fluorescence. Both the conversion of Tc to LTc and the abnormally shifted emission become insignificant in basic media.

Experimental Section

The experimental procedures have been detailed in previous papers in this series[1,2] or in the doctoral dissertation of G.O.

Solvents were MeOH and MeCN (Burdick and Jackson, high purity), DMSO, DMF, *n*-BuOH, *n*-PrOH, and anhydrous EtOH (Aldrich, high purity), and deionized water distilled through a Corning Megapure 3MP system. Tc and Tc·HCl were from Sigma and used as received. DTc was a gift from Dr. J. Hlavka, and ATc was previously prepared in these laboratories by Dr. R. E. Drexel. TcMeI was prepared by the literature procedure.[39] 2-Mercaptoethanol was purchased from Aldrich and used as received. All photolyses employed 7-mm quartz tubes with a Hanovia medium-pressure 450-W Hg lamp filtered by a uranium yellow glass sleeve (Houde glass; $\lambda > 330$ nm) as the light source unless otherwise noted. Solutions were degassed with argon for 20 min, sealed, and irradiated in a turnable. HPLC utilized a Varian Vista 5000 series chromatograph with a Varian UV-100 detector, a Hewlett-Packard HP-3376 recording integrator, and a 10-μm Alltech C-18 4.6 mm × 25 cm column. Acetophenone, *p*-methoxyacetophenone, or propiophenone was utilized as an internal standard for Tc, LTc, DTc, and ATc analysis. Analysis for *N,N*-dimethylbenzamide was carried out on a 5-μm Varian C-18 Micropak 4.6 mm × 20 cm column with acetophenone as the internal standard. CD data were collected on a Jasco J-600 polarimeter using a 1 cm path length quartz cell. Fluorescence and excitation spectra were obtained on an SLM-Aminco SPF-500 spectrofluorimeter operated in corrected mode using a 1-cm^2 quartz fluorescence cell with a filter passing light with $\lambda > 400$ nm on the emission side. Samples were deoxygenated with Ar for 20–30 min prior to study. Fluorescence data were corrected for absorbance and refractive index differences, with quinine sulfate in 0.1 N H_2SO_4 (absorbance at 355 nm ca. 0.1) utilized as a standard ($\phi = 0.55$)[40] for fluorescence quantum efficiencies. Solution pH values were determined with a Corning 125 pH meter, calibrated with Fisher pH 4.00, 7.00, and 10.0 standards prior to use.

Acknowledgment. We thank the National Institutes of Health (Grant 5 RO1 AR39286) for support of this research. We are grateful to Dr. David McMillin for the use of his fluorimeter, Dr. J. Hlavka for samples of compounds and useful discussion prior to the onset of this research, and Dr. T. Hasan for sharing with us the results of her ongoing photophysical studies on deoxytetracycline.

Registry No. Tc, 60-54-8; LTc, 115747-16-5.

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Pendant-Capped Porphyrins. 1. The Synthesis of a Biphenyl Pendant-Capped Iron(III) Porphyrin Model of Catalase

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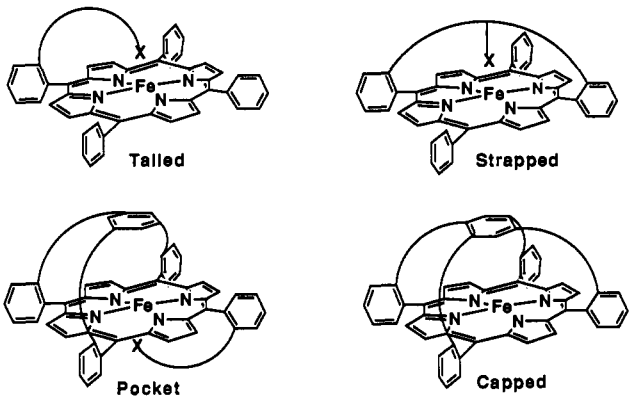
Abstract: A phenol pendant-capped porphyrin ((PHPCP)H_2) and its iron(III) complex ((PPCP)Fe^{III}) have been synthesized. ^1H and ^{13}C NMR were used to characterize all intermediates leading to the final product. In addition, the heteronuclear ^{13}C–^1H shift correlation experiment was used to further characterize the tetraaldehyde precursor of the pendant-capped porphyrin. Proton and carbon chemical shifts for the free base porphyrin (PHPCP)H_2 were assigned by using one-dimensional NMR experiments (including ^{13}C APT) and two-dimensional homonuclear COSY and ROESY experiments. In (PHPCP)H_2, the phenol that provides the ligand is hung from the ceiling of a vaulted dome or tepee with protected walls supported by four legs that are anchored to the 2-position of the phenyl rings at the 5,10,15,20-*meso*-carbons of (TPP)H_2. In the ground-state structure of (PPCP)Fe^{III}, the phenol is dissociated such that the resultant phenolate species is ligated to the high-spin ($S = {}^5/_2$) iron(III). Ligation of phenolate and iron moieties is established by (i) comparison of ^1H NMR to the ^1H NMR of the phenolate complex of $[(TPP)Fe^{III}]^+$; (ii) comparison of the UV/vis spectrum to that for the phenolate complex of $[(TPP)Fe^{III}]^+$; (iii) disappearance of the O–H stretch in the IR accompanying complexation of (PHPCP)H_2 with Fe(III); and (iv) laser desorption mass spectroscopy. At the active site of catalase, the protoporphyrin-IX iron(III) is ligated to the phenolate form of a tyrosine residue.

Introduction

The structures in Chart I depict the general structural characteristics of a number of modified 5,10,15,20-tetraphenylporphyrins $[(TPP)M^{n+}(X)_y]$. A tailed $(TPP)M^{n+}(X)_y$ possesses a chain of atoms extending from the 2-position of a single *meso*-phenyl substituent that terminates in a ligand species. The chain of atoms is of such a length that the ligand substituent may interact with the central M^{n+} moiety.[2] A strapped $(TPP)M^{n+}(X)_y$ possesses a chain of atoms (which holds a ligand in the vicinity of the M^{n+} moiety) extending from the 2-position of a phenyl substituted on the 5-*meso*-carbon of TPP to the 2-position of a phenyl on the 15-*meso*-carbon of TPP.[3] Pocket $(TPP)M^{n+}(X)_y$ structures possess three chains emanating from a common atom

Chart I



(1) Current address: Kang-weon National University, Chun-cheon, Korea.
(2) (a) Geibel, J.; Chang, C. K.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 5924. (b) Chang, C. K.; Traylor, T. G. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2647. (c) Battersby, A.; Hawson, W.; Hamilton, A. P. *J. Chem. Soc., Chem. Commun.* **1982**, 1266. (d) Collman, J. P.; Groh, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 1391. (e) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898. (f) Molinaro, F. S.; Little, R. G.; Iber, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5628. (g) Smith, K. M.; Bisset, G. M. F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2625.

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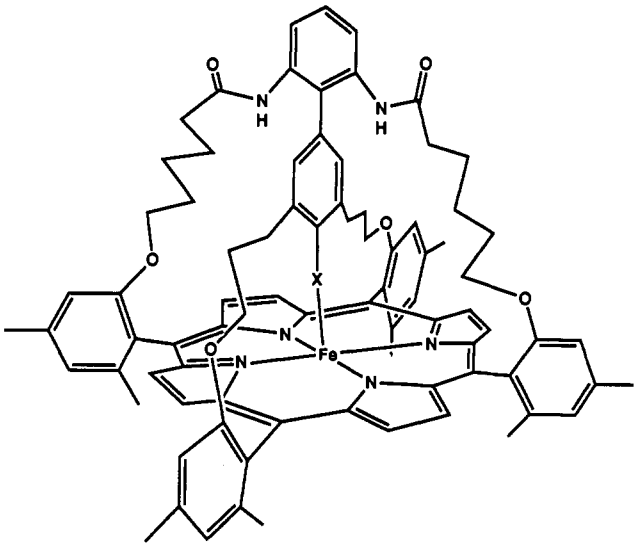
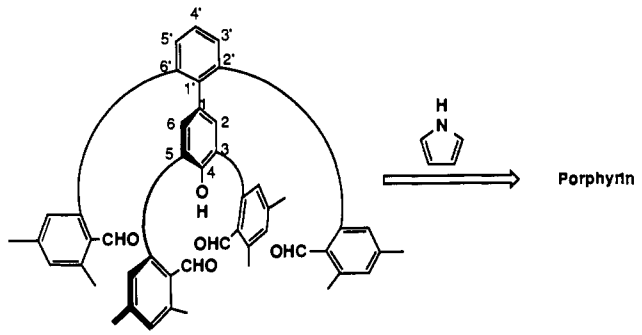


Figure 1. Structure of the iron(III) phenolate pendant-capped porphyrin of this study (PPCP)Fe^{III}, X = O, and the comparable iron(III) thiolate pendant-capped porphyrin structre (TPCP)Fe^{III}, X = S.

or ring and covalently link to the 2-positions of the 5,10,15-phenyl substituents of TPP.[4] Tailed, strapped, and pocket (TPP)$M^{n+}(X)_y$ allow approach of reagents to the metal from either plane of the porphyrin ring. A capped (TPP)$M^{n+}(X)_y$ possesses four chains emanating from a common ring structure that are covalently linked to the 2-positions of the 5,10,15,20-phenyl substituents of TPP.[5] The four legs of a capped (TPP)$M^{n+}(X)_y$ act as a sieve to screen out the approach of reagents to the plane of the porphyrin ring that is capped.[6] In principle, the circumference of the four legs and the distance of approach of the pinnacle of the capping structure to the M^{n+} moiety determine what ligand or reagents are allowed entrance under the cap. We describe here the details for the first synthesis of a pendant-capped porphyrin.[7] The structure of a pendant-capped (TPP)$M^{n+}(X)_y$ is designed such that a *desired pendant ligand* is hung from the ceiling of a vaulted dome or tepee capping structure with four legs that are anchored to the 2-positions of the four phenyl rings at the 5,10,15,20-*meso*-carbons of the TPP.

An ideal chemical model for a specific enzyme would include the following structural characteristics: (i) a domain that holds the catalytic functional groups at the active site in a geometry that mimics the active site structure of the enzyme; (ii) a binding domain for the substrate; and (iii) a capping structure that protects the catalytic functional groups from unwanted interaction with species other than the substrate. The concept of a pendant-capped (TPP)$M^{n+}(X)_y$ provides these features. To mimic a particular iron(III) porphyrin enzyme, the *desired ligand* (phenolic hydroxyl

Scheme I



of tyrosine in catalase, imidazole of histidine in peroxidase, and thiolate of cysteine in cytochrome P-450) is incorporated as the *desired pendant ligand* in the pendant-capped (TPP)$Fe^{III}(X)$.

The structure of the iron(III) ligated pendant-capped porphyrin, whose synthesis and complete characterization are described here, is shown in Figure 1. In the structure of Figure 1, (a) the distal phenolate is positioned within bonding distance of the metal and completely isolated from outside reagents; (b) an open face will allow oxidative oxygen addition to the metal; (c) the *o*-methyl substituents of the *meso*-phenyl groups will prevent stacking or μ-oxo dimer formation; and (d) the phenolate ligand is in a position to stabilize oxidation states $1e^-$ and $2e^-$ above the iron(III) state. The suggested abbreviation for the phenol pendant-capped porphyrin is $(PHPCP)H_2$. Iron(III) ligates to the two porphyrin pyrrole NH functions and the pendant OH such that Fe(III) + $(PHPCP)H_2 \rightarrow (PPCP)Fe^{III} + 3H^+$.

Results and Discussion

There are various means by which a tetraphenylporphyrin ring can be constructed.[8] One procedure is to react pyrrole with an appropriate benzaldehyde.[5,9-11] Baldwin and co-workers, in the synthesis of the so-called "C_2- and C_3-capped porphyrins",[5] introduced the idea of incorporating four benzaldehyde moieties into a single structure such that on reaction with pyrrole there was obtained a capped porphyrin (Chart I). We have used this general approach. In order to arrive at a pendant-capped porphyrin, a structural device is required that will support the four legs of the cap and also place the *desired pendant ligand* in bonding distance of the metal. The best candidate appeared to be a biphenyl derivative. As shown in Scheme I, the average conformation of the biphenyl structure has the two phenyl rings diagonal to each other. Utilizing the 3-, 5-, 2′-, and 6′-positions of a biphenyl to anchor the four legs has the advantage that the bonding of the legs to the phenyl rings points the latter downward toward what will become the porphyrin ring. Also, the 4-position of the biphenyl moiety serves to hold the *desired pendant ligand*, which in the case of $(PHPCP)H_2$ is a phenolic hydroxyl group. In principle, molecules such as thiophenol pendant-capped porphyrin $(THPCP)H_2$ could be synthesized, and its iron(III) complex would serve as a useful cytochrome P-450 model.

Synthesis. The synthesis of (PPCP)Fe^{III} has been completed in 15 steps, and the overall yields have been optimized. As shown in Scheme II, thermal coupling of *p*-iodoanisole and 2,6-dinitrochlorobenzene in the presence of copper powder at 220 °C yields **4** (90%). Demethylation of **4** with BBr_3 in methylene chloride at −70 °C provided the deprotected phenol **5** (90%). Treatment of **5** with sodium metal in absolute ethanol gave the phenoxide salt, which was directly reacted with excess allyl chloride

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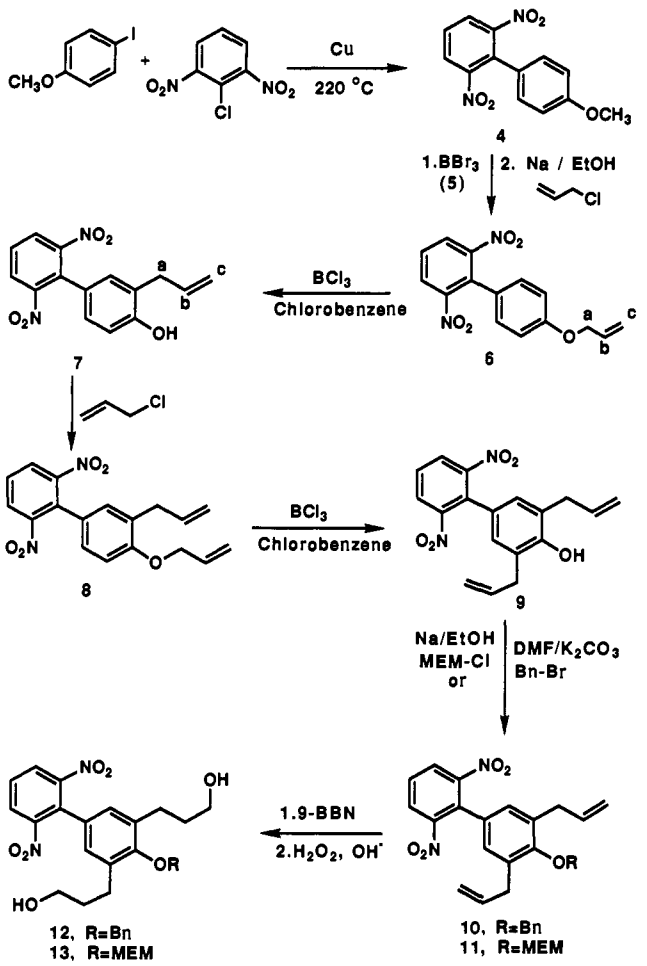
(11) (a) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. (b) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. S. *Tetrahedron Lett.* **1987**, *28*, 3069. (c) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.

Scheme II

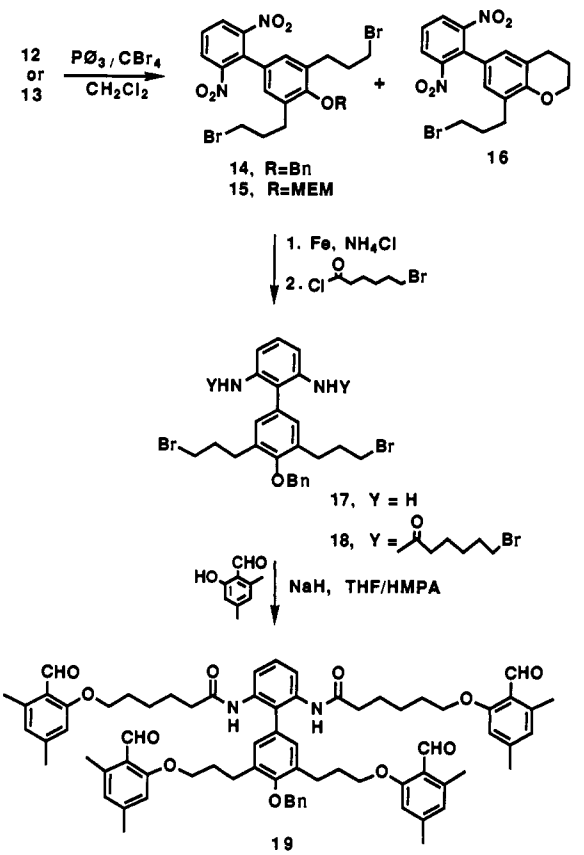


to afford allyl ether **6** (93%). Claisen rearrangement of the resultant allyl ether catalyzed by BCl_3 afforded **7** in 91% yield. 3,5-Diallyl-substituted biphenyl **9**, which is one of the key intermediates, was synthesized by repetitive allylation and Claisen rearrangement under the same conditions as used in the synthesis of **7**. Blocking of the phenolic functional group was carried out with benzyl bromide or (methoxyethoxy)methyl chloride to give benzyl- or MEM-protected biaryl **10** or **11**, respectively. In order to introduce a functional group at the terminal positions of the allyl groups that could be converted to a halide, terminal hydroboration–oxidation was chosen. Terminal hydroxylation by hydroboration–oxidation with 9-BBN/H_2O_2 provided **12** or **13** in 76% and 65% yield, respectively.

Substitution of the primary hydroxyl functions of **12** and **13** by bromide was carried out under mild conditions with PPh_3/CBr_4 in CH_2Cl_2/collidine at −3 °C to give **14** and **15** in 88% and 43% yields, respectively (Scheme III). The reaction is very sensitive to temperature, and the MEM protecting group was more labile to cleavage than the benzyl group under the conditions applied. Hence, the benzyl protecting group was used exclusively for the rest of the synthesis. Compound **16**, which is formed by intramolecular nucleophilic substitution between phenolic OH and alkyl bromide, was produced in larger quantities when the reaction was carried out at 4 °C. The remarkable temperature dependence of the reaction may be responsible for the rapid cleavage of the protecting group by generation of hydrogen bromide. The presence of collidine reduces this side reaction by trapping acidic residue.

Selective reduction of the nitro functions of **14** to amine groups by catalytic reduction with Pd or Raney nickel resulted in cleavage of either the benzyl protecting group or the primary alkyl bromide. In numerous attempts of different reaction conditions, ammonium chloride in the presence of iron dust proved best and gave diamine in 74% yield. Immediate reaction of diamine **17** with 6-bromohexanoyl chloride at −60 °C afforded the tetrabromide **18** (60%).

Scheme III



Reaction of the sodium salt of 2,4-dimethyl-6-hydroxybenzaldehyde, which was prepared by the Duff reaction[12] with **18** in THF/HMPA at 35 °C for 108 h, provided tetraaldehyde **19** (70%). The ^1H and ^{13}C NMR spectra of **19** indicate C_{2v} symmetry of the molecule since the two pairs of the bridges symmetrically substituted on the biphenyl core show identical chemical shifts.

The final stage of the pendant-capped porphyrin synthesis was completed as shown in Scheme IV. Removal of the benzylic protecting group of **19** without destroying other functional groups was possible by heating with CF_3COOH at 55 °C for 6 h to give the phenol **20** (70%). Complete removal of the protecting group was evidenced by the ^1H NMR spectrum since the single benzylic methylene resonance, shown at δ = 4.90 ppm, completely disappeared. Condensation of the phenolic tetraaldehyde **20** with 4 equiv of pyrrole to provide the desired phenol pendant-capped porphyrin **21** was carried out under the conditions developed by Lindsey.[11c] High dilution (10^{-3} M pyrrole in $CHCl_3$) is critical to give the desired porphyrin (see Experimental Section). After chromatographic separation, **21**, which is the only isolable porphyrin, was obtained in 7% yield. Baldwin's[5a] conditions were also tried, but only trace amounts of the desired porphyrin were isolated. Characterization of **21** was by FABMS, ^1H and ^{13}C NMR, IR, and UV/vis spectroscopy. Reaction of **21** with ferrous chloride tetrahydrate in dry DMF heated at 155 °C for 108 h under argon afforded the phenolate pendant-capped iron(III) porphyrin. A 55% yield of (PPCP)Fe^{III} was obtained after purification by silica gel flash column chromatography. The (PPCP)Fe^{III} was characterized by high-resolution laser desorption mass spectrometry, ^1H NMR, IR, and UV/vis spectrometry.

Physical Characterization. The commentary that follows pertains to the characterization of the tetraaldehyde porphyrin precursor **20**, the free base porphyrin (PHPCP)H_2 (**21**), and its iron(III) complex ((PPCP)Fe^{III}). *The phenolic tetraaldehyde porphyrin precursor **20** was carefully characterized* by both homonuclear ^1H decoupling and heteronuclear 2D ^{13}C–^1H chemical shift correlation experiments (Figure 2; see Scheme IV

(12) *Chem. Abstr.* **1947**, *41*, 110e.

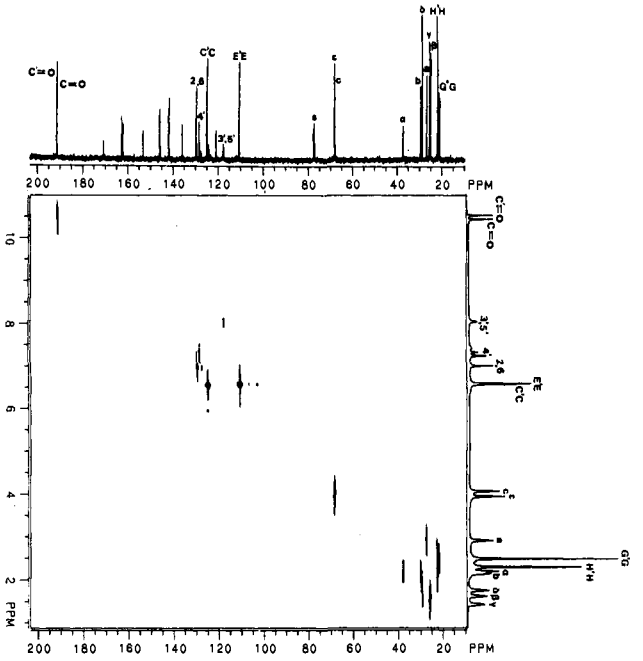
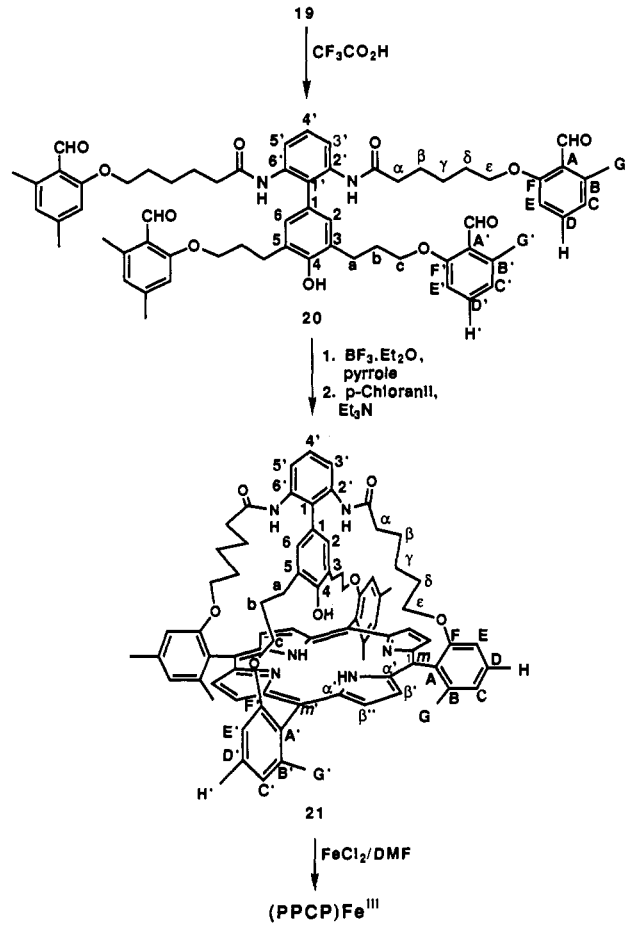


Figure 2. 500-MHz heteronuclear 2D ^{13}C–^{1}H NMR chemical shift correlation spectrum of 0.15 M tetraaldehyde **20** in $CDCl_3$ at 25 °C.

Scheme IV



for labeling of **20**). The strap methylene protons were assigned on the basis of the ^{1}H decoupling experiment, and assignments for the corresponding carbons in the ^{13}C NMR were made from the 2D experiment. Additionally, the characteristic ^{13}C assignments for the C,C′,E,E′ carbons (124.7, 124.9, 110.5, 110.6 ppm, respectively) allowed us to assign the correct proton singlet resonances (6.56, 6.55, 6.54, 6.54 ppm, respectively), and the characteristic ^{1}H shifts for the 2(6),G,G′,H,H′ protons (6.93, 2.465, 2.47, 2.265, 2.27 ppm, respectively) allowed us to assign the correct carbon resonances (129.5, 22.0, 22.0, 21.3, 21.0 ppm, respectively) with the use of the heteronuclear ^{13}C–^{1}H 2D experiment. The quarternary carbon assignments were based on calculations[13] and comparison with the ^{13}C NMR spectrum of 2,4-dimethyl-6-hydroxybenzaldehyde. The resonance assignments of the comparable carbons and protons on each of the two unequivalent 2-formyl-3,5-dimethylphenoxy groups were based on the different neighboring effects due to the different lengths for the two types of straps. The propyl strap holds the phenoxy ring in closer proximity to the biphenyl ring than does the amide strap, therefore causing a slight deshielding effect.

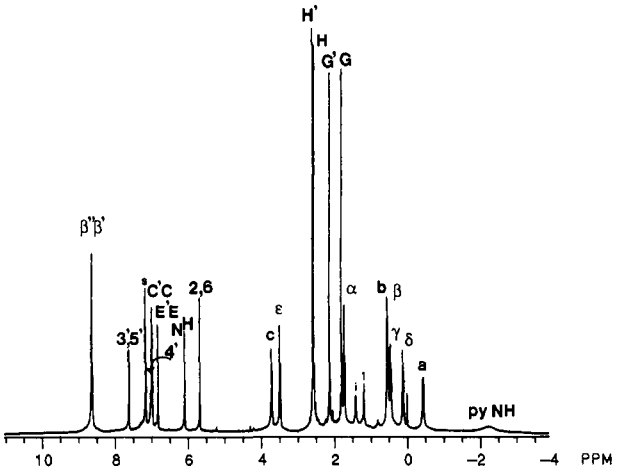


Figure 3. 500-MHz ^{1}H NMR spectrum of 10^{-2} M (PHPCP)H_2 (**21**) in $CDCl_3$ at 25 °C (s, solvent; i, impurity).

*The phenol pendant-capped porphyrin (PCHPCP)H_2 (see Scheme IV for labeling of **21**) was characterized* by ^{1}H and ^{13}C NMR experiments, UV/vis, IR, and FABMS. The 500-MHz ^{1}H NMR spectrum of (PHPCP)H_2, **21**, is shown in Figure 3. By conformational averaging in the NMR time scale, the free base porphyrin structure was found to possess C_{2v} symmetry. The β-pyrrolic resonances are observed at 8.67 and 8.70 ppm as two doublets, and the pyrrolic nitrogen protons are characteristically observed at −2.18 ppm as a broad singlet ($\nu_{1/2}$ = 360 Hz). The two protons in each bridging methylene group are enantiotopic and appear as individual multiplets. The assignments of the individual methylene groups are based on ^{1}H homonuclear decoupling, COSY, and ROESY experiments. The resonances of the methylene groups are shifted upfield due to their exposure to the porphyrin ring anisotropy. The individual chemical shifts of the bridging methylene protons are an indication of their relative distance from the porphyrin plane and the influence of the magnetic anisotropic effect. The a-methylene protons experience the strongest influence from the shielding effect with a 3.24 ppm upfield shift to −0.38 ppm since the protons are held in close proximity to the center of the porphyrin ring. The δ-methylene protons and the b-methylene protons experience similar shielding effects, 1.55 and 1.50 ppm upfield shifts, respectively, which is expected and consistent with the ball and stick figure imaged by molecular modeling[14] (Figure 4). The 2 and 6 aromatic protons

(13) (a) Breitmaier, E.; Voelter, W. *Carbon-13-NMR Spectroscopy*, 3rd ed.; VCH Publishers: New York, 1987. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; 4th ed.; John Wiley & Sons: New York, 1981.

(14) Minimized energy structures were created with the molecular modeling program Quanta (version 2.1A, Polygen Corp.) and coordinates generated by the energy minimization programs steepest descents and adopted basis Newton–Raphson until the energy-change tolerance was less than 10^{-9} kcal/mol (CHARMm, version 21.1.7, Polygen Corp.). During minimization, a distance-dependent dielectric constant and the CHARMm shift functions were used with nonbonded and hydrogen-bonded interaction cutoff distances of 12.5 and 7.5 Å, respectively. The nonbonded and hydrogen-bonded lists were updated every five steps. All computational analyses and graphics were carried out on a Silicon Graphics Iris 4D/220 GTX workstation. Initial coordinates and parameters for the porphyrin ring of **21** were obtained from the file PORPHYRIN·RTF supplied with Quanta and CHARMm.

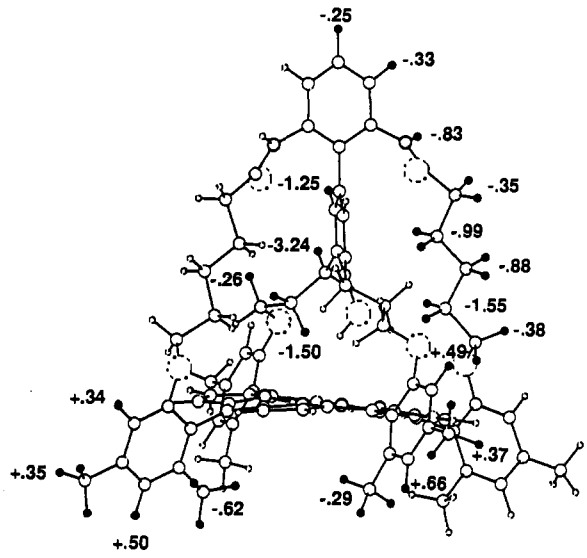


Figure 4. ^{1}H NMR $\Delta\delta$ (ppm) observed upon porphyrin formation. (−) denotes upfield shift, and (+) denotes downfield shift. The labeled protons are darkened for sake of clarity.

also experience a strong influence from the porphyrin ring anisotropy, and the resonance at 5.73 ppm with a difference of 1.25 ppm reflects this effect. Figure 4 demonstrates how the observed differences of the proton resonances due to the porphyrin ring anisotropy correlate to the minimized structure.

The methyl groups G, G′, H, and H′ (1.85, 2.18, 2.61, 2.64 ppm, respectively) were assigned according both to the ^{1}H NMR of tetramesitylporphyrin (TMP) where the comparable methyl groups are known[15] and to their different environments. The propyl strap causes the *meso*-phenyl ring to be held more rigidly than the *meso*-phenyl ring attached to the longer chain amide strap, and tilts the ring so that the G′ methyl group is less shielded than the G methyl group. The ^{1}H assignments for the G and H methyl groups are similar to the known resonances for the comparable methyl groups in TMP (1.84, 2.61 ppm, respectively), which is expected since the phenoxy group on the long chain strap is less restricted than the short strap phenoxy group and more able to obtain the favorable position of the phenyl ring in TMP.

The assignments of the *meso*-phenyl protons C′,C and E′,E (7.21, 7.05, 7.03, 6.88 ppm, respectively) were confirmed by the rotating frame NOE experiment (ROESY), Figure 5. The ROESY experiment, also known as CAMELSPIN (cross-relaxation appropriate for minimolecules emulated by spin-locking), permits the stereospecific assignments of the phenyl protons C′,C and E′,E. Although the ROESY cross peaks are obscrued by t_1 noise (not shown in Figure 5), they appear in negative phase relative to the t_1 noise, which allows the identification of these peaks possible. For our assignments, negative cross peaks between c–E′, ϵ–E, C′–G′, and C–G are significant. The E′ protons are shown to be in the proximity of the c protons, and the E protons are in the proximity of the ϵ protons. Since the assignment of c and ϵ protons can be made by the ^{1}H decoupling and COSY experiments on (PHPCP)H_2, we assigned E′ and E at 7.03 and 6.88 ppm, respectively. The same rationalization is applied to C and C′ protons. The ROESY spectrum, obtained with a spin-locking time (mixing time) of 200 ms, also gives ROESY peaks between α–β, ϵ–δ, c–b, and 3′(5′)–4′, which appear in negative phase and therefore cannot be cross peaks due to coherence transfer between scalar-coupled spins (J peaks).[16] Proximities between α–γ, c–a, 2(6)–β, NH–β and NH–α protons

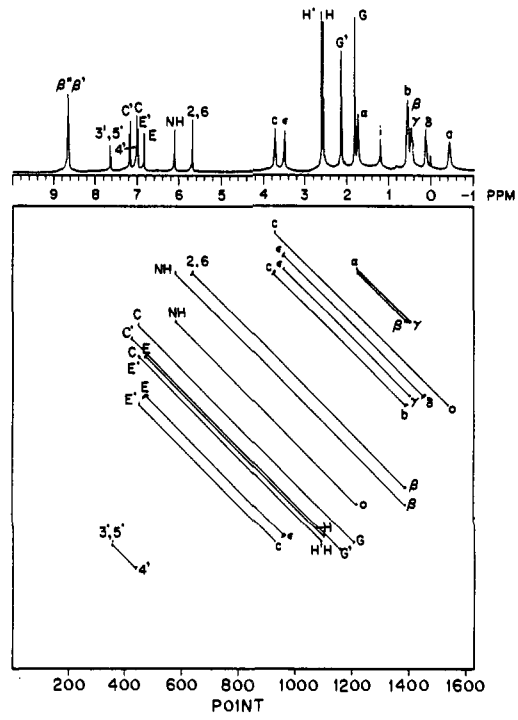


Figure 5. 500-MHz ROESY spectrum of 10^{-2} M (PHPCP)H_2 (**21**) in $CDCl_3$ at 25 °C with a mixing time of 200 ms; only negative peaks due to cross-relaxation in the rotating frame are shown.

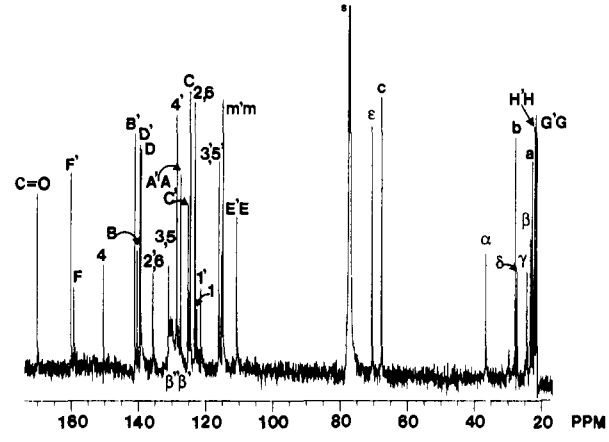


Figure 6. 500-MHz ^{13}C NMR spectrum of 10^{-2} M (PHPCP)H_2 (**21**) in $CDCl_3$ at 25 °C.

can be observed as ROESY peaks, which also confirm the ^{1}H assignments.

The ^{13}C NMR spectrum of **21** is shown in Figure 6, and assignments were made on the basis of an attached proton test experiment[17] (APT) of the porphyrin and by comparison with the ^{13}C NMR spectra of the precursor **20**, TMP,[15] and TOP,[18a] and calculations.[13,18a] The ^{13}C spectrum shows the characteristic pattern of free base tetraphenylporphyrins where N–H tautomerism is in effect.[18] The α-pyrrole carbon resonances are either broad and unresolved in the 145 ppm region or undetectable,[18d] and the β-pyrrole carbons, also affected by the exchange process, are seen as sharp or broad resonances in the 130 ppm region.[18a-d] Under our NMR operating conditions, the porphyrin **21** ^{13}C

(15) ^{1}H and ^{13}C NMR spectra were run (GN 500 MHz) on TMP (10^{-2} M, CD_2CL_2, 25 °C) for comparison studies and are included in the supplementary material.

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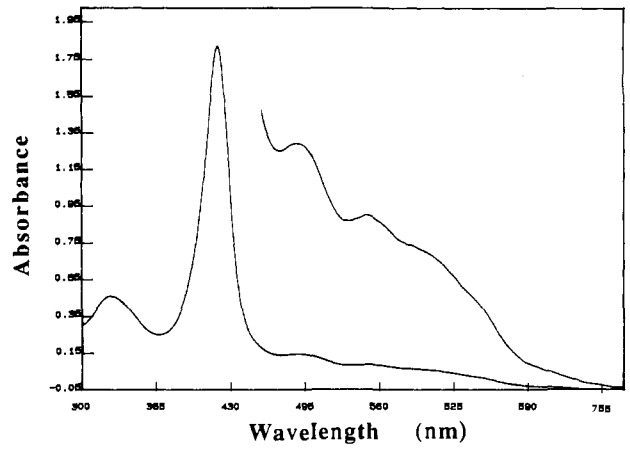

Figure 7. UV/vis spectrum of 1.3×10^{-5} M (PPCP)Fe^{III} in $CHCl_3$ at 25 °C (inset is enlarged 9-fold).

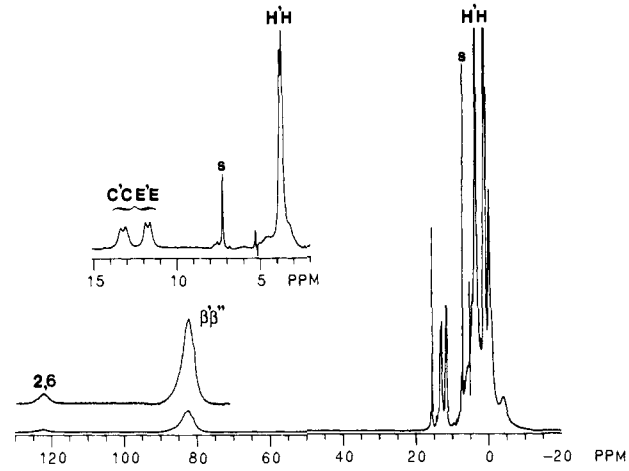

Figure 8. 500-MHz ^1H NMR spectrum of 4×10^{-3} M (PPCP)Fe^{III} in $CDCl_3$ at 25 °C. Resonance assignments: 2,6 = phenolate meta protons; β', β'' = β-pyrrole protons; C', C, E', E = *meso*-phenyl meta protons; H', H = *meso*-phenyl p-methyl protons.

spectrum (10^{-2} M, $CDCl_3$, 25 °C) was comparable to the ^{13}C spectra of TMP (10^{-2} M, CD_2Cl_2, 25 °C)[15] and TPP (3×10^{-2} M, $CDCl_3$, 25 °C, 35 °C, 45 °C)[19] where the α-pyrrole carbons were undetectable and the β-pyrrole carbons (β', β'') were seen as broad peaks at 129–131 ppm ($\nu_{1/2}$ = 72 Hz). The APT experiments for both **21** (10^{-2} M, $CDCl_3$, 35 °C) and TPP (3×10^{-2} M, $CDCl_3$, 35 °C) showed the negative phase pattern characteristic for tertiary carbon atoms for the β-pyrrole carbons. The quarternary *meso*-carbon resonances for **21** (m, m') were within the expected range for tetraphenylporphyrins[18e] at 114.6 and 115.0 ppm.

The thoroughly characterized ^{13}C spectrum of **20** contributed valuable information for the carbon assignments of **21** since the majority of the comparable carbon resonances showed chemical shift differences less than 2%. The porphyrin ring anisotropy contributes equally to the observed chemical shifts in both the ^1H and ^{13}C NMR spectra, but in the carbon spectrum this shift effect is in the order of a few percent because of the range of the observed chemical shifts (200 ppm).[18e] Therefore, the anisotropic effect of the porphyrin ring causes little influence on the carbon resonances, whereas in the proton spectrum the effect is dramatic. The APT experiment helped to confirm the assignments in the complex region 131–114 ppm where quarternary and tertiary carbons had similar chemical shifts. A significant change in chemical shifts (Δ6.6 ppm) on formation of the porphyrin was observed for carbons A and A' (127.2 ppm), which was expected because of their proximity to the porphyrin ring and calculations.[18a] Two of the quarternary carbon resonances, 1C (122.3 ppm) and 1'C (121.2 ppm) in the biphenyl portion of the molecule, were observed as low-intensity peaks in the ^{13}C spectra of all the intermediates, which helped in their assignments.

The UV/vis spectrum of $(PHPCP)H_2$ is characterized by absorption bands at 402 (sh), 420 (Soret), 512, 551, 589, and 643 nm. The phenolic –OH stretching band is clearly shown at 3450 cm^{-1} in the IR spectrum.

The following observations pertain to the (PPCP)Fe^{III}. The laser desorption mass spectrum calculated for $(C_{82}H_{79}N_6OFe + Na)^+$ is *m/e* 1338.526, and the mass found for $(M + Na)^+$ was *m/e* 1338.546. This indicates that there is no proton on the phenolic oxygen. Further evidence supports this contention. The electronic spectrum of (PPCP)Fe^{III} (Figure 7) is comparable to the spectrum of phenoxide ligated (tetraphenylporphinato)iron(III) [(TPP)Fe^{III}(OPh)],[20] exhibiting UV/vis absorption bands at 325, 420 (Soret), 490, 552, 608, and 653 nm. Also of note is the fact that the UV/vis spectrum of chloro ligated (tetraphenylporphinato)iron(III) [(TPP)Fe^{III}(Cl)] exhibits a λ_{max} just prior to the Soret absorbance and the UV/vis spectrum of (PPCP)Fe^{III} does not. This shows that chloride is not ligated to (PPCP)Fe^{III}. Additionally, the IR spectrum of (PPCP)Fe^{III} clearly shows that there is no absorbance that can be attributed to a phenolic –OH stretch. That the phenolate ligand is indeed ligated to the iron(III) moiety in (PPCP)Fe^{III} is shown from the 500-MHz ^1H NMR spectrum recorded at 25 °C. As shown in Figure 8, the large downfield shift of the β-pyrrolic resonances (β', β'') at 83 ppm is distinctive for a high-spin ($S = {}^5/_2$), five-coordinated iron(III).[20-23] The broad line width of the β-pyrrolic resonances (1796 Hz) is consistent with an oxygen donor occupying the fifth coordination site.[21] Moreover, the distinctive downfield resonance at 122.4 ppm corresponds to the axially coordinated phenolate meta proton (2,6-protons) resonances.[20,23] The methyl substituents (H', H) on the para positions of the *meso*-phenyl groups show two distinctive chemical shifts (3.81 and 3.70 ppm), and the protons on the meta positions of the *meso*-phenyl groups (C', C, E', E) also show two different sets of chemical shifts at 13.1, 13.4 and 11.9, 11.6 ppm.

Summary

The synthetic sequences of Schemes II–IV were designed to provide the tetraaldehyde **20**, which was then converted to the phenol pendant-capped porphyrin $(PHPCP)H_2$ (**21**). The intermediates leading to **20** were characterized by ^1H and ^{13}C NMR and MS. For **20**, ^1H and ^{13}C assignments were made with knowledge gained from ^1H decoupling and the 2D ^{13}C–^1H chemical shift correlation experiments. The free base porphyrin **21** possesses C_{2v} symmetry and was characterized by ^1H and ^{13}C NMR, UV/vis, IR, and FAB mass spectroscopy. ^1H homonuclear decoupling and COSY experiments indicated significant upfield shifts (compared with **20**) of the methylene resonances (Δppm = –0.26 to –3.24 ppm) and the aromatic resonances of the biphenyl ring (Δppm = –0.25 to –1.25 ppm) due to porphyrin ring anisotropy. Negative cross peaks of the ROESY experiment indicated proximities between (i) the meta E and E' protons of the *meso*-phenyl groups with both the ε- and c-methylene protons and H and H' protons of the para methyl groups and (ii) the meta C and C' protons of the *meso*-phenyl groups with G and G' protons of the ortho methyl groups. Additionally, ROESY peaks indicated proximities between the α and β methylene groups and the amide NH protons and proximities between the β methylene groups and the 2,6-biphenyl protons meta to the OH.

For **21**, the ^{13}C NMR experiments established the presence of a free base porphyrin structure with the characteristic β-pyrrole

(19) ^{13}C NMR spectra were run (GN 500 MHz) on TPP (3×10^{-2} M, $CDCl_3$, 25, 35, 45 °C) for comparison studies and are included in the supplementary material.

(20) Goff, H.; Shimomura, E. T.; Lee, Y. J.; Sheheit, W. R. *Inorg. Chem.* **1984**, *23*, 315.

(21) Cheng, R.; Lechoslaw, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412.

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carbon resonances at 129–131 ppm region and the meso carbon resonances at 114.6 and 115.0 ppm. The ^{13}C resonances showed chemical shift differences from the precursor **20** of less than 2%.

The iron(III) ligated species (PPCP)Fe^{III} was characterized by ^1H NMR, UV/vis, IR, and laser desorption mass spectroscopy. In the ground-state structure of (PPCP)Fe^{III}, the phenol is dissociated such that the resultant phenolate species is ligated to the iron(III), which exists in a high-spin ($S = {}^5/_2$) state. The large downfield shifts of the β'- and β''-pyrrole proton resonances (82.6 ppm) show the presence of a five-coordinated high-spin iron(III) porphyrin. The coordination of phenolate and iron(III) in the structure (PPCP)Fe^{III} has been firmly established. The 2,6-biphenyl protons meta to the ligand O have a large downfield resonance at 122.4 ppm, which is characteristic of phenolate axially coordinated to an iron(III) porphyrin. Further, the IR spectrum of (PPCP)Fe^{III} shows the absence of the O–H stretch observed with **21**, and laser desorption MS $(M + Na)^+$ shows the absence of H. Also, the UV/vis spectrum of (PPCP)Fe^{III} is virtually superimposable on the spectrum of phenoxide ligated iron(III) tetraphenylporphyrin. Coordination of phenolate and iron(III) porphyrin is a feature shared by the protoporphyrin-IX iron(III) tyrosine structure at the active site of catalase.

Experimental Section

General Procedures. Melting points were taken on a Melt-Temp apparatus equipped with a calibrated thermometer. Nuclear magnetic resonance spectra (^1H, ^{13}C) were obtained with a Nicolet NT-300 or General Electric GN-500 spectrometer. Chemical shifts are reported relative to the signal of TMS, $CDCl_3$, CD_2Cl_2, or $[(CD_3)_2CO]$, which were assigned 0.00, 7.24, 5.32, or 2.04 ppm, respectively, for ^1H NMR, and 0.0, 77.0 (3), 53.8 (5), and 29.8 (7) ppm, respectively, for ^{13}C NMR. ROESY spectra were recorded at 25 °C on a GN 500-MHz spectrometer using the Kessler pulse sequence 90_x–t_1–$(\beta_y$–$\tau)_n$–aquisition.[24] Spectra were collected into 4 K data blocks for 422 t_1 increments with a relaxation delay of 3 s, $\beta = 24°$, $\tau = 3$ μs, and $n = 7491$ to give a mixing time of 200 ms with a locking field of 2.5 kHz and spectral width in both dimensions of 6993 Hz. Data were processed on a VAX computer workstation-3100 using the FTNMR program of Hare Research Inc. (version 4.5, October 1987). The pulse sequence for the attached proton test experiment[17] is designed to produce decoupled ^{13}C spectra with only carbons of selected multiplicity. The interpulse delay was set at 7 ms to obtain quarternary and methylene carbons as positive peaks and methyl and methine carbons as negative peaks. The spectrum was recorded at 500 MHz and 35 °C. 2D ^{13}C–^1H heteronuclear shift correlation data were recorded at 500 MHz and 25 °C by using a pulse sequence,[25] ^1H, $90°_{\phi 1}$–t_1–Δ_1–$90°_{\phi 2}$–τ–Δ_2–decouple; ^{13}C, $t_1/2$–$180°_{\phi 1}$–$t_1/2$–Δ_1–τ–$90°_{\phi 3}$–Δ_2–aquisition$_{\phi R}$, with a 90°(^{13}C) pulse of 17.5 μs and 90°(^1H) = 32 μs calibrated before the experiment. To afford quadrature detection in both frequency domains, an eight-step phase cycling has been applied.[25] Spectra were collected into 4 K data blocks for 256 t_1 increments with a relaxation delay of 1.5 s, $\Delta_1 = 3.2$ ms, $\Delta_2 = 2.1$ ms, and $\tau = 10$ μs. Spectral width in the first dimension was 24 390.2 Hz and 5050.5 Hz in the second dimension. The data matrix was zero filled to 1 K and apodized with an exponential function to give a line broadening of 2 Hz in both dimensions. IR spectra were obtained with a Perkin-Elmer monochromator grating spectrometer in spectral-grade chloroform. Low-resolution and high-resolution mass spectra were obtained with a VCT analytical spectrometer by electron impact (EI) or fast atomic bombardment (FAB) using *m*-nitrobenzyl alcohol as the liquid matrix. Laser desorption mass spectral analysis was obtained from University of California at Riverside. UV–vis spectra were recorded with Cary-14 or Perkin-Elmer 553 spectrophotometers. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Column chromatography was performed on silica gel 60 (70–230 mesh) from Merck or on flash silica gel (200–425 mesh) from Fisher Scientific. Thin-layer chromatography was performed on silica gel 60, F254-backed plates (0.25 cm) purchased from Merck. THF was distilled from potassium in the presence of benzophenone. All other solvents and reagents were purchased and further purified under standard conditions.

4-Methoxy-2′,6′-dinitrobiphenyl (4). A mixture containing 2.0 g (8.5 mmol) of *p*-iodoanisole and 1.7 g (8.5 mmol) of 2,6-dinitrochlorobenzene was heated to 220 °C, and 2.0 g (32 mmol) of copper powder (99.5%, fresh bottle, 155 mesh) was added slowly over a 5-min period. The resultant dark mixture was heated for 30 min at 220 °C with vigorous stirring and then cooled to 50 °C in air, and 200 mL of acetone was added while the mixture was stirred. The solid was filtered and washed thoroughly with acetone. The filtrate was evaporated under reduced pressure, and the solid residue was purified by column chromatography on SiO_2 (70–230 mesh, toluene). The fast-moving orange fraction was collected. Evaporation of solvent and recrystallization from hexane/toluene (9/1) afforded pure **4**: yield 2.1 g (90%); mp 117–119 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.93 (d, 2 H, $J = 8.1$ Hz, 3′,5′-Hs), 7.62 (t, 1 H, $J = 8.1$ Hz, 4′-H), 7.16 (d, 2 H, $J = 8.7$ Hz, 2,6-Hs), 6.93 (d, 2 H, $J = 8.7$ Hz, 3,5-Hs), 3.84 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) (ppm) 160.4 (4C), 151.1 (2′C, 6′C), 129.7 (1′C), 129.3, 128.9 (3′C, 4′C, 5′C), 126.3 (2C, 6C), 122.2 (1C), 114.3 (3C, 5C), 55.2 (CH_3); MS *m/e* 274.0 (M^+).

4-Hydroxy-2′,6′-dinitrobiphenyl (5). To a mixture of 2.3 g of **4** (8.4 mmol) and 100 mL of methylene chloride was added 1.0 mL of BBr_3 (10 mmol) dropwise over a 5-min period at −78 °C. The mixture was warmed to 25 °C and stirred under N_2 (~1.2 h) until no further starting material was consumed as observed by TLC ($CHCl_3$). The mixture was then combined with chloroform (200 mL), washed with water once, saturated $NaHCO_3$ once, and water twice, and dried over $MgSO_4$. The solvent was evaporated to yield **5**, which was recrystallized from hot ethanol/water (20/80): yield 1.99 g (91%); mp 191–193 °C; ^1H NMR ($CDCl_3$) δ 7.94 (d, 2 H, $J = 8$ Hz, 3′,5′-Hs), 7.63 (t, 1 H, $J = 8$ Hz, 4′-H), 7.12 (d, 2 H, $J = 8.5$ Hz, 2,6-Hs), 6.86 (d, 2 H, $J = 8.5$ Hz, 3,5-Hs), 5.00 (s, 1 H, OH); ^{13}C NMR [$(CD_3)_2CO$] (ppm) 159.2 (4C), 152.0 (2′C, 6′C), 130.7, 130.4 (3′C, 4′C, 5′C), 129.7 (1′C), 127.3 (2C, 6C), 122.4 (1C), 116.4 (3C, 5C); MS *m/e* 260.0 (M^+).

4-(2-Propenyloxy)-2′,6′-dinitrobiphenyl (6). A solution containing **5** (16.0 g, 0.061 mol) and ethanol (100%, 200 mL) was added to a solution of dissolved sodium (1.6 g, 0.069 mol) in ethanol (100%, 300 mL), and then 5.0 mL of allyl chloride (0.061 mol) was added slowly by using a dropping funnel. The resultant dark brown mixture was stirred for 1 h at 25 °C, followed by heating at 65 °C for 24 h. When most of the starting material was consumed as observed by TLC, the solvent was evaporated to a small volume (~50 mL). The residue was combined with 200 mL of water, and then the mixture was extracted with diethyl ether (200 mL) two times. The ether layer was washed with water and dried over anhydrous $MgSO_4$. Evaporation of solvent afforded crude product, which was purified by column chromatography (SiO_2, 70–230 mesh, $CHCl_3$) to give 17.1 g (93%) of pure **6**, mp 56–57 °C. The nonpolar product was easily separated from the more polar starting material: ^1H NMR ($CDCl_3$, TMS) δ 7.95 (d, 2 H, $J = 8.5$ Hz, 3′,5′-Hs), 7.64 (t, 1 H, $J = 8.5$ Hz, 4′-H), 7.17 (d, 2 H, $J = 9$ Hz, 2,6-Hs), 6.96 (d, 2 H, $J = 9$ Hz, 3,5-Hs), 6.06 (m, 1 H, O-allylic-b-H), 5.43 (dm, 1 H, $J = 16.5$ Hz, O-allylic-c-H), 5.31 (dm, 1 H, $J = 10.5$ Hz, O-allylic-c-H′), 4.56 (d, 2 H, $J = 6$ Hz, O-allylic-a-Hs); ^{13}C NMR ($CDCl_3$) (ppm) 154.4 (4C), 151.0 (2′C, 6′C), 132.8 (bC), 129.6 (1′C), 129.3, 129.0 (3′C, 4′C, 5′C), 126.3 (2C, 6C), 122.3 (1C), 117.9 (cC), 115.1, 115.0 (3C, 5C), 68.8 (aC); MS *m/e* 340.1 (M^+). Anal. Calcd for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 60.15; H, 4.16; N, 9.36.

4-Hydroxy-5-(2-propenyl)-2′,6′-dinitrobiphenyl (7). A slow stream of BCl_3 gas was bubbled through a solution of **6** (17.0 g, 0.056 mol) in 500 mL of chlorobenzene for 1.5 h at 25 °C. The progress of the reaction can be followed by TLC. When no more starting material was observed, methanol (250 mL) was added dropwise and the reaction was stirred for 1 h. The solvent was evaporated to give a brown solid, which was purified by column chromatography (SiO_2, 70–230 mesh, $CHCl_3$) and recrystallized from $CHCl_3$/petroleum ether: yield 15.4 g (91%); mp 105–107 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.95 (d, 2 H, $J = 8.5$ Hz, 3′,5′-Hs), 7.64 (t, 1 H, $J = 8.5$ Hz, 4′-H), 7.04–7.00 (m, 2 H, 2,6-Hs), 6.85 (d, 1 H, $J = 8.5$ Hz, 5-H), 6.04–5.96 (m, 1 H, 3-allylic-b-H), 5.19–5.11 (m, 2 H, 3-allylic-c-Hs), 5.09 (s, 1 H, 4-OH), 3.41 (d, 2 H, 3-allylic-a-H); ^{13}C NMR [$(CD_3)_2CO$] (ppm) 156.8 (4C), 152.0 (2′C, 6′C), 137.2 (bC), 130.7, 130.6 (3′C, 4′C, 5′C), 129.8 (1′C), 128.1, 127.1 (2C, 6C), 127.8 (3C), 122.5 (1C), 116.0, 115.9 (5C, cC), 34.3 (aC); MS *m/e* 300.1 (M^+).

3-(2-Propenyl)-4-(2-propenyloxy)-2′,6′-dinitrobiphenyl (8). A solution containing **7** (15.4 g, 0.051 mol) and ethanol (200 mL) was added to a solution containing sodium (1.2 g, 0.052 mol) predissolved in 400 mL of ethanol, and then allyl chloride (3.92 g, 0.051 mol) was added. After the mixture was heated for 24 h at 65 °C, additional allyl chloride (1 mL) was added and the heating was continued for another 24 h. The dark brown mixture was cooled, and the solvent was evaporated to 50 mL and then combined with water (300 mL). The suspension was extracted with chloroform (200-mL portion) three times. The organic layer was washed with aqueous 2 N NH_4Cl, dried over anhydrous $MgSO_4$, and evaporated to yield crude product that was slightly contaminated with unreacted starting material. Column chromatography (SiO_2, 70–230

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(25) Martin, G. E.; Zekter, A. S. *Two Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH Publishers: New York, 1988; p 178.

mesh, $CHCl_3$) afforded pure product: yield 14.7 g (85%); mp 42–43 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.93 (d, 2 H, J = 8.0 Hz, 3′,5′-Hs), 7.63 (t, 1 H, J = 8.0 Hz, 4′-H), 7.07–7.03 (m, 2 H, 2,6-Hs), 6.86 (d, 1 H, J = 8.5 Hz, 5-H), 6.09–6.03 (m, 1 H, 4-O-allylic-b-H), 6.00–5.93 (m, 1 H, 3-allylic-b-H), 5.43 (dm, 1 H, J = 16 Hz, 4-O-allylic-c-H), 5.29 (dm, 1 H, J = 11 Hz, 4-O-allylic-c-H′), 5.07–5.01 (m, 2 H, 3-allylic-c-Hs), 4.58–4.56 (m, 2 H, 4-O-allylic-a-Hs), 3.41 (d, 2 H, J = 6.5 Hz, 3-allylic-a-Hs); ^{13}C NMR ($CDCl_3$) (ppm) 157.1 (4C), 151.0 (2′C, 6′C), 136.0 (3-allylic-bC), 132.9 (4-O-allylic-bC), 129.8 (1′C), 129.5, 128.8 (3′C, 4′C, 5′C), 129.4 (3C), 127.0, 126.2 (2C, 6C), 122.1 (1C), 117.2 (4-O-allylic-cC), 116.0 (3-allylic-cC), 111.5 (5C), 68.7 (4-O-allylic-aC), 33.8 (3-allylic-aC); MS m/e 341.1 (M^+).

3,5-Bis(2-propenyl)-4-hydroxy-2′,6′-dinitrobiphenyl (9). Compound **9** was prepared following the same procedure as for the synthesis of **7**. A slow stream of BCl_3 was bubbled through a solution of **8** (5.3 g, 0.015 mol) in chlorobenzene (400 mL) for 2 h at 25 °C. The resultant yellow solution of boric acid ester was decomposed by slow addition of methanol (100 mL) followed by stirring for 1 h. The solvent was evaporated, and the residue was purified by column chromatography (SiO_2, 70–230 mesh, $CHCl_3$). The fast-moving fraction was the desired product, which was solidified either by overnight vacuum or treatment with CH_2Cl_2/petroleum ether (1/9): yield 4.6 g (87%); mp 72–74 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.93 (d, 2 H, J = 8.0 Hz, 3′,5′-Hs), 7.62 (t, 1 H, J = 8.0 Hz, 4′-H), 6.90 (s, 2 H, 2,6-Hs), 6.03–5.94 (m, 2 H, allylic-b-Hs), 5.33 (s, 1 H, 4-OH), 5.18–5.12 (m, 4 H, allylic-c-Hs), 3.40 (d, 4 H, J = 6.5 Hz, allylic-a-Hs); ^{13}C NMR ($CDCl_3$) (ppm) 153.6 (4C), 151.0 (2′C, 6′C), 135.7 (allylic-bC), 129.8 (1′C), 128.8 (3C, 5C), 128.3, 126.2, 126.1 (3′C, 4′C, 5′C, 2C, 6C), 122.2 (1C), 116.9 (allylic-cC), 34.7 (allylic-aC); MS m/e 341.1 (M^+). Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.53; H, 4.74; N, 8.23. Found: C, 63.26; H, 4.60; N, 8.19.

3,5-Bis(2-propenyl)-4-(benzyloxy)-2′,6′-dinitrobiphenyl (10). A solution of benzyl bromide (5.56 g, 32.5 mmol) in DMF (10 mL) was added to a solution of powdered K_2CO_3 (3.62 g, 26.3 mmol) and **9** (8.5 g, 25 mmol) in DMF (90 mL) at 25 °C under N_2. The dark brown slurry was stirred for 18 h, at which time the slurry became pale yellow in color. The mixture was combined with ice–water and then extracted with diethyl ether (300 mL). The combined organic layers were washed with water until neutral and with brine. The layer was dried over $MgSO_4$ and evaporated to yield product. It was purified by flash column chromatography (EtOAc/hexene = 10/90) to yield 10.4 g (97%): mp 73–74.5 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.96 (d, 2 H, J = 8.0 Hz, 3′,5′-Hs), 7.65 (t, 1 H, J = 8.0 Hz, 4′-H), 7.45–7.35 (m, 5 H, benzylic-Ar), 6.98 (s, 2 H, 2,6-Hs), 5.98–5.90 (m, 2 H, allylic-b-Hs), 5.09 (dm, 2 H, J = 10 Hz, allylic-c-Hs), 5.01 (dm, 2 H, J = 17 Hz, allylic-c-H's), 4.86 (s, 2 H, benzylic-CH_2-), 3.44 (d, 4 H, J = 6.5 Hz, allylic-a-Hs); ^{13}C ($CDCl_3$) (ppm) 156.0 (4C), 150.9 (2′C, 6′C), 137.1 (benzylic Ar-1′′C), 136.5 (allylic-bC), 130.0 (1′C), 129.0 (3C, 5C), 133.9, 128.5, 128.5, 128.0, 127.6, 126.4 (3′C, 4′C, 5′C, 2C, 6C, benzylic Ar-2′′C, -3′′C, -4′′C, -5′′C, -6′′C), 126.1 (1C), 116.5 (allylic-cC), 75.5 (benzylic methylene-C), 33.6 (allylic-aC); MS m/e 430.2 (M^+).

4-(Benzyloxy)-3,5-bis(3-hydroxypropyl)-2′,6′-dinitrobiphenyl (12). A solution containing **10** (8.35 g, 19.4 mmol) and THF (100 mL) was added slowly to a solution of THF (300 mL) and 9-BBN (83.4 mL of 0.5 M solution, 41.7 mmol) under nitrogen. The mixture was stirred for 30 min at 25 °C and then heated to 65 °C for 2.5 h. The mixture was cooled in an ice bath, and 3 M NaOH solution (60 mL) was added slowly, followed by slow addition of 30% H_2O_2 solution (60 mL). The temperature was kept less than 28 °C. The mixture was stirred for 30 min and then combined with 500 mL of chloroform and washed with saturated NH_4Cl solution, saturated Na_2SO_3, and brine. After drying over $MgSO_4$, evaporation of the solvent yielded crude product, which was column chromatographed (SiO_2, 200–425 mesh), EtOAc/hexane = 50/50) to afford pure product: yield 6.9 g (76%); mp 104–105 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.97 (d, 2 H, J = 7.5 Hz, 3′,5′-Hs), 7.67 (t, 1 H, J = 7.5 Hz, 4′-H), 7.47–7.37 (m, 5 H, benzylic-Ar), 6.99 (s, 2 H, 2,6-Hs), 4.91 (s, 2 H, benzylic-CH_2-), 3.53 (q, 4 H, J = 6.0 Hz, (3-hydroxypropyl)-c-CH_2s-), 2.77 (t, 4 H, J = 7.0 Hz, (3-hydroxypropyl)-a-CH_2s-), 1.84 (quin, 4 H, J = 6.0 Hz and J = 7.0 Hz, (3-hydroxypropyl)-b-CH_2s-), 1.59 (t, 2 H, J = 6.0 Hz, (3-hydroxypropyl)-c-OHs)); ^{13}C ($CDCl_3$) (ppm) 156.3 (4C), 150.9 (2′C, 6′C), 136.7 (benzylic Ar-1′′C), 129.8 (1′C), 135.6, 129.1, 128.7, 128.3, 128.1, 127.7, 126.3 (3′C, 4′C, 5′C, 2C, 3C, 5C, 6C, benzylic Ar-2′′C, -3′′C, -4′′C, -5′′C, -6′′C), 126.6 (1C), 76.1 (benzylic methylene-C), 63.3 (cC), 33.0 (bC), 26.0 (aC); MS m/e 466.2 (M^+). Anal. Calcd for $C_{25}H_{26}N_2O_7$: C, 64.37; H, 5.62; N, 6.06. Found: C, 64.33; H, 5.62; N, 5.87.

4-(Benzyloxy)-3,5-bis(3-bromopropyl)-2′,6′-dinitrobiphenyl (14). To a solution of **12** (2.0 g, 4.29 mmol) in dry CH_2Cl_2 (150 mL) at 23 °C under N_2 was added triphenylphosphine (4.5 g, 17.2 mmol) and collidine (1.13 g, 8.6 mmol). The homogeneous reaction was cooled to −3 °C, and carbon tetrabromide (2.85 g, 8.6 mmol) in methylene chloride (25 mL) was added dropwise over 10 min. The pale yellow homogeneous reaction was stirred at −5 to −3 °C for 2 h, and the reaction was monitored on TLC to ensure complete formation of the bis(bromo) product. The product was isolated by pouring the reaction into ice-cold 1% HCl, followed by washing with saturated $NaHCO_3$, water, and brine. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed to yield crude bis(bromo) product. Flash chromatography (EtOAc/hexane = 50/50) gave 2.23 g (88%) of white crystals: mp 58–60 °C; ^1H NMR ($CDCl_3$, TMS) δ 7.99 (d, 2 H, J = 8.0 Hz, 3′,5′-Hs), 7.68 (t, 1 H, J = 8.0 Hz, 4′-H), 7.47–7.35 (m, 5 H, benzylic-Ar), 7.00 (s, 2 H, 2,6-Hs), 4.91 (s, 2 H, benzylic-CH_2-), 3.35 (t, 4 H, J = 6.6 Hz, (3-bromopropyl)-c-CH_2s-), 2.80 (t, 4 H, J = 7.2 Hz, (3-bromopropyl)-a-CH_2s-), 2.14 (quin, 4 H, J = 6.6 Hz and J = 7.2 Hz, (3-bromopropyl)-b-CH_2s-); ^{13}C NMR ($CDCl_3$) (ppm) 156.4 (4C), 150.8 (2′C, 6′C), 137.0 (benzylic Ar-1′′C), 129.8 (1′C), 134.9, 129.2, 128.6, 128.4, 128.1, 127.6, 126.4 (3′C, 4′C, 5′C, 2C, 3C, 5C, 6C, benzylic Ar-2′′C, -3′′C, -4′′C, -5′′C, -6′′C), 126.3 (1C), 75.7 (benzylic methylene-C), 33.2, 32.8, 28.6 (aC, bC, cC); MS m/e 592.0 (M^+).

4-(Benzyloxy)-3,5-bis(3-bromopropyl)-2′,6′-diaminobiphenyl (17). A solution of ammonium chloride (153 mg, 2.87 mmol) in 1 mL of water was added to **14** (85 mg, 0.14 mmol) in ethanol (2 mL). The mixture was heated to 65 °C, and iron powder (85 mg, 1.52 mmol) was added in portions over 15 min. The reaction slurry was heated at 65–70 °C for 90 min and monitored by TLC. The TLC indicates formation of intermediates during the reaction before the reaction goes to completion. The reaction was cooled to room temperature and filtered through Celite with additional ethanol. The majority of ethanol was removed under vacuum, and the residue was taken up in ether, washed with water and brine, and dried over Na_2SO_4. Evaporation of the solvent yielded 0.64 g (84%) of crude product that was pure enough to carry out the next step without further purification. Purification attempts caused decomposition of product: ^1H NMR ($CDCl_3$, TMS) δ 7.52–7.39 (m, 5 H, benzylic-Ar), 7.10 (s, 2 H, 2,6-Hs), 6.95 (t, 1 H, J = 7.8 Hz, 4′-H), 6.23 (d, 2 H, J = 7.8 Hz, 3′,5′-Hs), 4.90 (s, 2 H, benzylic-CH_2-), 3.45 (br s, 4 H, NHs), 3.39 (t, 4 H, J = 6.6 Hz, (3-bromopropyl)-c-CH_2s-), 2.84 (t, 4 H, J = 7.6 Hz, (3-bromopropyl)-a-CH_2s-), 2.19 (m, 4 H, (3-bromopropyl)-b-CH_2s-).

4-(Benzyloxy)-3,5-bis(3-bromopropyl)-2′,6′-bis(6-bromohexanamido)biphenyl (18). 6-Bromohexanoyl chloride (56 mg, 0.26 mmol) was added dropwise to a solution containing diamine **17** (64 mg, 0.12 mmol) and pyridine (28 mg, 0.36 mmol) in dry THF (1 mL) at −60 °C. The reaction slurry was warmed slowly to 10 °C over a 1.5-h period. A drop of water was added to the reaction mixture, and the mixture was stirred for 1 h to hydrolyze the excess acid chloride. The reaction was poured into ether and water. The ether layer was washed with dilute HCl, saturated $NaHCO_3$ solution, water, and brine and dried over $MgSO_4$. Evaporation of solvent afforded 92 mg of crude product, which was flash chromatographed on SiO_2 (EtOAc/hexane = 40/60). Yield was 60% as a white crystalline solid: mp 99.5–102 °C; ^1H NMR ($CDCl_3$, TMS) δ 8.05 (m, 2 H, 3′,5′-Hs), 7.51–7.39 (m, 5 H, benzylic-Ar), 7.37 (t, 1 H, J = 8.4 Hz, 4′-H), 7.04 (s, 2 H, 2,6-Hs), 6.69 (s, 2 H, N-Hs), 4.98 (s, 2 H, benzylic-CH_2-), 3.39 (t, 4 H, J = 6.6 Hz, (3-bromopropyl)-c-CH_2s-), 3.38 (t, 4 H, J = 6.6 Hz, ϵ-CH_2s-), 2.88 (t, 4 H, J = 7.5 Hz, (3-bromopropyl)-a-CH_2s-), 2.20 (m, 4 H, (3-bromopropyl)-b-CH_2s-), 2.13 (t, 4 H, J = 7.2 Hz, α-CH_2s-), 1.82 (m, 4 H, δ-CH_2s-), 1.58 (m, 4 H, β-CH_2s-), 1.42 (m, 4 H, γ-CH_2s-); ^{13}C NMR ($CDCl_3$) (ppm) 170.3 (amide C), 156.1 (4C), 136.7 (2′C, 6′C), 136.5 (benzylic Ar-1′′C), 135.5, 130.3, 129.1, 128.6, 128.5, 127.6 (4′C, 1C, 2C, 3C, 5C, 6C, benzylic Ar-2′′C, -3′′C, -4′′C, -5′′C, -6′′C), 121.8 (1′C), 117.3 (3′C, 5′C), 75.8 (benzylic methylene-C), 37.4 (αC), 33.5, 33.1, 33.0, 32.3, 29.1, 27.5 (γC, δC, ϵC, aC, bC, cC), 24.4 (βC); FABMS m/e 882 ($M^+ - 4$), 884 ($M^+ - 2$), 886 (M^+), 888 ($M^+ + 2$), 890 ($M^+ + 4$).

4-(Benzyloxy)-3,5-bis[3-(2-formyl-3,5-dimethylphenoxy)propyl]-2′,6′-bis[6-(2-formyl-3,5-dimethylphenoxy)hexanamido]biphenyl (19). A solution of 2-hydroxy-4,6-dimethylbenzaldehyde (1.1 g, 7.34 mmol) in 5 mL of THF was added dropwise to NaH (0.17 g, 7.14 mmol) in 25 mL of THF followed by HMPA (5 mL) at 23 °C. After 0.5 h, compound **18** (0.6 g, 0.68 mmol) in 5 mL of THF was added to the mixture. The reaction was heated at 35 °C for 108 h, and then the reaction was poured into water and extracted with ether (500 mL). The ether layer was washed twice with 10% NaOH and water until neutral. After washing with brine, it was dried over $MgSO_4$. The solvent was removed, and the residue was purified by flash column chromatography (EtOAc/hexane = 60/40) to give 0.55 g (70%) of pure product: mp 116–118 °C; ^1H NMR ($CDCl_3$, TMS) δ 10.52 and 10.29 (s, 4 Hs, four aldehydes), 7.99 (m, 2 H, 3′,5′-Hs), 7.37 (m, 6 Hs, 4′-H and benzylic-Ar), 7.09 (s, 2 H, 2,6-Hs), 7.02 (s, 2 H, N-Hs), 6.53, 6.57 (s, 8 H, C-Hs, C′-Hs, E-Hs, E′-Hs), 4.90 (s, 2 H, benzylic-CH_2-), 4.01 (t, 4 H, J = 6.0 Hz, c-CH_2s-), 3.96 (t, 4 H, J = 6.5 Hz, ϵ-CH_2s-), 2.87 (t, 4 H, J = 7.0 Hz, a-CH_2s-), 2.49, 2.48 (s, 12 H, G′-CH_3s, G-CH_3s), 2.29 (s, 12 H, H-CH_3s, H′-

CH_3s), 2.17 (t, 4 H, J = 7.5 Hz, α-CH_2s-), 2.12 (m, 4 H, b-CH_2s-), 1.77 (m, 4 H, δ-CH_2s-), 1.63 (m, 4 H, β-CH_2s-), 1.44 (m, 4 H, γ-CH_2s-); ^{13}C NMR ($CDCl_3$) (ppm) 191.6 (aldehyde' C), 191.4 (aldehyde C), 170.8 (amide C), 162.7 (F'C), 162.5 (FC), 155.7 (4C), 145.8 (D'C), 145.6 (DC), 141.8 (B'C), 141.8 (BC), 137.0 (2'C, 6'C), 136.7 (1''C), 135.6, 129.8, 129.2, 128.8, 128.6, 128.2, 127.1 (1C, 2C, 3C, 5C, 6C, 1'C, 4'C, 2''C, 3''C, 4''C, 5''C, 6''C), 125.0 (C'C), 124.8 (CC), 120.8 (A'C), 120.7 (AC), 118.5 (3'C, 5'C), 110.5 (E'C), 110.4 (EC), 75.4 (benzylic methylene-C), 68.2 (ϵC), 68.0 (cC), 37.2 (αC), 30.0 (bC), 28.9 (δC), 27.2 (aC), 25.6 (γC), 25.0 (βC), 22.1 (H'C, HC), 21.4 (G'C, GC); FABMS m/e 1164 $(M + H)^+$, calcd for $C_{73}H_{83}N_2O_{11}$ 1164.0.

3,5-Bis[3-(2-formyl-3,5-dimethylphenoxy)propyl]-4-hydroxy-2',6'-bis-[6-(2-formyl-3,5-dimethylphenoxy)hexanamido]biphenyl (20). Benzyl-protected compound **19** (66.5 mg, 0.057 mmol) was added to trifluoroacetic acid (0.6 mL), and the reaction was heated under Ar for 5 h at 50 °C. Then chloroform and water were added to the reaction, the mixture was washed with saturated $NaHCO_3$, water, and brine and dried over $MgSO_4$. The solvent was removed and the residue purified by flash column chromatography (EtOAc/hexane = 60/40) to yield 43 mg (70%) of product, which is an amorphous solid with no distinct melting point: ^{1}H NMR ($CDCl_3$, 10^{-2} M) δ 10.48 (s, 2 H, aldehyde-H's), 10.38 (s, 2 H, aldehyde-Hs), 8.00 (m, 2 H, 3',5'-Hs), 7.31 (t, 1 H, J = 8.25 Hz, 4'-H), 6.98 (br s, 2 H, N-Hs), 6.94 (br s, 1 H, OH), 6.93 (s, 2 H, 2,6-Hs), 6.56, 6.55 (s, 4 H, C'-Hs, C-Hs), 6.54 (s, 4 H, E'-Hs, E-Hs), 4.03 (t, 4 H, J = 6.0 Hz, c-CH_2s-), 3.92 (t, 4 H, J = 6.5 Hz, ϵ-CH_2s-), 2.86 (t, 4 H, J = 7.3 Hz, a-CH_2s-), 2.47, 2.465 (s, 12 H, G'-CH_3s, G-CH_3s), 2.27, 2.265 (s, 12 H, H'-CH_3s, H-CH_3s), 2.12 (t, 4 H, J = 7.5 Hz, α-CH_2s-), 2.08 (m, 4 H, b-CH_2s-), 1.72 (tt, 4 H, J = 6.5 Hz and J = 7.25 Hz, δ-CH_2s-), 1.57 (tt, 4 H, J = 7.5 Hz and J = 7.5 Hz, β-CH_2s-), 1.39 (m, 4 H, γ-CH_2s-); ^{13}C ($CDCl_3$) (ppm) 191.6 (aldehyde' C), 191.4 (aldehyde C), 170.7 (amide C), 162.7 (F'C), 162.0 (FC), 153.1 (4C), 145.9 (D'C), 145.7 (DC), 142.0 (B'C), 141.7 (BC), 135.7 (2'C,6'C), 129.6 (3C, 5C), 129.5 (2C, 6C), 128.3 (4'C), 127.5 (1C), 124.9 (C'C), 124.7 (CC), 124.0 (1'C), 120.7 (A'C), 120.6 (AC), 117.4 (3'C, 5'C), 110.6 (E'C), 110.5 (EC), 67.9 (ϵC), 67.6 (cC), 37.3 (αC), 29.4 (bC), 28.7 (δC), 26.7 (aC), 25.4 (γC), 25.0 (βC), 22.0 (H'C, HC), 21.3 (G'C), 21.0 (GC); FABMS m/e 1074 $(M + H)^+$, calcd for $C_{66}H_{77}N_2O_{11}$ 1074.0.

Free Base of the Phenolate Pendant-Capped Porphyrin (21). Freshly prepared 2.5 M BF_3·Et_2O/chloroform (71 μL, 0.18 mmol) was added to the mixture of compound **20** (142 mg, 0.132 mmol), distilled pyrrole (36.3 mg, 0.54 mmol), and chloroform (550 mL, freshly distilled over K_2CO_3) at 23 °C under argon. The reaction was stirred for 3.25 h, p-chloranil (99.8 mg, 0.41 mmol) followed by triethylamine (25 μL, 0.18 mmol) were added, and the reaction was heated to 65 °C for 1.75 h. The reaction was cooled, and the solvent was removed to give a black residue. This crude reaction product was purified twice by silica flash column chromatography to give 11.7 mg (7%) of desired porphyrin, mp >300 °C. The solvents employed were first column, EtOAc/$CHCl_3$ (5/95); and second column, CH_3OH/$CHCl_3$ (4/96): ^{1}H NMR ($CDCl_3$, 10^{-2} M) δ 8.70 (d, 4 H, J = 4.8 Hz, β-pyrrolic Hs), 8.67 (d, 4 H, J = 4.8 Hz, β-pyrrolic Hs), 7.67 (d, 2 H, J = 8.4 Hz, 3',5'-Hs), 7.21 (s, 2 H, C'-Hs), 7.06 (t, 1 H, J = 8.4 Hz, 4'-H), 7.05 (s, 2 H, C-Hs), 7.03 (s, 2 H, E'-Hs), 6.88 (s, 2 H, E-Hs), 6.14 (s, 2 H, amide N-Hs), 5.73 (s, 2 H, 2,6-Hs), 3.77 (t, 4 H, J = 5.0 Hz, c-CH_2s-), 3.54 (t, 4 H, J = 7.3 Hz, ϵ-CH_2s-), 2.64 (s, 6 H, H'-CH_3s), 2.61 (s, 6 H, H-CH_3s), 2.18 (s, 2 H, G'-CH_3s), 1.85 (s, 6 H, G-CH_3s), 1.77 (t, 4 H, J = 7.0 Hz, α-CH_2s-), 0.55–0.63 (m, 8 H, b-CH_2s- and β-CH_2s-), 0.46–0.53 (m, 4 H, γ-CH_2s-), 0.14–0.19 (m, 4 H, δ-CH_2s-), −0.41 to −0.36 (m, 4 H, a-CH_2s-), −2.18 (br s, 2 H, pyrrolic NHs); ^{13}C NMR ($CDCl_3$, 10^{-2} M) (ppm) 169.9 (amide C), 159.9 (F'C), 159.1 (FC), 150.2 (4C), 140.8 (B'C), 140.1 (BC), 139.3 (D'C), 139.0 (DC), 135.4 (2'C, 6'C), 130.7 (3C, 5C), 130.1–129.6 (β'- and β''-pyrrole C), 128.3 (4'C), 127.2 (AC, A'C), 125.0 (C'C), 124.3 (CC), 123.0 (2C, 6C), 122.3 (1C), 121.2 (1'C), 115.8 (3'C, 5'C), 115.0, 114.6 (m,m'C), 110.5 (E'C, EC), 70.3 (ϵC), 67.5 (cC), 36.4 (αC), 27.6 (bC), 27.1 (δC), 24.2 (γC), 23.1 (βC), 22.6 (aC), 21.9 (H'C), 21.8 (HC), 21.4 (G'C), 21.2 (GC); UV/vis ($CHCl_3$) λ_{max} (nm) ($\epsilon \times 10^4$ M^{-1} cm^{-1}), 402 (sh), 420 (32.2), 512 (12.5), 551 (3.0), 589 (3.0), 643 (0.5); IR ($CHCl_3$) 3450 (br, OH), 3415 (m, amide NH), 3340 (w, pyrrole NH), 1680 (s, C=O) cm^{-1}; FABMS m/e 1263 (M^+), calcd for $C_{82}H_{82}N_6O_7$ 1263.

Phenolate Pendant-Capped Porphyrin Iron(III) [(PPCP)Fe^{III}]. $FeCl_2$·$4H_2O$ (142 mg, 0.71 mmol) was added to the mixture of **21** (8.7 mg, 6.9×10^{-3} mmol) and dry DMF (4 mL) under argon. The reaction was heated to 155 °C for 108 h. The reaction mixture was added to chloroform (30 mL) and water (50 mL) and extracted with chloroform (3 × 30 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4. The solvent was removed, and the crude product was purified by silica flash column chromatography to yield 5 mg (55%) of pure product: ^{1}H NMR ($CDCl_3$, 4×10^{-3} M, 25 °C) δ 122.4 (br s, 2,6-Hs), 82.6 (br s, β'- and β''-pyrrolic Hs), 13.4, 13.1, 11.9, 11.6 (s, C', C, E', E protons), 3.8, 3.7 (H-CH_3s, H'-CH_3s), see Figure 8; UV/vis ($CHCl_3$) λ (nm) ($\epsilon \times 10^4$ M^{-1} cm^{-1}), 325 (3.3), 420 (13.5), 490 (1.1), 552 (0.66), 608, 653; IR ($CHCl_3$) 3415 (m, amide NH), 1680 (s, C=O) cm^{-1}; laser desorption MS m/e 1338.546 $(M + Na)^+$, calcd for $(C_{82}H_{79}N_6O_7Fe + Na)^+$ 1338.526.

Acknowledgment. This investigation was supported by a grant from the National Institute of Health.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of the intermediates of $(PHPCP)H_2$, including enlarged portions of the 2D ^{13}C–^{1}H chemical shift correlation spectrum of the tetraaldehyde **20**, the enlarged portions of the ^{1}H and ^{13}C NMR spectra of **21** and its APT spectrum and UV/vis and IR spectra along with the ^{1}H and ^{13}C NMR spectra of TMP and the ^{13}C NMR spectra of TPP (25, 35, 45 °C) and its APT spectrum, and the IR spectrum of (PPCP)Fe^{III} (51 pages). Ordering information is given on any current masthead page.