Linked Porphyrin Systems

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Porphyrin monomers, 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin (**1**), 5,10-(dipyridyl)-15,20-(diphenyl)-porphyrin (**2**), and 5,15-(dipyridyl)-10,20-(diphenyl)porphyrin (**3**), were linked by hydrocarbon chains to form a series of dimers, trimers and polymers. The 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin monomers were linked by 2, 4, 6, 8 and 10 carbon chains through the alkylation of the pyridine nitrogens using the appropriate diiodoalkane to form positively charged linked dimers **4-8**. A trimer **12** was synthesized from two 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin and one 5,10-(dipyridyl)-15,20-(diphenyl)porphyrin linked by a six carbon chain. Hydrocarbon linked (5,10-(dipyridyl)-15,20-(diphenyl)porphyrin)$_n$ (**13**) and (5,15-(dipyridyl)-10,20-(diphenyl)porphyrin)$_n$ (**14**) were also prepared.

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Introduction.

Porphyrins have been covalently linked to form dimers since 1977 [2]. Single interporphyrin linkages formed by amides, esters, ethers, pure hydrocarbon chains and rigid spacers such as anthracene and biphenylene have been studied [2,3-8]. Dolphin, Hiom and Paine [2] have reviewed such research, including their own work involving amide linked octaalkylporphyrins and conclude that, although amides, esters and ethers provide fairly easy synthetic routes to covalently linking porphyrins, these systems are of inherently low solubility. Many of these systems have been used to study porphyrin-porphyrin interactions as photosynthetic 'special pair' models and as electron transfer agents. Recently, flexible ether linked porphyrins have been synthesized to explore the anti-cancer activity of porphyrins in phototherapy [9].

Trimeric and polymeric porphyrin systems have also been investigated. Anton and coworkers [10] synthesized a tetraarylporphyrin derivative which bound through an ester linkage to two other tetraaryl porphyrins. Ester linked trimers of an octaalkylporphyrin and it's zinc and copper derivatives were synthesized by Ichimura [11,12].

Several other trimeric systems involving actinide metalloporphyrins have been studied. Buchler *et al.* [13,14] has investigated triple decker systems of the type $(P)_3M_2$ where P is a porphyrin and M is an actinide. Additionally, the x-ray structures of two porphyrin trimers, $[TPP(Th)(OH)_2]_3$ and $[(OEP)Ga]_3F_2(BF_4)_2$, were determined recently by Kadish [15,16].

Porphyrins with polymerizable peripheral substituents have been synthesized to form polymers for a variety of functions. Tetraarylporphyrin derivatives have been copolymerized with acrylic acid and a quinone derivative to form a polymer with a structured porphyrin-quinone orientation designed to model photosynthesis [17]. Tsuchida and coworkers [18,19] synthesized an iron porphyrin-phospholipid copolymer which is designed to transport oxygen and which displays oxygen binding affinities similar to that of hemoglobin. Additionally, electropolymerization of porphyrins has recently been explored by several groups [20,21] as a method of forming thin polymeric films on electrodes for electrocatalysis.

In this study, the 5-(monopyridyl)-10,15,20-(triphenyl)-porphyrin, 5,10-(dipyridyl)-15,20-(diphenyl)porphyrin, and 5,15-(dipyridyl)-10,20-(diphenyl)porphyrin monomers were linked by alkane chains. The linkage was formed by the alkylation of a pyridine nitrogen on one porphyrin with one terminus of an alkane chain and the alkylation of an adjacent porphyrin pyridine with the other alkane terminus. The alkylation of the pyridine ring produced a quaternized nitrogen and, therefore, a charged porphyrin species of relatively high solubility.

The linked dimers **4-8** were formed from two 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin and a diiodoalkane

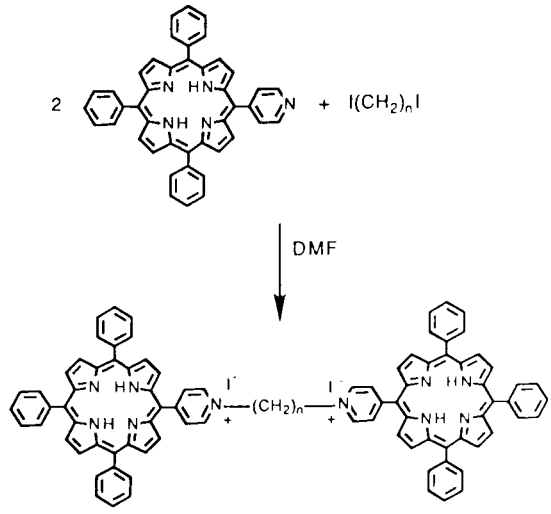


Figure 1

Syntheses of Linked Dimers

(Figure 1). Higher order oligomers **12-14** were formed using 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin, 5,10-(dipyridyl)-15,20-(diphenyl)porphyrin, or 5,15-(dipyridyl)-10,20-(diphenyl)porphyrin and a diiodoalkane such as the trimer shown in Figure 2 or the polymer illustrated in Figure 3.

Additionally, the zinc **9** and cobalt **10**, **11** derivatives of the hexamethylene-linked dimer have also been prepared.

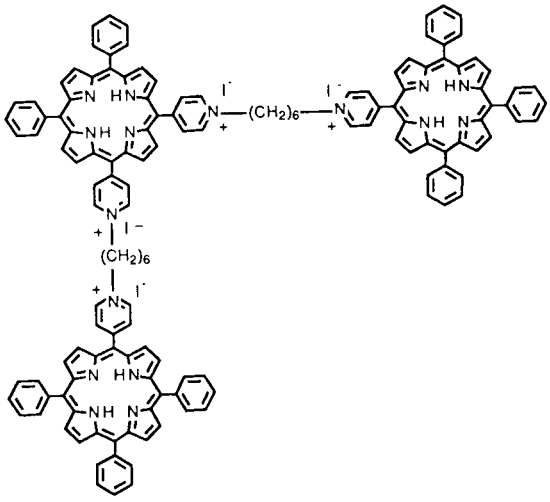
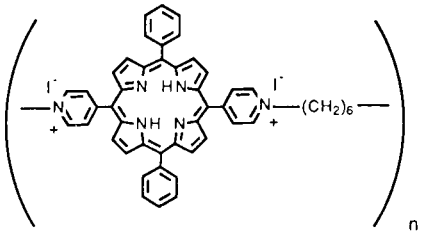
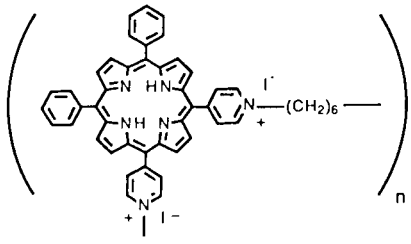


Figure 2

Linked Trimer



A



B

Figure 3

Linked Polymers

a) 5,15-(Dipyridyl)-10,20-(diphenyl)porphyrin linked polymer.

b) 5,10-(Dipyridyl)-15,20-(diphenyl)porphyrin linked polymer.

Results and Discussion.

Visible Spectra of Linked Systems.

The absorption spectra of the alkane linked systems were solvent dependent. In dimethylformamide, dimethyl sulfoxide, ethanol, and benzene, the linked systems have absorption spectra essentially equivalent to that of their related monomers. In chloroform, a broadening of the Soret and a red shift of the Q bands was observed. Figure 4 shows the solvent dependent spectra of the octamethylene-linked dimer (iodide counterions). Several dimers were synthesized with hydroxide and chloride counterions. The hydroxide, a by product in the general synthesis, and the chloride species showed the same solvent dependences as the iodine species. Additionally, the metallodimers with acetate and chloride counterions and the alkylated monomer [3] demonstrated the same solvent dependent absorption spectra as all the linked systems.

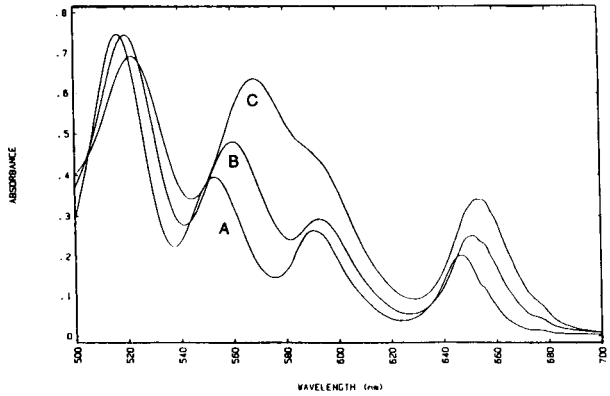


Figure 4

Solevent Dependence of the Octamethylene Linked DimerAbsorption Spectra

A) Dimethylformamide B) Benzene C) Chloroform

The solvent dependent spectra was the result of aggregation of the charged porphyrins in solution. Stacking of porphyrins either by linking porphyrins together or as a result of aggregation generally induces marked change in visible absorption [2,22-27]. For tetraarylporphyrin derivatives [22-27], stacking is accompanied by a broadening of the Soret band and a red shift of the Q bands. A blue shift of the Soret, as well as, broadening and a red shift of the Q bands is also observed for octaethylporphyrin and chlorophyll dimers [2,28]. The singlely linked dimers of Boxer and Closs [29] show a solvent dependent red shift of the Q bands, with polar solvents inducing the shift. Little, *et al.* [30] also report some slight spectral changes in a polar solvent (chloroform) for ether linked dimers. Chang, *et al.* [31] and Paine, *et al.* [40] found no spectral changes for their singlely linked free base dimers in non-polar solvents. The absorption spectra of doublely and quadruplely linked face-to-face dimers display a definite dimerization

effect in both the Soret and the Q bands, without illustrating any solvent dependence [2,22,28,29,31-39]. These results indicate that face-to-face dimers formed either by locking them face-to-face with more than one linkage or by aggregation effects generally exhibit distinct absorption changes. The linked dimers of this study displayed a broadening of the Soret band and a red shift in chloroform and slightly in benzene, but had absorption similar to a monomer in dimethylformamide. These results are consistent with aggregate formation through π interactions.

Linked Dimer Proton NMR Spectra.

The ^{1}H nmr spectra showed a slight solvent dependence. The proton resonances of the hexamethylene-linked dimer in d_6-dimethylsulfoxide were generally shifted slightly up field from those observed in deuteriochloroform. Spectral variations such as these have also been reported in similar tetrapyridylporphyrin systems [41] and have been attributed to aggregation effects.

EXPERIMENTAL

All uv-visible spectra were obtained on a Hewlett Packard 8451A diode array spectrophotometer and plotted by a Hewlett Packard 7470A plotter. Automatic baseline corrections were applied by the spectrophotometer from reference solvent and cell absorption measurements. Either 0.1, 1.0, 5.0, or 10.0 cm quartz cells or 1.0 cm glass cells were used. The ^{1}H nuclear magnetic resonance spectra were obtained with a Varian VXR-300 spectrometer in deuteriochloroform unless otherwise noted; chemical shifts are given in ppm. Flash column chromatography was carried out on silica gel (Merck, grade 60, 230-400 mesh, 60 Å). Lipophilic Sephadex (60-120 μ) was used for the size exclusion chromatography with dimethylformamide as the solvent. Thin layer chromatography was performed with Kodak silica gel plates. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, Georgia, USA. Unless noted, all reagents were reagent grade and used as received.

General Procedure for the Synthesis of the Porphyrin Monomers **1-3**.

The porphyrin monomers were prepared according to standard literature methods [8]. Pyrrole (7.0 ml, 100 mmoles), benzaldehyde (7.5 ml, 74 mmoles) and 4-pyridine carboxyaldehyde (2.5 ml, 26 mmoles) were refluxed in 250 ml of 99% propionic acid for one hour. The reaction mixture was then cooled and allowed to stand overnight. Filtration and methanol washing afforded 2.07 g (13% yield) of a purple crystalline product. The product was analyzed by silica gel thin layer chromatography and found to be a mixture of the six possible porphyrin isomers: 5,10,15,20-(tetraphenyl)porphyrin, 5-(pyridyl)-10,15,20-(triphenyl)porphyrin (**1**), 5,10-(dipyridyl)-15,20-(diphenyl)porphyrin (**2**), 5,15-(dipyridyl)-10,20-(diphenyl)porphyrin (**3**), 5,10,15-(tripyridyl)-20-(phenyl)-porphyrin, and 5,10,15,20-(tetrapyridyl)porphyrin. The R_f values of the isomers were 0.88 (5,10,15,20-(tetraphenyl)porphyrin), 0.60 (**1**), 0.42 (**3**), 0.22 (**2**), 0.12 (5,10,15-(tripyridyl)-20-(phenyl)porphyrin), and 0.08 (5,10,15,20-(tetrapyridyl)porphyrin) in 98% chloroform/2% ethanol. The R_f values were assigned according to literature values [42].

The isomers were separated using flash chromatography with silica gel and a chloroform/ethanol solvent system consisting initially of 98% chloroform/2% ethanol and gradually ending with 100% ethanol. Upon separation, the product mixture consisted of 30% 5,10,15,20-(tetraphenyl)porphyrin, 20% (**1**), 2% (**3**), 8% (**2**), 15% (5,10,15-(tripyridyl)-20-(phenyl)porphyrin), 25% (5,10,-15,20-(tetrapyridyl)porphyrin).

The mixed aldehyde procedure was followed for several small scale syntheses in which 1.5-2.5 g of the porphyrin mixture were produced and for several large scale syntheses which produced 10 to 12 g of porphyrin product.

5-(Monopyridyl)-10,15,20-(triphenyl)porphyrin (**1**).

This compound was obtained as purple crystals; uv (chloroform): λ (nm) (ϵ x 10^4 cm^{-1} M^{-1}) 418 (25), 516 (1.7), 550 (0.7), 590 (0.6), 646 (0.4); ^{1}H nmr: δ 9.04 (2 H, d, 2,6-pyridyl), 8.86 (8 H, m, β-pyrrole), 8.22 (8 H, m, *o*-phenyl and 3,5-pyridyl), 7.77 (9 H, m, *m*- and *p*-phenyl), and -2.83 (2 H, s, internal pyrrole).

Anal. Calcd. for $C_{43}N_5H_{29}\cdot(H_2O)_{1/2}$: C, 82.67; H, 4.84; N, 11.21; O, 1.28. Found: C, 82.61; H, 4.61; N, 11.11; O, 1.39.

5,10-(Dipyridyl)-15,20-(diphenyl)porphyrin (**2**).

This compound was obtained as purple crystals; uv (chloroform): λ (nm) (ϵ x 10^4 cm^{-1} M^{-1}) 416 (22), 514 (1.8), 548 (0.7), 590 (0.6), 646 (0.3); ^{1}H nmr: δ 9.06 (4 H, d, 2,6-pyridyl), 8.86 (8 H, h, β-pyrrole), 8.20 (8 H, m, *o*-phenyl and 3,5-pyridyl), 7.81 (6 H, m, *m*- and *p*-phenyl), -2.84 (2 H, s, internal pyrrole).

Anal. Calcd. for $C_{42}N_6H_{28}\cdot(H_2O)_{1/2}$: C, 80.62; H, 4.67; N, 13.43; O, 1.28. Found: C, 81.11; H, 4.47; N, 13.49; O, 0.81.

5,15-(Dipyridyl)-10,20-(diphenyl)porphyrin (**3**).

This compound was obtained as purple crystals; uv (chloroform): λ (nm) (ϵ x 10^4 cm^{-1} M^{-1}) 418 (23), 514 (1.0), 548 (0.4), 590 (0.3), 644 (0.2); ^{1}H nmr: δ 9.06 (4 H, d, 2,6-pyridyl), 8.90 (8 H, d, β-pyrrole), 8.22 (8 H, m, *o*-phenyl and 3,5-pyridyl), 7.79 (6 H, m, *m*- and *p*-phenyl), -2.86 (2 H, s, internal pyrrole).

Anal. Calcd. for $C_{42}N_6H_{28}\cdot(H_2O)$: C, 79.48; H, 4.76; N, 13.24; O, 2.52. Found: C, 79.42; H, 4.73; N, 12.83; O, 2.53.

Dimethylene-Linked Dimer **4**.

One hundred mg (0.16 mmole) of **1** and 0.065 g (0.23 mmole excess) of 1,2-diiodoethane were refluxed in 40 ml of anhydrous dimethylformamide under argon, using dry glassware. The reaction was monitored by silica gel tlc using a solvent system of dichloromethane/ethanol in a 9:1 ratio. After six hours, a trace amount of a product (yellow) with an R_f of 0.30 began to appear on the tlc, along with unreacted monomer, **1**, (R_f = 0.86). The reaction was quenched when the tlc no longer exhibited significant change (forty-eight hours). The dimethylformamide was then rotavaped off and the reaction mixture was dissolved in a few milliliters dichloromethane in preparation for purification. Using flash column chromatography with a 25 cm x 3 cm column of silica gel and an initial solvent system of 95% dichloromethane and 5% ethanol, the reaction mixture was separated. The unreacted **1** was the first compound to elute off the column, with a trace amount of a dark green product following off the column. A trace amount of a third red product eluted off the column last. After **1** eluted, increasing amounts of ethanol were added to elute the other products.

The green product was confirmed to be the *N,N'*-pyrrole alkylated porphyrin by visible spectroscopy. The absorbances of **4b** (λ = 448 nm and 674 nm) are similar to those of *trans-N,N'* dialkylated compounds found in the literature [43] (λ = 460 nm and 710 nm).

Compound **4** was obtained as a red glass; uv (chloroform): λ (nm) (relative intensity) [44] 420 (10.2), 520 (1.0), 570 (0.82), 590 (sh), 656 (0.49); uv (dimethylformamide): λ (nm) (relative intensity) 420 (21.3), 516 (1.0), 554 (0.43), 592 (0.21), 648 (0.10).

Tetramethyl-Linked Dimer **5**.

One hundred mg (0.16 mmole) of **1** and 10.6 μl (0.08 mmole) of 1,4-diiodobutane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, two products appeared on the tlc, R_f = 0.37 and 0.25, respectively. The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. After the dimethylformamide was rotavaped off, the reaction mixture was dissolved in a dichloromethane/ethanol solution (9:1) and sodium iodide was added. The mixture was stirred for one hour then a tlc was taken. The tlc showed **1** (R_f = 0.86) and one other product (**5** with an R_f = 0.78). The reaction mixture dimer R_f values were lower than 0.78 due to the presence of dimethylformamide in the reaction mixture solvent system.

The mixture was separated by flash chromatography (silica gel, 25 cm x 3 cm) with unreacted **1** eluting first, followed by the yellow dimer product. After **1** eluted, increasing amounts of ethanol were added to elute the dimer product. The product was further purified using size exclusion chromatography with lipophilic. Sephadex as the stationary phase and dimethylformamide as the mobile phase. Two products eluted off the Sephadex column; with the first being the largest in size. The first product was confirmed to be the diiodo dimer product, while the second product was unreacted monomer.

The diiodo dimer **5** was obtained as a red glass; uv (chloroform): λ (nm) (relative intensity) 422 (11.3), 522 (1.0), 568 (0.86), 590 (sh), 656 (0.49); uv (dimethylformamide): λ (nm) (relative intensity) 422 (19.0), 516 (1.0), 554 (0.43), 592 (0.21), 648 (0.10); ^{1}H-nmr: δ 9.64 (4 H, d, α-py), 8.94 (4 H, m, β-py), 8.83 (16 H, m, β-pyrrole), 8.16 (12 H, m, *o*-phenyl), 7.74 (18 H, m, *m*, *p*-phenyl), -2.77 (4 H, s, pyrrole N), 5.31 (4 H, m, α-link), and 2.19 (4 H, m, β-link).

Anal. Calcd. for $C_{90}N_{10}H_{66}I_2 \cdot (H_2O)_6$: C, 65.50; H, 4.76; N, 8.49; O, 5.8. Found: C, 66.48; H, 6.14; N, 5.47; O, 6.51. The elemental analysis of the **5** indicated that the dimer was impure; however, analyses of dimeric compounds synthesized under similar conditions and discussed below are consistent with calculated formulations.

Hexamethylene-Linked Dimers **6a,b,c**.

One hundred mg (0.16 mmole) of **1** and 13.4 μl (0.08 mmole) of 1,6-diiodohexane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, two products **6a** and **b** appeared on the tlc (R_f = 0.58 for **6a** and R_f = 0.32 for **6b**). The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. The products were separated by flash chromatography (silica gel, 25 cm x 3 cm) with unreacted **1** eluting first, followed by the two dimer products. Initially, a solvent system of 95% dichloromethane and 5% ethanol was used. After **1** eluted, increasing amounts of ethanol were added to elute the dimer products. The dimer products were the diiodo and the dihydroxy linked dimers with the addition of sodium iodide to the dimer mixture produces only one product **6a** with an R_f = 0.50. The addition of sodium chloride produces one product **6c** with an R_f = 0.67. Also, contacting the diiodo dimer product with water resulted in the exchange of the counterion to produce a mixture of both the diiodo and the dihydroxy species (original tlc). Compound **6c** was also obtained using ion-exchange chromatography (Dowex).

The dimeric product was further purified using size exclusion chromatography with lipophilic Sephadex as the stationary phase and dimethylformamide as the mobile phase. Three products eluted off the Sephadex column with the first being the largest in size. The first product was confirmed to be the diiodo dimer product, while the second product was a small amount of the dihydroxy product, and the third was unreacted monomer.

The diiodo dimer **6a** was obtained in a yield of 9%; uv (chloroform): λ (nm) (relative intensity) 420 (9.4), 522 (1.0), 570 (0.91), 592 (sh), 658 (0.54); uv (dimethylformamide): λ (nm) (relative intensity) 420 (14.0), 516 (1.0), 552 (0.51), 592 (0.37), 648 (0.29); ^{1}H nmr: δ 9.59 (4 H, d, α-py), 8.93 (4 H, m, β-py), 8.81 (16 H, m, β-pyrrole), 8.17 (12 H, m, *o*-phenyl), 7.76 (18 H, m, *m*, *p*-phenyl), -2.82 (4 H, s, pyrrole N), 5.19 (4 H, m, α-link), 2.27 (4 H, m, β-link), and 1.71 (4 H, m, γ-link).

Anal. Calcd. for $C_{92}N_{10}H_{70}I_3 \cdot (H_2O)_3$: C, 63.13; H, 4.38; N, 8.00; O, 2.74. Found: C, 63.14; H, 4.62; N, 7.41; O, 3.01.

Compound **6c** was characterized by visible and nmr spectroscopy; uv (chloroform): λ (nm) 420, 522, 570, 654; ^{1}H nmr: δ 9.51 (4 H, d, α-py), 8.97 (4 H, m, β-py), 8.86 (16 H, m, β-pyrrole), 8.19 (12 H, m, *o*-phenyl), 7.77 (18 H, m, *m*, *p*-phenyl), -2.75 (4 H, s, pyrrole N), 5.21 (4 H, m, α-link), 2.19 (4 H, m, β-link), and 1.74 (4 H, m, γ-link).

Octamethylene-Linked Dimer **7**.

One hundred mg (0.16 mmole) of **1** and 15.8 μl (0.08 mmole) of 1,8-diiodooctane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, two products appeared on the tlc (**7a** with R_f = 0.48 and **7b** with R_f = 0.19). The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. The products were separated by flash chromatography (silica gel, 25 cm x 3 cm) with unreacted **1** eluting first, followed by the two dimer products. Initially, a solvent system of 95% dichloromethane and 5% ethanol was used. After **1** eluted, increasing amounts of ethanol were added to elute the dimer products. The dimer products were the diiodo dimer and the dihydroxide dimer with the addition of sodium iodide to the dimer mixture yielding one product **7a** with an R_f = 0.62.

The product was further purified using size exclusion chromatography with lipophilic Sephadex as the stationary phase and dimethylformamide as the mobile phase. Three products eluted off the Sephadex column with the first being the largest in size. The first product was confirmed to be the diiodo dimer product, while the second product was a trace amount of the dihydroxy species and the last product was unreacted monomer.

The diiodo dimer **7a** was obtained in a yield of 11%; uv (chloroform): λ (nm) (relative intensity) 420 (10.0), 522 (1.0), 568 (0.92), 590 (sh), 656 (0.49); uv (dimethylformamide): λ (nm) (relative intensity) 420 (13.0), 516 (1.0), 554 (0.53), 590 (0.36), 646 (0.27); ^{1}H nmr: δ 9.53 (4 H, d, α-py), 8.93 (4 H, m, β-py), 8.84 (16 H, m, β-pyrrole), 8.19 (12 H, m, *o*-phenyl), 7.73 (18 H, m, *m*, *p*-phenyl), -2.79

(4 H, s, pyrrole N), 5.30 (4 H, m, α-link), 2.28 (4 H, m, β-link), and 1.0-2.0 (m, γ, δ links).

Anal. Calcd. for $C_{94}N_{10}H_{74}I_3\cdot(H_2O)_2$: C, 64.14; H, 4.24; I, 21.6; N, 7.96. Found: C, 65.85; H, 5.08; I, 21.84; N, 7.45.

Decamethyl-Linked Dimer **8**.

One hundred mg (0.16 mmole) of **1** and 0.0500 g (12.7 mmoles) of 1,10-diiododecane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction mixture was monitored using tlc. After two hours, two products **8a** and **8b** appeared on the tlc with R_f values of 0.53 and 0.21 respectively. The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. The products were separated by flash chromatography (silica gel, 25 cm x 3 cm) with unreacted **1** eluting first, followed by the two dimer products. Initially, a solvent system of 95% dichloromethane and 5% ethanol was used. After **1** eluted, increasing amounts of ethanol were added to elute **8a** and **8b**. The dimer products are the diiodo dimer **8a** and the dihydroxide dimer **9b**.

The products were further purified using size exclusion chromatography. Two products eluted off the Sephadex column with the first being the largest in size. The first product was confirmed to be the diiodo dimer product, while the second product was a trace amount of the dihydroxy dimer and the last product was unreacted monomer.

The diiodo dimer **8a** was obtained in a yield of 27%; uv (chloroform): λ (nm) (relative intensity) 422 (11.9), 522 (1.0), 568 (0.88), 590 (sh), 656 (0.66); uv (dimethylformamide): λ (nm) (relative intensity) 422 (17.8), 516 (1.0), 554 (0.51), 592 (0.31), 648 (0.22); ^{1}H nmr: δ 9.48 (4 H, d, α-py), 8.92 (4 H, m, β-py), 8.81 (16 H, m, β-pyrrole), 8.19 (12 H, m, ortho-phenyl), 7.77 (18 H, m, *m*, *p*-phenyl), -2.79 (4 H, s, pyrrole N), 5.10 (4 H, m, α-link), 2.26 (4 H, m, β-link), 1.0-2.0 (m, γ, δ, *etc.* links).

Anal. Calcd. for $C_{96}N_{10}H_{78}I_2\cdot(H_2O)$: C, 70.16; H, 4.91; N, 8.52. Found: C, 69.92; H, 5.03; N, 8.33.

Zinc Hexamethylene-Linked Dimer **9a,b**.

Zinc(II) was inserted into the porphyrin dimers by standard methods [45]. An excess of zinc acetate (7.0 mg, 32 μmoles) was added to 5 mg (3.2 μmoles) of **6a** in 25 ml of dimethylformamide. The solution was refluxed for one hour, after which a small sample of the reaction mixture was extracted and analyzed using visible spectroscopy. The spectrum indicated that the metal insertion was complete, with the four Q bands of the free base (λ = 512 nm, 550 nm, 590 nm, and 648 nm) collapsing to two peaks (λ = 562 nm, 628 nm). The dimethylformamide was then removed by rotary evaporation and the zinc product, **9a**, was purified using a silica gel column with a chloroform/ethanol solvent system.

Compound **9a** was obtained as a red powder in stoichiometric yield; uv (chloroform): λ (nm) (relative intensity) 426 (11.4), 560 (1.0), 624 (0.60); uv (dimethylformamide): λ (nm) (relative intensity) 428 (7.2), 560 (1.0), 606 (0.55).

The zinc dimer was also synthesized with a chloride counterion using zinc chloride. An excess of zinc chloride (5.0 mg, 32 μmoles) was added to 5 mg (3.2 μmoles) of **6a** in 25 ml of dimethylformamide. The solution was refluxed for one hour, after which a small sample of the reaction mixture was extracted and analyzed using visible spectroscopy. The spectrum indicated that the metal insertion was complete, with the four Q bands of the free base (λ = 512 nm, 550 nm, 590 nm, and 648 nm) collapsing to two peaks (λ = 562 nm, 615 nm). The dimethylformamide was then removed by rotary evaporation, and the zinc product was purified by using a 6 cm x 2.5 cm silica gel column with a chloroform/ethanol solvent system. The reddish yellow **9b** dichlorodimer powder was obtained in stoichiometric yield; uv (chloroform): λ (nm) (relative intensity) 428 (14.0), 560 (1.0), 618 (0.48); uv (dimethylformamide): λ (nm) (relative intensity) 426 (8.4), 560 (1.0), 606 (0.54).

Cobalt(II) and Cobalt(III) Hexamethylene-Linked Dimers **10** and **11**.

Cobalt(II) was inserted into the porphyrin dimers by standard methods [45]. Excess of cobalt(II) acetate (10 mg, 37 μmoles) was added to 12 mg (7.7 μmoles) of **6a** in 25 ml of dimethylformamide and refluxed. Cobalt insertion was monitored by visible spectroscopy. After 3 hours, the spectrum indicated that the insertion was completed, with a split Soret occurring at 414 nm and 432 nm and the Q bands occurring at 546 nm, and 600 (sh) nm in chloroform. The dimethylformamide was removed by rotary evaporation. The red product was purified by passing it through a 6 cm x 2.5 cm silica gel column with a chloroform/ethanol solvent system.

Compound **10** was obtained as a red glass; uv (chloroform): λ (nm) (relative intensity) 410 (8.4), 540 (1.0), 580 (sh); uv (dimethylformamide): λ (nm) (relative intensity) 410 (8.6), 5.34 (1.0).

Oxidation of cobalt was achieved by suspending 5 mg of Co(II) **6a** in 40 ml of methanol and adding 0.12 ml of concentrated hydrochloric acid. The mixture was stirred overnight and the cobalt(III) derivative **11** was obtained as a red powder in stoichiometric yield; uv (chloroform): λ (nm) (relative intensity) 442 (6.4), 544 (1.0), 610 (0.71); uv (dimethylformamide): λ (nm) (relative intensity) 442 (9.21), 554 (1.0), 600 (0.56).

Linked Trimer **12**.

One hundred mg (0.16 mmole) of **1**, 50 mg (0.08 mmole) of **2**, and 26.8 μl (0.16 mmole) of 1,6-diiodohexane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, several products appeared on the tlc. The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. The products were separated by flash chromatography (silica gel, 25 cm x 3 cm) with unreacted **1** eluting first, followed by unreacted **2**, and three unknown products. Initially, a solvent system of 95% dichloromethane and 5% ethanol was used. After **1** and **2** eluted, increasing amounts of ethanol were added to elute the other products. The three products were the dimer **6a**, trimer **12** and the polymer **13**.

Each of these products was purified further using Sephadex. The trimer **12** was obtained as a red-purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (12.5), 522 (1.0), 570 (0.94), 592 (sh), 656 (0.58); uv (dimethylformamide): λ (nm) (relative intensity) 422 (6.9), 516 (1.0), 554 (0.52), 590 (0.36), 646 (0.25); ^{1}H nmr (d_6-dimethyl sulfoxide): δ 9.59 (4 H, s, α-py), 9.48 (4 H, s, α-py), 9.05 (8 H, m, β-py), 8.86 (24 H, m, β-pyrrole), 8.17 (16 H, m, *o*-phenyl), 7.78 (24 H, m, *m*, *p*-phenyl), -3.00 (6 H, s, pyrrole N), 4.98 (4 H, m, α-link), 4.92 (4 H, s, α-link), 2.38 (4 H, s, β-link), 2.22 (4 H, s, β-link), 1.78 (4 H, m, γ-link), and 1.58 (4 H, s, γ-link).

The polymer (**13**) was also a red-purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (10.1), 522 (1.0), 566 (0.81), 592 (sh), 656 (0.48); uv (dimethylformamide): λ (nm) (relative intensity) 422 (7.6), 516 (1.0), 554 (0.51), 590 (0.36), 646 (0.24); ^{1}H nmr (d_6-dimethyl sulfoxide): δ 9.56 (2 H, d, α-py), 8.90 (12 H, m, β-py and β-pyrrole), 8.18 (4 H, m, *o*-phenyl), 7.79 (6 H, m, *m*, *p*-phenyl),

-2.97 (2 H, s, pyrrole N), 4.97 (2 H, m, α-link), 2.24 (2 H, m, β-link), and 1.79 (2 H, m, γ-link).

The proton nmr spectra, specifically, the β-pyrrole resonances, of these products indicated that **6a** was the dimer (hexamethylene-linked 5-(monopyridyl)-10,15,20-(triphenyl)porphyrin), while **12** was the trimer and **13** was a higher order polymer. The β-pyrrole splitting of **13** resembles that of the hexamethylene-linked dimer; however, the splitting of **12** is indicative of a mixture of β-pyrrole proton shifts from both monomers **1** and **2**. Additionally, for the pyridine and alkane protons, two resonances appeared, indicating again that the two different monomers **1** and **2** were present. Spectral integration confirmed these assignments.

5,10-(Dipyridyl)-15,20-(diphenyl)porphyrin-Linked Polymers **13a,b,c**.

Fifty mg (0.08 mmole) of **2** and 13.4 μl (0.08 mmole) of 1,6-diiodohexane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, one product appeared on the tlc. The reaction was quenched after two additional hours, when no substantial change in the tlc was observed. The reaction mixture was separated by size exclusion chromatography. A large band of the oligomeric product eluted first, followed by a small amount of unreacted 5,10-(dipyridyl)-15,20-(diphenyl)porphyrin. The oligomeric product mixture was further separated using flash chromatography. Initially, a solvent system of 95% dichloromethane and 5% ethanol was used. Five fractions were obtained. The first was unreacted monomer, while fractions 2 (**13a**), 3 (**13b**) and 4 (**13c**) were oligomers. Fraction 5 remained adsorbed in the silica gel.

Compound **13a** was a red-purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (9.6), 522 (1.0), 568 (0.81), 656 (0.34); uv (dimethylformamide): λ (nm) (relative intensity) 424 (10.0), 516 (1.0), 552 (0.46), 592 (0.35), 646 (0.21); ^{1}H nmr: δ 9.55 (2 H, d, α-py), 8.80 (12 H, m, β-py and β-pyrrole), 8.16 (4 H, m, *o*-phenyl), 7.76 (6 H, m, *m*, *p*-phenyl), -2.92 (2 H, s, pyrrole N), 5.23 (2 H, m, α-link), 2.34 (2 H, m, β-link), and 1.78 (2 H, m, γ-link).

Compound **13b** was obtained as a red-purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (8.24), 526 (1.0), 568 (0.76), 590 (sh), 656 (0.42); uv (dimethylformamide): λ (nm) (relative intensity) 424 (8.1), 516 (1.0), 552 (0.50), 590 (0.36), 646 (0.21); ^{1}H nmr: δ 9.49 (2 H, d, α-py), 8.83 (12 H, m, β-py and β-pyrrole), 8.18 (4 H, m, *o*-phenyl), 7.75 (6 H, m, *m*, *p*-phenyl), -2.83 (2 H, s, pyrrole N), 5.20 (2 H, m, α-link), 2.39 (2 H, m, β-link), and 1.80 (2 H, m, γ-link).

Compound **13c** was also a red-purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (7.82), 526 (1.0), 572 (0.83), 590 (sh), 656 (0.30); uv (dimethylformamide): λ (nm) (relative intensity) 374 (sh), 422 (8.7), 518 (1.0), 556 (0.54), 592 (0.41), 646 (0.2).

5,15-(Dipyridyl)-10,20-(diphenyl)porphyrin Polymer (**14**).

Compound **3** (24.5 mg, 0.04 mmole) and 13.4 μl (0.08 mmole) of 1,6-diiodohexane were refluxed in 40 ml of anhydrous dimethylformamide under argon. The reaction was monitored using tlc. After two hours, one product appeared on the tlc. The reaction was quenched after two additional hours, when the monomer was no longer detected by tlc. The product was purified on a Sephadex column with dimethylformamide as the eluent. Only one product eluted from the Sephadex column. Preliminary tests with silica gel indicated that the highly polar *trans*-polymer readily adsorbs on the silica gel and can not be removed. Consequently, the polymer was not purified further using silica gel flash chromatography.

The *trans*-polymer was obtained as a purple glass; uv (chloroform): λ (nm) (relative intensity) 422 (12.5), 520 (1.0), 568 (0.94), 590 (sh), 656 (0.58); uv (dimethylformamide): λ (nm) (relative intensity) 420 (8.5), 516 (1.0), 554 (0.61), 592 (0.39), 648 (0.30); ^{1}H nmr (d_6-dimethyl sulfoxide): δ 9.53 (4 H, d, α-py), 8.99 (16 H, m, β-pyrrole), 8.19 (12 H, m, *o*-phenyl), 7.79 (18 H, m, *m*, *p*-phenyl), -3.03 (4 H, s, pyrrole N), 5.05 (4 H, m, α-link), 2.23 (4 H, m, β-link), 1.60 (m, γ-link).

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