420 (434)
15	649 (6.2)	593 (5.6)	553 (8.5)	518 (19.0)	481 (3.6) (c)	421 (487)
15 (e)	652 (6.9)	594 (5.8)	551 (9.3)	517 (19.9)	485 (4.0) (c)	422 (475)
16	649 (5.1)	593 (5.2)	555 (10)	519 (17.8)	485 (3.5) (c)	422 (494)
<i>o,o</i> - C_3 -TTP	647 (7.5)	592 (10.5)	554 (16.5)	518 (34.5)	486 (6.5) (e)	420 (663) (f)
<i>o,o</i> - C_3 -TTP (e)	648 (7.8)	593 (10.5)	551 (17.7)	517 (36.7)	487 (7.5) (c)	420 (681) (f)
<i>o,o</i> - C_5 -TTP	649 (11.5)	593 (10.6)	552 (16.5)	518 (34.2)	487 (7.0) (c)	419 (712)
<i>o,p</i> - C_3 -TTP		592 (11.4) (c)	553 (18.8)	516 (34.4)	487 (7.3) (c)	420 (654)
Cu(TTP)		574 (3.2)	540 (21.2)	504 (3.7) (c)		417 (495)
Cu_2 - <i>o,o</i> - C_3 -TTP		575 (5.5) (c)	540 (44.1)	503 (7.6) (c)		419 (750)
Cu_2 - <i>o,p</i> - C_3 -TTP		575 (6.3) (c)	542 (43.3)	502 (7.5) (c)		419 (669)
13		590 (8.0) (c)	551 (29)	517 (19.6) (c)		426, 421 (488) (f)

(a) The spectra were recorded on 10^{-5} and 10^{-7} M chloroform solutions unless otherwise stated. Solid potassium carbonate was present in the cell to remove acidic impurities. (b) The values in parentheses should be multiplied by 10^3 . (c) Shoulder. (d) The spectrum of TTP has been previously reported by F. R. Longo, M. G. Finarelli and J. B. King, *J. Heterocyclic Chem.*, **6**, 927 (1969). (e) Benzene solvent. (f) Broad or double maxima.

particularly evident in the absorption spectrum of *o,o*-C₃-TTP where a new band appears as a distinct shoulder on the low energy side of the 420 nm band. The possibility that the decrease in the intensity of the Soret band was due to the presence of more than one absorbing specie (folded and unfolded conformers) was ruled out by the fact that identical spectra were obtained in both chloroform and benzene solvent. The two solvents would be expected to have appreciably different effects on any conformational or dimerization process. A splitting of the Soret absorption of matrix isolated porphine has previously been observed by Leonard and Longo (17). They conclude that the porphine was trapped as pairs or "dimers" in the matrix and that the splitting was due to Davydov splitting of molecular states in the pairs. Gouterman, *et al.*, (18) have observed a similar, temperature dependent splitting of the Soret band in μ -oxo-metalloporphyrin dimers. Dolphin, *et al.*, (6) in their study of covalently linked octaalkylporphyrins did not study the free-base dimers. Instead they prepared mixed metalloporphyrin dimers. The compounds did not show a splitting of the Soret band. By contrast, the di-copper complexes prepared in this work do show a decrease in the intensity of the Soret band.

These results may be compared to those of Boxer and Closs (19) who observed an appreciable red shift in the 656 nm absorption of a covalently linked, dimeric derivative of pyrochlorophyllide *a*. The red shift was dependent on the state of solvation of the dimer. Boxer and Closs proposed that two water molecules hold the two halves of the dimer together by coordinating to the Mg atom of one chromophore and hydrogen-bonding to the keto-carbonyl group of the other. In this tightly locked dimer exciton interactions presumably give rise to the observed red shift. Gouterman, *et al.*, (18) have examined the absorption spectra of μ -oxoporphyrin dimers and presented a model for exciton coupling in these compounds. The different electronic interactions observed in the μ -oxo-dimers, the cyclophane porphyrins, and the dimeric compounds reported here suggests that very subtle stereochemical factors can have significant effects on electronic structure in these dimers. This subject is under further investigation.

The possibility of a long range interaction between porphyrins containing paramagnetic metal ions was briefly investigated. The electron spin resonance spectrum of a mixed copper-vanadium dimer, **14**, was recorded. The observed spectrum is the sum of that observed for simple copper ($g_{av} = 2.11$) and vanadyl ($g_{av} = 2.03$) porphyrins (20-23). Within experimental error there appears to be no through-space coupling of the unpaired electron spin on the two ions in the mixed dimer.

This result contrasts with the observations of Collman, *et al.*, (8). Collman found that A_{\parallel} in the dimeric dicobalt

or dicopper porphyrins prepared in their study was roughly twice that observed in metalloporphyrin monomers. This significant result must be attributed to a greater orbital overlap in the doubly-linked porphyrins with which they worked. The doubly-linked porphyrins are constrained to a face-to-face conformation whereas the present compounds have a good deal of conformational freedom and this apparently leads to a decrease in metal-metal interaction.

Finally, it is of interest that the unsymmetrically substituted porphyrin monomers prepared in this work, 5-(2-(2-phenyl-1-ethoxy)phenyl)-10,15,20-tritolyldiporphyrin, **15**, and 5-(4-propoxy)phenyl-10,15,20-tritolyldiporphyrin, **16**, show a slight increase in the intensities of the Soret bands over that observed in TTP, (Table I).

Acknowledgments.

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EXPERIMENTAL

The nmr spectra were obtained on a Perkin-Elmer R24B spectrometer operating at 60 MHz. Unless otherwise specified, the solvent was deuteriochloroform with TMS as an internal standard. The shifts, δ , are given in ppm and the coupling constants are in Hz. The spectra were generally taken on nearly saturated solutions. It should be noted that the shifts are often concentration dependent (24). This is especially true of the protons of the functionalized ring of mono-substituted porphyrins. The protons at the 2,3,7,8,12,13,17,18 positions of the porphyrin ring are referred to below as the β -pyrrole protons. Absorption spectra were obtained in chloroform solution on a Cary 16 recording spectrophotometer. Electron spin resonance spectra were obtained in chloroform solutions or glasses on a Varian E-4 spectrometer, operating at 9Ghz.

Analyses were performed by Chemanalytics, Inc., Tempe, Arizona. The compounds were analyzed as their copper derivatives.

The chromatographic separations described below were effected by the dry-column procedure (25) using either alumina (Fisher Scientific A-540) or silica gel (Woelm-04526; obtained through ICN Pharmaceuticals, Inc.). The copper derivatives were chromatographed on neutral alumina (Baker 0540) Brockmann activity grade 1. The thin layer chromatographic plates were obtained from the Eastman Kodak Company (Eastmann Chromagram sheets; 13252 and 13181). The dimeric porphyrins were separated from the corresponding monomers by gel permeation chromatography using styrene-divinylbenzene copolymer beads (BioRad Laboratories, Biobeads S-X2, 200-400 mesh).

5-(2-(3-Bromo-1-propoxy)phenyl)-10,15,20-tritolyldiporphyrin (**3**).

A mixture of 1.00 g. (1.49 mmoles) of compound **1**, 4.1 g. (19.8 mmoles) of 1,3-dibromopropane and 3.0 g. of anhydrous potassium carbonate was stirred magnetically with 30 ml. of dimethylformamide for 24 hours. The reaction mixture was then poured into a mixture of 170 ml. of water and 30 ml. of methanol. The precipitated porphyrin was filtered off using a Buchner funnel and washed with a little methanol. The porphyrin was dried in

an oven at 100° to remove excess dibromopropane and then chromatographed on a 30 x 2 cm column of alumina using chloroform as the eluant to give 1.14 g. (96%) of pure **3**.

The porphyrin **3** moves with the solvent front and any unreacted **1** remains on the column as a slow moving purple band; nmr: δ , 8.83 (s, 6H, β -pyrrole); 8.78 (s, 2H, β -pyrrole); 7.93 (d, 6H, tolyl-2,6-protons); 7.34 (d, 6H, tolyl-3,5-protons); 7.2-7.1 (m); 3.95 (t, 2H, -CH₂-O-); 3.25 (t, 2H, -CH₂-Br); 2.15 (s, 9H, methyl); 1.6 (m, 2H, -CH₂-).

Anal. Calcd. for C₅₀H₄₁BrN₄O, M.W. 793.59: C, 75.67; H, 5.17. Found: C, 75.43; H, 5.13.

5-(2-(5-Bromo-1-pentoxy)phenyl)-10,15,20-tritolylporphyrin (**4**).

The porphyrin **4** was prepared by a procedure analogous to that given for **3**. The yield was 93%; nmr: δ , 8.83 (s, 6H, β -pyrrole); 8.78 (s, 2H, β -pyrrole); 7.98 (d, 6H, tolyl-2,6-protons); 7.33 (d, 6H, tolyl-3,5-protons); 7.2-1.0 (m); 3.96 (t, 2H, -CH₂-O-); 7.33 (t, 2H, -CH₂-Br-); 2.15 (s, 9H, methyl); 1.6 (m, 6H, -(CH₂)₃-).

Anal. Calcd. for C₅₂H₄₅BrN₄O, M.W. 821.65: C, 76.01; H, 5.48. Found: C, 76.23; H, 5.57.

5-(4(5-Bromo-1-pentoxy)phenyl)-10,15,20-tritolylporphyrin (**5**).

The porphyrin **5** was prepared by a procedure analogous to that given for **3** except that 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin, **2**, was used. The product was chromatographed on silica gel. The yield of **5** was 93%; nmr: δ , 8.83 (s, 8H, β -pyrrole), 8.05 (d, 8H, tolyl-2,6-protons); 7.46 (d, 6H, tolyl-3,5-protons); 7.10 (d, 2H, phenyl-3,5-protons); 4.08 (t, 2H, -CH₂-O-); 3.41 (t, 2H, -CH₂-Br); 2.13 (s, 9H, methyl); 1.16 (m, 6H, -(CH₂)₃-).

Anal. Calcd. for C₅₂H₄₅BrN₄O, M.W. 821.65: C, 76.01; H, 5.48. Found: C, 76.13; H, 5.37.

5-(4(6-Bromo-1-hexoxy)phenyl)-10,15,20-tritolylporphyrin (**6**).

The porphyrin **6** was prepared in 96% yield by a procedure exactly analogous to that given for the preparation of **5**. The nmr spectrum of **6** was identical to that of **5** except that the resonance at 1.6 ppm had an integral which corresponded to eight hydrogen atoms.

Anal. Calcd. for C₅₃H₄₇BrN₄O, M.W. 835.68: C, 76.17; H, 5.63. Found: C, 76.01; H, 5.41.

Oxo[5,10,15-tritolyl-20-(2-hydroxyphenyl)porphinato(2-)]vanadium(IV) (**7**).

The vanadyl ion was inserted into the *o*-hydroxyporphyrin **1** by the method of Erdman, *et al.*, (26). The porphyrin **1**, 0.16 g. (0.235 mmole) was dissolved in a mixture of 40.5 ml. of glacial acetic acid and 19.5 ml. of pyridine and 0.40 g. (2.0 mmoles) of vanadyl sulfate dihydrate was added. The reaction mixture was gently refluxed overnight. The visible spectrum of an aliquot of the reaction mixture showed that the four bands characteristic of the free base porphyrin had been replaced by a single band at 540 nm. The reaction mixture was poured into 100 ml. of water and the precipitated porphyrin filtered off with the aid of a Büchner funnel. The product was dried in an oven at 100° and then chromatographed on a 20 x 2 cm silica gel column using chloroform as the eluant. The vanadyl porphyrin, **7**, moves as a cherry red band just behind the solvent front and is preceded by red material which has a greenish yellow tinge. The portion containing **7** was collected and taken to dryness on a rotary evaporator, 0.151 g. (87%). The compound has a R_f value of 0.6 on silica gel plates with chloroform as the eluant. The compound was used directly in the synthesis of the *o,o*-VO-C₃-TTP dimer.

Oxo[5,10,15-tritolyl-20-(4-hydroxyphenyl)porphinato(2-)]vanadium(IV) (**8**).

The porphyrin **2**, 0.15 g. (0.22 mmole) was dissolved in a mixture of 40.5 ml. of glacial acetic acid and 19.5 ml. of pyridine and 0.40 g. (2.0 mmoles) of vanadyl sulfate was added. The reaction mixture was heated just below the reflux temperature for 12 hours and then poured into 100 ml. of water. The precipitated porphyrin was filtered off and dried at 100°. Chromatography on a 20 x 2 cm silica gel column using chloroform as the eluant gave a single cherry red band which moved slowly down the column. The band containing the complex was collected and flashed down to give 0.14 g. of **10** (84%). The compound has an R_f value of 0.4 on silica gel plates with chloroform as the eluant. The compound was used directly in the synthesis of **13**.

5,10,15-Tri-*p*-tolyl-20-[2-[3-[*o*-(10,15,20-tri-*p*-tolyl-5-porphinyl)-phenoxy]propoxy]phenyl]porphine (**9**).

A mixture of 0.50 g. (0.74 mmole) of the *o*-hydroxyporphyrin **1** and 0.185 g. (0.23 mmole) of the *o*-propyl bromide **3** were stirred for 48 hours with 1.10 g. of anhydrous potassium carbonate in 15 ml. of dimethylformamide. The product was precipitated by pouring the reaction mixture into 100 ml. of a 10% aqueous methanol solution, and then heating the mixture to coagulate the porphyrin. The product was filtered off, dried at 100° and then chromatographed on a 18 x 2 cm alumina column using chloroform as the eluant. The major band which moves with the solvent front contains the dimer and any unreacted **3**. A slower moving second band contains unreacted **1**.

The dimer was separated from the monomer by gel permeation chromatography on a 90 x 4 cm column of styrene-divinylbenzene beads using chloroform as the solvent. Small aliquots containing approximately 10 mg. chromatographed reaction mixture were loaded on the column. The first and major band which develops is the dimer, the second band, the monomer. On a freshly prepared column the first band is sometimes preceded by a yellow-green band of protonated porphyrins.

The bands containing the dimer were collected and passed through the column a second time, using much larger amounts of porphyrin. The material was judged pure when no second band due to any monomeric species was observed. The combined portions containing the pure dimer were then rechromatographed on a 45 x 2 cm column of silica gel using chloroform as the eluant, 0.220 g. (69%). The compound moves with an R_f value of 0.85 on silica gel plates with toluene as the eluant.

The dimer, **9**, was converted to the di-copper complex by dissolving the porphyrins, 80 mg. (0.058 mmole) in 12 ml. of warm pyridine and then adding 0.2 g. (1 mmole) of copper acetate monohydrate. The mixture was heated momentarily to reflux and the disappearance of the 650 nm band of the free base was followed spectrophotometrically. Continued heating produced decomposition products which have an absorption maxima at 620 nm. The pyridine was removed on a rotary evaporator and the solid material which remained dried at 100°. The porphyrins were dissolved in chloroform and chromatographed on Baker 0540, neutral alumina, using chloroform as the eluant. The copper complex moved with the solvent front and separated easily from several minor, slower moving bands. No separation of these materials could be achieved on any absorbants other than Baker, neutral alumina. The band containing the copper complex was collected and yielded 83 mg. (95%) of the pure copper dimer. A sample suitable for analysis was prepared by adding absolute ethanol to a filtered chloroform solution of the porphyrin. The mixture was taken to dryness by rotary evaporation and the resultant powder repeatedly washed by decantation with ether. The complex was then dried at 100° under vacuum for 24 hours.

Anal. Calcd. for Cu₂C₉₇H₇₂N₈O₂, M.W. 1508.7: C, 77.22; H, 4.81. Found: C, 77.37; H, 4.72.

5,10,15-Tri-*p*-tolyl-20-[2-[3-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]propoxy]phenyl]porphine (**10**).

The dimer **10** was prepared from 0.156 g. (0.20 mmole) of **3** and 0.315 g. (0.47 mmole) of **2** by the method given for the preparation of **8**. The dimer is relatively insoluble in dimethylformamide and precipitates out as the reaction proceeds. Chromatographic separation of the dimer from the reaction mixture gave 0.210 g. (76%) of pure **9**; R_f 0.75 (toluene, silica gel).

The dimer **10** was converted to the di-copper complex for analysis. The di-copper complex, when pure, is only slightly soluble in chloroform.

Anal. Calcd. for $Cu_2C_{97}H_{72}N_8O_2$: C, 77.22; H, 4.81. Found: C, 77.02; H, 4.93.

5,10,15-Tri-*p*-tolyl-20-[2-[5-[*o*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]pentoxy]phenyl]porphine (**11**).

The dimer **11** was prepared in 69% yield by a procedure analogous to that given for compound **8**. R_f 0.85 (toluene, silica gel). The compound was converted to the di-copper derivative for analysis.

Anal. Calcd. for $Cu_2C_{99}H_{76}N_8O_2$, M.W. 1536.8: C, 77.37; H, 4.98. Found: C, 76.98; H, 4.81.

5,10,15-Tri-*p*-tolyl-20-[4-[6-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]hexoxy]phenyl]porphine (**12**).

The dimer **12** was prepared in 71% yield by a procedure analogous to that given for compound **10**. The purified dimer has a limited solubility in chloroform, pyridine or dimethylformamide and was not examined further. The compound moves with an R_f value of 0.65 on silica gel plates with toluene as the eluant.

Oxo[μ -[5,10,15-Tri-*p*-tolyl-20-[2-[3-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]propoxy]phenyl]porphinato(2-)]]vanadium(IV) (**13**).

A mixture of 0.082 g. (0.11 mmole) of the vanadyl porphyrin **8** and 0.135 g. (0.170 mmole) of compound **3** were stirred for one week with 1 g. of anhydrous potassium carbonate in 25 ml. of dimethylformamide. A thin layer chromatographic examination of an aliquot of the reaction mixture, using silica gel plates and toluene, showed that the reaction had gone to about 90% of completion. The reaction mixture was poured into water and the precipitated porphyrins collected and dried. Chromatography on a 30 x 2 cm column of silica gel using chloroform as the eluant gave two bands. The first which moved with the solvent front contained unreacted **3** and the dimer, **13**. The second and slowest moving band contained **8**.

The band containing the dimer was collected and loaded in small portions on a 90 x 4 cm column of polystyrene beads using chloroform as the solvent. The material separated into two bands, the first of which contained **13**. The dimer was collected and rechromatographed on the polystyrene beads and then on silica gel to give pure **13**. The yield was 0.130 g. (81%). The dimer moves with an R_f value of 0.6 on silica gel plates with toluene as the eluant. The esr spectrum ($g_{av} = 2.03$) was nearly identical to that reported by Roberts, *et al.*, for vanadyl etioporphyrin II, (18).

Oxo[μ -[5,10,15-Tri-*p*-tolyl-20-[2-[3-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]propoxy]phenyl]porphinato(4-)]]copper(II) vanadium(IV) (**14**).

A solution of 0.036 g. (0.025 mmole) of the vanadyl dimer, **13**, in 10 ml. of pyridine was refluxed briefly with 0.16 (0.8 mmole) of copper acetate monohydrate until the visible spectrum of the reaction mixture indicated that the insertion of copper was

complete. The pyridine was then flashed off and the remaining solids dried at 100°. Chloroform as the eluant gave the mixed dimer (0.036 g. (96%)) as the major band, which moves slightly behind the solvent front. The complex, **14**, moves with an R_f value of 0.6 on silica gel plates with toluene as the eluant.

Anal. Calcd. for $CuVO_3C_{97}H_{72}N_8$, M.W. 1511.7: C, 77.06; H, 4.80. Found: C, 77.23; H, 4.69.

Attempted Preparation of an *o,o*-VO-C₃-TTP Dimer.

A mixture of 0.14 g. (0.18 mmole) of **3** and 0.13 g. (0.18 mmole) of **7** were stirred with 1 g. of anhydrous potassium carbonate in 25 ml. of dimethylformamide. After three days a portion of the reaction mixture was chromatographed on a silica gel plate using toluene as the solvent. The plate indicated that the reaction had not gone to completion and so the reaction mixture was stirred for three more weeks. Examination of an aliquot of the reaction mixture indicated that an appreciable amount of the starting materials, particularly **7**, were still present.

The reaction was not investigated further.

5(2(2-Phenyl-1-ethoxy)phenyl)-10,15,20-tritolylporphyrin (**15**).

The porphyrin **15** was prepared by a procedure exactly analogous to that described for the preparation of **3** except that a large excess of 2-phenylbromoethane was substituted for 1,3-dibromopropane. The material was first chromatographed on alumina and then on silica gel.

Anal. Calcd. for $CuC_{55}H_{42}N_4O$, M.W. 838.28: C, 78.80; H, 6.02; N, 6.68. Found: C, 78.69; H, 5.89; N, 6.50.

5(4-Propoxy)phenyl-10,15,20-tritolylporphyrin (**16**).

The porphyrin **16** was prepared by a procedure exactly analogous to that described for the preparation of **5** except that a large excess of bromopropane was substituted for 1,5-dibromopentane. The material was twice chromatographed on silica gel and then once on alumina.

Anal. Calcd. for $CuC_{50}H_{40}N_4O_1$, M.W. 776.21: C, 77.37; H, 5.16; N, 7.22. Found: C, 77.53; H, 5.20; N, 7.31.

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- (10) The abbreviations used in this paper: TPP = 5,10,14,20-tetraphenylporphyrin, TTP = any 5-R,10,15,20-tritolylporphyrin, Chl = chlorophyll. For convenience the covalently linked tritolylporphyrins discussed in this paper will be referred to by the following system of nomenclature; *x,y*-C_n-TTP refers to a TTP dimer in which the two porphyrins are linked together by an

n-carbon alkyl chain *via* ether linkages at respectively the *x* and *y* positions of the phenyl groups of the first and second porphyrins. Thus *o,p*-C₃-TTP is 5,10,15-tri-*p*-tolyl-20-[2-[3-[*p*-(10,15,20-tri-*p*-tolyl-5-porphinyl)phenoxy]propoxy]-*p*-phenyl]porphine.

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