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Synthesis of Porphyrins Tailored with Eight Facially-Encumbering Groups. An Approach to Solid-State Light-Harvesting Complexes[1]

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Abstract: Synthetic models of the photosynthetic antenna complexes must achieve long-range 3-dimensional order encompassing a large number of porphyrinic pigments with limited direct contact of the pigments. In order to develop solid-state antenna complexes, we have synthesized porphyrins bearing benzyloxy groups projecting over both faces and optionally also around the periphery of the porphyrin. Routes have been established for prefunctionalizing benzaldehydes with various benzyloxy groups. Reaction of 2,6-bis, 3,5-bis, or 2,4,6-tris(benzyloxy)benzaldehydes with pyrrole via the room temperature two-step one-flask porphyrin reaction provides direct access to the facially-encumbered porphyrins. The benzyloxybenzaldehydes react as efficiently as methoxybenzaldehydes, indicating the utility of the -OCH_2- unit for introducing large substituents near the face of the porphyrin. The octakis and dodecakis(benzyloxy)porphyrins exhibit characteristic porphyrin absorption and fluorescence properties in solution. The crystal structure of *meso*-tetrakis[2,6-bis(2,3,4,5,6-pentafluorobenzyloxy)phenyl]porphyrin has been determined. The pentafluorobenzyloxy substituents provide a cavity on each side of the porphyrin plane which has an approximate cylindrical shape with a diameter of ~7.5 Å and a height of ≥ 4.5 Å. The porphyrin core parameters are those obtained for free base derivatives in which the inner hydrogen atoms are ordered. Crystal data: a = 14.759 (1) Å, b = 25.519 (2) Å, c = 13.100 (1) Å, α = 100.04 (1), β = 99.83 (1), γ = 88.25 (1), V = 4767.3 (6) $Å^3$, all measurements at 127 K, triclinic, space group $P\bar{1}$, Z = 2 $R_1(F)$ = 0.097, for 10020 "observed" data, and $wR_2(F^2)$ = 0.275 for 17761 total unique (all) data.

Porphyrinic pigments lie at the heart of the light-harvesting complexes of photosynthetic organisms.[2] The concentration of pigments in the antenna complexes is ~0.1 M,[3] yet structural analysis of one bacteriochlorophyll-protein complex shows that the π-systems of the pigments are not in van der Waals contact.[4] These structural determinations, as well as a large body of data concerning the strong distance dependencies of photosynthetic energy transfer processes, point up the importance of holding the interacting pigments at intermediate distances: too far apart and the reactions do not occur within the lifetime of the porphyrin excited state; too close and non-energy transfer quenching interactions often predominate. The design of a light-harvesting model system must bring a large number of porphyrins in close proximity yet maintain limited pigment contact. Porphyrinic pigments have a pronounced tendency to undergo face-to-face dimerization, and this aggregation process must be controlled in any model system for light-harvesting.

One approach to the construction of light-harvesting complexes is the synthesis of covalent arrays of porphyrins with the porphyrins held apart by relatively rigid linkers.[5] A second approach, co-crystallizing tetraphenylporphyrin with small organic compounds, has yielded a large family of crystals with regular sponge-like structures.[6] A third approach is to introduce bulky groups on both faces of the porphyrin, thereby establishing a minimum distance of separation of the porphyrin macrocycles in the crystalline state.

We sought to prepare a family of facially-encumbered tetraarylporphyrins with each porphyrin having all eight *ortho*-phenyl positions substituted with bulky groups of selected size and polarity (Figure 1). Facially-encumbered porphyrins have been the object of widespread attention in porphyrin biomimetic chemistry, and substituents (excluding halogens) that have been incorporated at all eight *ortho*-positions of tetraarylporphyrins include methyl groups,[7,8] larger alkyl groups,[9] phenyl or aryl units,[10] amines,[11,12] amides,[12] methoxy,[13-16] ethoxy,[16] alkoxy straps,[13,17] acyloxy groups,[14,18] and a few combinations of these.[8,19,20] Recently porphyrins bearing bulky groups at all eight β-pyrrole positions also have been synthesized.[21]

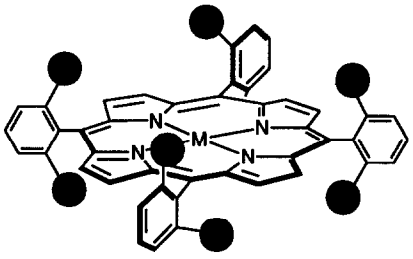


Figure 1. A facially-encumbered tetraaryl-metalloporphyrin with eight *ortho*-substituents.

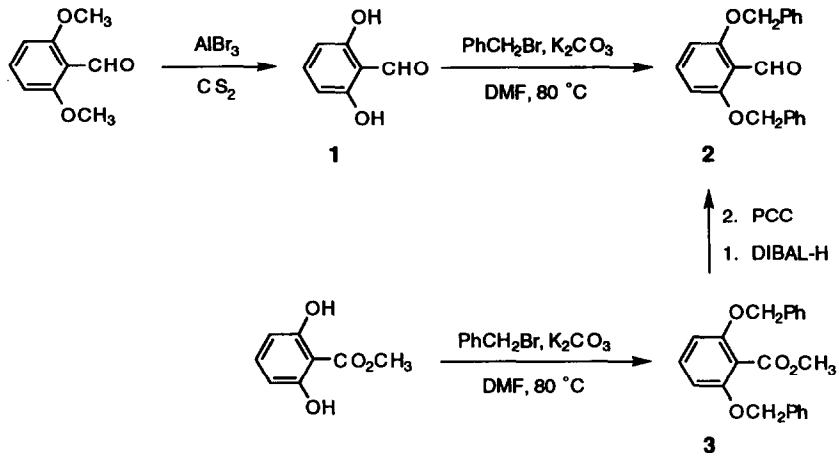
We felt *ortho*-benzyloxy groups would satisfy several molecular design and synthesis constraints in preparing facially-encumbered porphyrins, including a) use of pre-functionalized aldehydes, thereby minimizing porphyrin manipulations, b) ease of synthesis of the substituted aldehyde, c) compatibility of the *ortho* -OCH_2- unit with the porphyrin-forming reaction, d) ability to incorporate groups of variable size and polarity, enabling a tailor-made family of facially-encumbered porphyrins, and e) coverage of both faces of the porphyrin.[22] In addition to potential solid-state applications, the ability to prepare facially-encumbered porphyrin building blocks[23] is a key element in the design of soluble multi-porphyrin arrays.[5] In this paper we report the synthesis of various 2,6-bis and 2,4,6-tris(benzyloxy)benzaldehydes and their conversion to facially-encumbered porphyrins, characterize the solution spectral properties of the porphyrins, and present the X-ray structural determination of one facially-encumbered porphyrin.

RESULTS AND DISCUSSION

Aldehyde Preparation

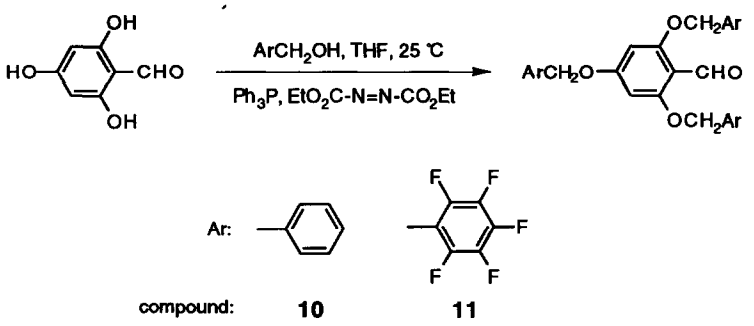
We explored methods for preparing benzyloxy-substituted aldehydes that have broad applicability and can be easily scaled-up to multigram quantities. Alkylation of 2,6-dihydroxybenzaldehyde (**1**), prepared by $AlBr_3$-mediated demethylation of 2,6-dimethoxybenzaldehyde, was performed with benzyl bromide using K_2CO_3 at 80 °C for 1 h (K_2CO_3 method) (Scheme 1). Similar benzylation of the less expensive methyl 2,6-dihydroxybenzoate afforded **3**, which upon treatment with diisobutylaluminum hydride followed by pyridinium chlorochromate gave the aldehyde. A related route to **2** via **3** has been described.[24]

In general the reaction of 2,6- or 3,5-dihydroxybenzaldehyde with various benzyl bromides using the K_2CO_3 method gave good yields and afforded a direct route to aldehydes **4-6**, **8**, and **9**. The synthesis of the ester-substituted aldehyde **7** gave low yields with K_2CO_3 and was prepared at room temperature with KF in 25% yield. The aldehydes were purified by flash chromatography. In many cases the aldehyde was the fastest moving component, no unreacted alkylating agent remained, and the other materials remained bound at the top of the column.



Scheme 1.

Reaction of 2,4,6-trihydroxybenzaldehyde (phloroglucinol carboxaldehyde) with benzyl bromide and K_2CO_3 in DMF at 80 °C gave a red oil composed of multiple components. The same reaction at room temperature for 48 h[25] gave 50% yields of **10** or **11** but the product was contaminated with significant amounts of C-alkylated material (6% or 10% of the total, respectively), a well-known problem in the alkylation of phloroglucinol carbonyl compounds.[26] These side-products were not easily separated chromatographically. Application of the Mitsunobu reaction[27] with the appropriate benzyl alcohol and phloroglucinol carboxaldehyde cleanly gave **10** or **11** in about 40% yield following flash chromatography (Scheme 2).

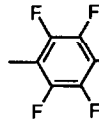


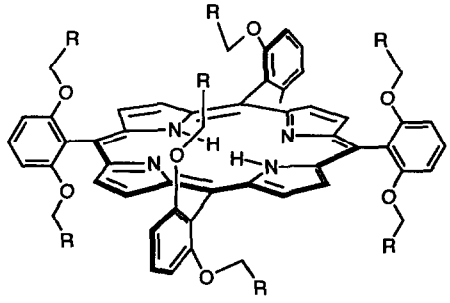
Scheme 2.

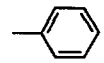
Porphyrin Synthesis

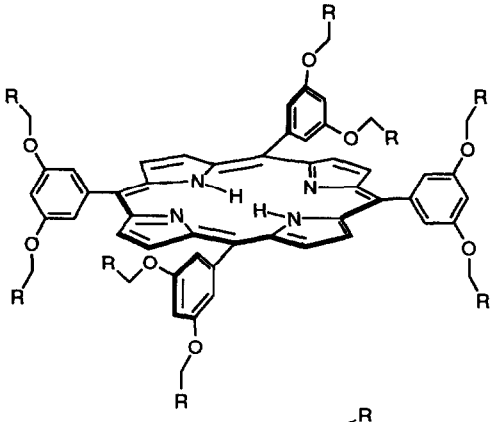
The condensation of 2,6-dibenzyloxybenzaldehyde with pyrrole was performed at 0.01 M using BF_3-ethanol cocatalysis (3.3 mM BF_3-$O(Et)_2$ in $CHCl_3$ containing 0.75% ethanol) at room temperature, the conditions found optimal for mesitaldehyde.[8] Oxidation of the porphyrinogen with DDQ at room temperature afforded the corresponding porphyrin **12**. The porphyrin was purified easily by chromatography on silica gel in 20% overall yield. The similar reaction of 2,6-dimethoxybenzaldehyde gave porphyrin **13** in 26% overall yield, indicating the steric effects of the benzyl groups in the condensation and oxidation processes are minimal.

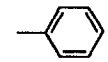
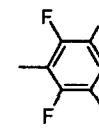
Table 1. Porphyrins synthesized.

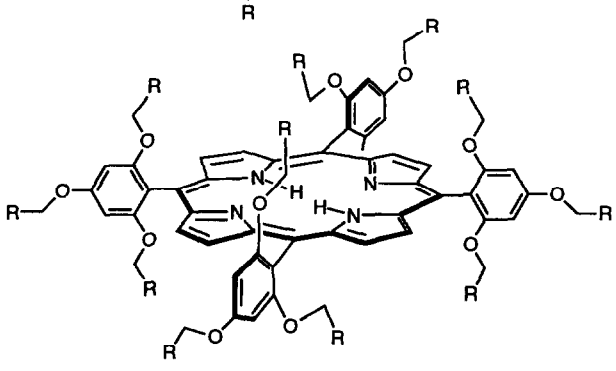
R group	Porphyrin	% Yield
	**12**	20%
—H	**13**	26%
	**14**	9.3%
	**15**	17%
	**16**	52%
	**17**	11%



R group	Porphyrin	% Yield
	**18**	41%
	**19**	15%



R group	Porphyrin	% Yield
	**20**	15%
	**21**	44%
—H	**22**	11%



A limited survey was performed of the effects of catalysts, cocatalysts, and oxidant. The yield of porphyrin **12** was quite sensitive to the oxidant, giving 0% with *p*-chloranil in place of DDQ at room temperature. Trifluoroacetic acid as a catalyst gave no porphyrin, and the reaction with $BF_3{\cdot}O(Et)_2$ in the absence of ethanol gave only 7.1% yield of porphyrin **12**.

Porphyrins **14-22** were obtained in yields of 9-52% (Table 1). The lowest yield was for the *para*-bromobenzyl porphyrin **14** (9.3%). In this reaction the condensation yielded a cloudy orange mixture, indicative of aggregation. Higher acid concentrations did not increase the porphyrin yield. The reactions of 2,4,6-tribenzyloxybenzaldehyde and 2,4,6-trimethoxybenzaldehyde gave yields of 15% and 11%, respectively, illustrating the absence of adverse steric effects caused by the benzyloxy groups in the reaction. The porphyrins with fluorinated benzyloxy groups (**16, 21**) are formed in 2.5-3-times higher yields than their non-fluorinated counterparts (**12, 20**), but the mechanistic origins of the yield differential are not clear.

The generally good yields obtained for all 2,6-bis(benzyloxy)benzaldehydes illustrate the attractive features of the $-OCH_2-$ linker. The $-OCH_2-$ unit is compatible with the porphyrin-forming reaction and enables a variety of groups to be incorporated over the face of the porphyrin, with synthetic yields comparable to those obtained with *o*-methoxy groups.

Porphyrin Spectral Features

The absorption and fluorescence spectra of the benzyloxy-porphyrins closely resemble those of tetraphenylporphyrin (TPP). The absorption spectra of the *ortho*-substituted octakis and dodecakis (benzyloxy)porphyrins exhibit slightly broadened Soret bands (12.5 nm fwhm) and phyllo patterns in the visible region. The fluorescence quantum yields of the porphyrins in CH_2Cl_2 at room temperature were generally within a factor of two of that of TPP.[28] Thus the eight *ortho*-benzyloxy groups hardly perturb the intrinsic spectral properties of the porphyrin.

During the syntheses we noticed that the porphyrins with electron-rich methoxy or benzyloxy groups in the 2,6 or 2,4,6- positions (**12, 13, 15, 20, 22,** but not **14, 16-19,** or **21**) have enhanced affinity for acid compared with TPP, tetramesitylporphyrin (TMP), or *meso*-tetrakis(2-methoxyphenyl)porphyrin. The absorption spectra of TPP, TMP, and **12** were measured in the presence of trifluoroacetic acid (TFA) for comparison with the literature standard, TPP in $CHCl_3$ acidified with gaseous HCl (Table 2).

Table 2. Spectral properties of porphyrins in neutral and acidic media.

		Free base porphyrin		Diprotonated Porphyrin		
Porphyrin		Soret	Acid medium	Soret	II	I
TPP	λ (nm)	419	HCl, $CHCl_3$[a]	445	608	661
	ε ($M^{-1}cm^{-1}$)	478,000		431,000	9,000	50,900
	λ	417	TFA, CH_2Cl_2	437	600-615	656
	ε	478,000[b]		430,000	10,600	47,500
	fwhm (nm)	11.4		17.5		
TMP	λ	418	TFA, CH_2Cl_2	434	580	630
	ε	427,000[c]		272,000	10,600	19,300
	fwhm	10.1		20.6		
12	λ	420	TFA, CH_2Cl_2	441	579	632
	ε	316,000		131,000	8,300	11,500
	fwhm	12.5		41		

[a]Literature data in $CHCl_3$ acidified with gaseous HCl.[29] [b]From ref. 29 (in $CHCl_3$). [c]From ref. 8.

TPP exhibits a broad intense band at 660 nm whereas the *ortho*-disubstituted TMP and **12** show two weaker bands at ~580 (band II) and 630 nm (band I). The bathochromic shift of diprotonated TPP relative to natural (*meso*-unsubstituted) porphyrins has been attributed to the increased resonance of the phenyl and porphyrin rings that accompanies rotation of the phenyl rings toward coplanarity with the porphyrin nucleus.[29] The spectra of acidified TMP and **12** are consistent with this interpretation, as the *ortho*-disubstituted phenyl groups are unable to achieve coplanarity. The distinctive spectral features of **12** are a consequence of *ortho*-disubstitution at all sites but the enhanced affinity for acid is due to the electron-rich 2,6-bis(benzyloxy) groups.

Chemical Stability

The benzyloxy groups examined are stable to the mild acid and oxidative conditions (DDQ) of the porphyrin-forming reaction. Because benzyloxy groups are labile to strong acid and to strong oxidants,[30] we performed two experiments to assess the stability of various octakis(benzyloxy)porphyrins. The parent octakis(benzyloxy)porphyrin (**12**) decomposed upon exposure to 50% trifluoroacetic acid in CH_2Cl_2 for 1 h at room temperature, but the octakis(perfluorobenzyloxy)porphyrin (**16**) was recovered intact upon identical treatment. The zinc chelate of **12** (**Zn-12**) could be reversibly oxidized without decomposition, indicating the stability of the benzyloxy group to the formation of the zinc-porphyrin radical cation.

Physical Properties

The relative rates of metalation were examined by parallel experiments with TPP and the parent octakis(benzyloxy)porphyrin (**12**). 1.5 equiv $Zn(OAc)_2$ was added to each of the porphyrin solutions in $CHCl_3$/methanol (9:1) and zinc insertion was monitored spectroscopically. The $t_{1/2}$ points for metalation of TPP and **12** were 4 and 21 min, respectively, indicating the benzyloxy groups slow the metalation by about 5-fold. The NMR spectra indicate the *ortho*-benzyloxy groups in all the porphyrins experience an averaged magnetic environment and thus are freely rotating. The slower metalation of **12** is opposite to the accelerated metalation observed in a bis-picket fence porphyrin, which has been attributed to hydrogen-bonding by the *ortho*-amines.[12]

The porphyrin with eight *para*-bromobenzyloxy groups (**14**) provided a convenient probe of the conformation of the benzyl groups. The fluorescence spectrum and yield of **14** were essentially identical to the corresponding methoxy-porphyrins without bromo-substituents, indicating the absence of an external heavy atom quenching due to the eight *para*-bromo groups. Though external heavy-atom perturbations[31] are sluggish reactions (the fluorescence yield of TPP decreased only 17% in the presence of 1 M bromobenzene in CH_2Cl_2 at room temperature),[32] it seems unlikely that the bromobenzyloxy group could rest on the porphyrin macrocycle without quenching the porphyrin fluorescence. A reasonable interpretation is that the benzyloxy groups are conformationally mobile in a generally upright orientation.

Solid-state Structure

All of the porphyrins exhibited high solubility in CH_2Cl_2 and $CHCl_3$ (~0.1 M) but were essentially insoluble in hexane or methanol. Crystals of **12** were obtained by slow evaporation over two weeks from a $CHCl_3$/methanol solution. The crystals were hexagonal needles up to 2.5 cm in length. However, the X-ray data for these crystals fell off rapidly with scattering angle and the structure has not been solved.

Crystals of **16** were obtained by similar procedures. The molecular structure of **16** is shown in Figure 2 along with the atom labeling scheme. A brief summary of structural parameters is given in Table 3.

The pentafluorobenzyloxy substituents on the *meso*-aryl groups provide a substantial "protecting cover" over the two faces of the porphyrin ring (Figure 2). Interestingly, this facial encumbrance also provides a large cavity above the center of each face. The cavity has an approximate cylindrical shape with a diameter of ~7.5 Å and a height of ≥ 4.5 Å. The cavity is deeper and substantially more protected than that observed with *ortho*-methoxy groups.[15] The zinc incorporation rates suggest that the movement of the walls of this cavity must be reasonably facile, but it seems probable that the cavity must remain.

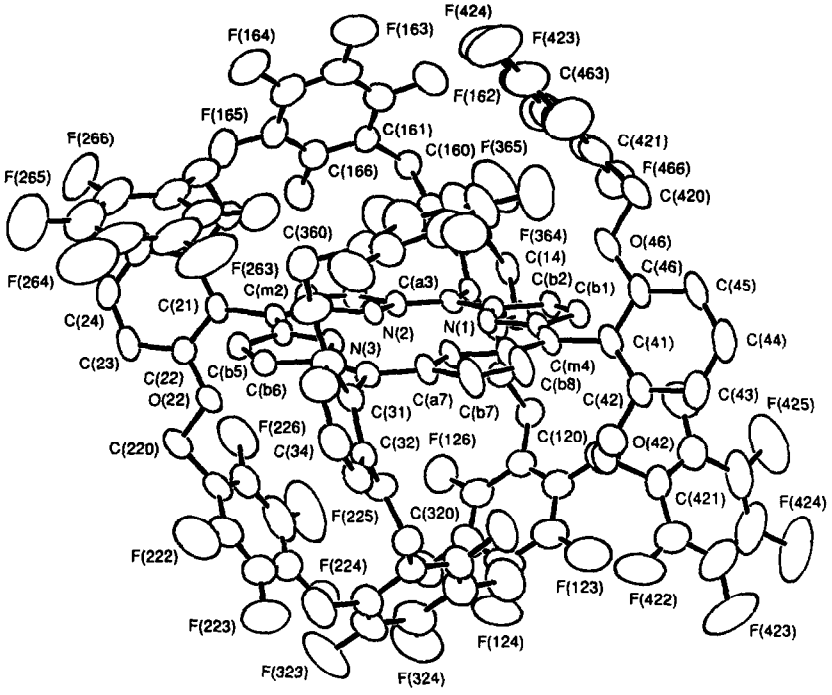


Figure 2. ORTEP diagram of **16**. Thermal ellipsoids are drawn at the 50% probability level. Porphyrin hydrogen atoms are omitted for clarity.

Table 3. Crystallographic data and data collection parameters for porphyrin **16**·2CHCl$_3$.

Formula	$C_{102}H_{40}Cl_6F_{40}N_4O_8$
FW, amu	2422.08
a, Å	14.7587 (12)
b, Å	25.519 (2)
c, Å	13.1004 (7)
α, deg	100.045 (6)
β, deg	99.834 (8)
γ, deg	83.253 (6)
V, Å^3	4767.3 (6)
Space group	P $\bar{1}$
Crystal system	triclinic
Z	2
μ, mm^{-1}	0.322
Temp, K	127 (2)
Final R indices [I>2s(I)]	R_1 = 0.097, wR_2 = 0.212
R indices (all data)	R_1 = 0.166, wR_2 = 0.275
Goodness-of-fit on F^2	1.04

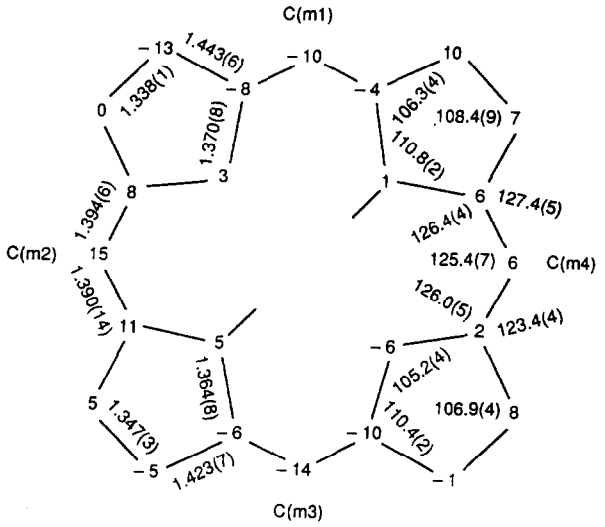


Figure 3. Formal diagram of the porphinato core in **16** displaying the perpendicular displacement of each unique atom from the 24-atom mean plane. All displacements are given in units of 0.01 Å. Also shown are the averaged values of all bond distances and angles of the core, which have been averaged in accord with the two-fold symmetry of the molecule. Transannular distances are $N_H \cdots N_H$ = 4.199 Å and N··N = 3.998 Å.

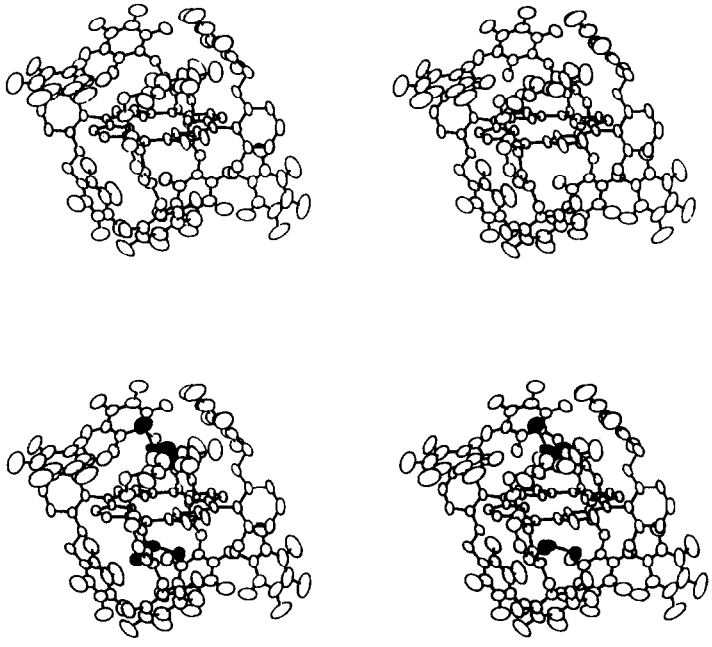


Figure 4. Stereoscopic diagrams of **16** illustrating the cavity formed by the pentafluorobenzyloxy substituents. In the top drawing, the chloroform solvate molecules are absent while they are included in the bottom drawing, where they are shown as filled black ellipsoids.

Figure 3 shows the displacements, in units of 0.01 Å, of the porphyrin core atoms from the 24-atom mean plane for **16**. The porphyrin core displays a modest amount of nonplanarity (an idealized S_4-ruffling) which is presumably the consequence of the very bulky *ortho*-substituents. The two inner hydrogen atoms of the free base porphyrin appear well-ordered. Such ordering of the inner hydrogen atoms is not always observed in free base porphyrin structures.[33] Figure 3 also shows the averaged bond distances in the two types of five-membered rings of the free base. The pattern of distances and angles in the two ring types is similar to that observed in other free-base porphyrins.[34]

In the present crystal structure, each of the cavities formed by the four protruding pentafluorobenzyloxy groups contains a $CHCl_3$ solvate molecule. These solvent packing arrangements are shown in Figure 4 which presents stereoviews of the porphyrin molecule with and without the two $CHCl_3$ solvate molecules. Finally, the porphyrin macrocycles are indeed well-separated in the solid state. Close contacts to the edges of the porphyrin rings (C_β atoms) primarily occur with the fluorine atoms on the pentafluorobenzyloxy substituents.

CONCLUSION

The ability to convert a wide variety of benzyloxybenzaldehydes to the corresponding porphyrins, without significant steric hindrance, provides access to a tailor-made family of facially-encumbered porphyrins. The *ortho* -OCH_2- unit provides compatibility with the porphyrin-forming reaction and enables the porphyrin faces to be covered with a variety of bulky groups. Interestingly, *meso*-tetrakis(*o*-hydroxyphenyl)porphyrin was examined in the earliest quest for picket fence porphyrins, but was abandoned because the reaction conditions for derivatizing the hydroxy groups led to porphyrin atropisomerization.[35] The symmetric placement of hydroxy groups in both *ortho*-positions circumvents isomerization difficulties, and prefunctionalizing the phenolic aldehyde sidesteps problems of derivatizing multiple *ortho*-phenoxy groups on the porphyrin. In effect, the symmetric coverage of both faces of the porphyrin is a less difficult design problem than coverage of only one. The crystal structure of **16** shows the porphyrin macrocyle embedded in a protective cover. This approach toward light-harvesting systems is complementary to the synthesis of covalent arrays of porphyrins and to the cocrystallization of porphyrins with small organic guests, and enables organized arrangement of a large number of porphyrins at close distances with limited direct contact of the porphyrin macrocycles.

EXPERIMENTAL

General. Preparative centrifugal TLC was performed with a Harrison Research Chromatotron Model 7924T. Column chromatography was performed on silica (Merck, 70 - 230 mesh). Flash chromatography was performed on Baker flash silica. Pyrrole was distilled at atmospheric pressure. All reagents were obtained from Aldrich unless noted otherwise. All the reported elemental analyses (Oneida Research Services, Inc., Whitesboro, NY) were within the accepted ± 0.4% limit for C, H, N. Porphyrin mass spectra were determined by plasma desorption mass spectrometry.[36] Absorption and emission spectra were collected in CH_2Cl_2/ethanol (3:1) unless stated otherwise. Fluorescence quantum yields (Spex Fluoromax) were determined by ratioing the total integrated corrected emissions obtained in CH_2Cl_2 at room temperature with that of TPP ($\Phi_f = 0.11$).[21]

Solvents. CH_2Cl_2 (Fisher, reagent grade) and $CHCl_3$ (Fisher certified A.C.S.) were subjected to simple distillation from K_2CO_3. The commercially-available $CHCl_3$ contained ethanol (0.75%) as a stabilizer. All references to $CHCl_3$ in this paper pertain to $CHCl_3$ containing 0.75% ethanol. We have previously shown that simple distillation does not significantly alter the ethanol content.[8] CS_2 (Aldrich, HPLC grade) and anhydrous DMF (Aldrich) were used as received. THF (Fisher certified A.C.S.) was distilled from $LiAlH_4$.

Acid Catalysts. Stock solutions of BF_3·$O(Et)_2$ were prepared by diluting BF_3·$O(Et)_2$ (Aldrich, 8.1 M) to 2.5 M in $CHCl_3$. Stock solutions remained viable for at least two weeks. Trifluoroacetic acid was used as obtained from Aldrich.

Reaction monitoring. Reactions were monitored following the procedures outlined previously.[8,37] A 25 μL aliquot of the condensation solution was removed via syringe and injected into 150 μL of a 10^{-2} M solution of DDQ in toluene. After about 10-20 seconds with occasional agitation a 50 μL aliquot of this oxidized solution was diluted into 3 mL CH_2Cl_2/ethanol (3/1) in a cuvette. The sharp Soret band enables the yield to be determined directly after correcting for the rather broad absorption of the non-porphyrin components. With most porphyrins CH_2Cl_2/ethanol (3/1) is adequate to buffer the residual acid catalyst in porphyrin-forming reactions. Some of the benzyloxy-porphyrins have high affinity for acid and are not completely neutralized upon dilution into CH_2Cl_2/ethanol (3/1). Simulation of the reaction monitoring conditions by addition of 7 μL of 3.3 mM $BF_3{\cdot}O(Et)_2$ to **12** in 3 mL CH_2Cl_2/ethanol (3/1) gave the Soret band diminished ~2-fold (ε = 166,000 $M^{-1}cm^{-1}$) and broadened (fwhm 28.7 nm) but only shifted 7 nm (λ_{max} 427 nm) compared with a 20 nm shift with tetraphenylporphyrin (TPP). The absence of a significant red-shift under the reaction monitoring conditions could easily lead to artefactually low yield values during reaction-monitoring. Neutralization with triethylamine (10 μL, or a few drops) regenerates the Soret band typical of neutral porphyrins.

Porphyrin Cation Radical. The zinc chelate of **12** (**Zn-12**) (5 mg, 3.27 μmol) was dissolved in 5 mL CH_3CN and treated with $Fe(ClO_4)_3{\cdot}6H_2O$ (3 mg, 6.55 μmol), yielding a green solution. After 30 min 10 μL of triethylamine was added and the Soret band was restored to 96% of its original magnitude. Subsequent TLC analysis (silica, CH_2Cl_2) revealed one major and one minor porphyrin component. The leading component co-chromatographed with authentic **Zn-12** and was estimated to comprise 95% of the porphyrin components on TLC. The radical cation was also generated on the analytical scale in a cuvette by addition of 20 μL of 1 mM $Fe(ClO_4)_3$ in CH_3CN. The radical cation of **Zn-12** exhibited a peak at 413 nm in CH_3CN with intensity 0.31 times that of the Soret of the neutral **Zn-12** (λ_{max} 424.5 nm in CH_3CN), which compares well with the properties of the radical cation of ZnTPP (λ_{max} 409 nm, ε_{409} = 190,000 $M^{-1}cm^{-1}$).[38]

Structure Determination. A black crystal of **16** was examined on an Enraf-Nonlus FAST area detector diffractometer at 127 K with graphite monochromated MoKa radiation. Unit cell determination and data collection procedures with the area detector have been described elsewhere.[39] A brief summary of parameters is given in Table 3. A total of 30330 reflections were collected of which 17761 were unique and the intensities of 10020 unique reflections were greater than 2.0σ(I). The structure was solved by direct methods with the MITHRIL program,[40] but overall temperature and scale factors were taken from a normalization procedure in MULTAN.[40] More than 60% of the non-hydrogen atoms were found. The remaining atoms were found in several difference Fourier maps (FORDAP).[40] For one perfluorophenyl ring, very large temperature factors were observed and suggest a disorder problem. Careful study of the Fourier maps led to finding two orientations, both of which were refined without any constraints. All non-hydrogen atoms of the structure were refined anisotropically with the use of the SHELXL-93 program.[40] Hydrogen atoms were included as fixed, idealized contributors; those connected to the pyrrole nitrogens were clearly seen in a difference Fourier map but all others were idealized. The two occupancies of the disordered ring were refined to final values of 61 and 39%. The refinement converged to a value of R_1 = 0.097 and wR_2 = 0.212 for observed unique reflections ($I \geq 2.0\sigma(I)$) and R_1 = 0.166 and wR_2 = 0.275 for all unique reflections including also negative intensities (the weighted R-index is based on F^2).

2,6-Dihydroxybenzaldehyde (1): Following the procedure of Adams,[41] a solution of 2,6-dimethoxybenzaldehyde (5.5 g, 33 mmol) in 500 mL CS_2 was placed in a 2 liter three-neck round bottom flask equipped with a mechanical stirrer. $AlBr_3$ (100 mL of 1 M solution in CH_2Br_2, 100 mmol, 3 equiv) was added at room temperature and stirring was continued under nitrogen for 1 h during which the product precipitated as a red gum. The CS_2 was decanted from the red gum into a separatory funnel for subsequent extraction. Crushed ice, 180 mL 3 N HCl, and 240 mL ether were added to the reaction mixture. The CS_2 was extracted with 60

mL 3 N HCl and the acidic aqueous layer was added to the reaction flask. The reaction mixture was stirred until the addition complex had dissolved (1-2 h). Then the layers were separated and the aqueous layer was extracted with ether (2 x 240 mL). The ether extracts were combined and extracted with 1 N NaOH (3 x 60 mL). The basic extracts were combined and cooled in an ice water bath, followed by the dropwise addition of 18 mL conc HCl. The crude brown product was collected by vacuum filtration, washed with H_2O (2 x 25 mL), and purified by flash chromatography (silica, CH_2Cl_2/ethyl acetate 19:1, 3 runs, 2.5 x 13 cm), yielding 2.45 g (54% yield) of a light yellow powder. mp 157-158 °C; ^1H NMR (DMSO-d_6) δ 6.36 (d, 2 H, J = 8.1 Hz, ArH), 7.36 (t, 1 H, J = 8.1 Hz, ArH), 10.24 (s, 1 H, CHO), 11.27 (s, 2 H, OH); Anal. ($C_7H_6O_3$) C, H.

2,6-Dibenzyloxybenzaldehyde (2). General K_2CO_3 method: A sample of 2,6-dihydroxybenzaldehyde (829 mg, 6 mmol) was dissolved in 20 mL DMF at room temperature. K_2CO_3 (4.97 g, 36 mmol; dried in vacuo at 140 °C overnight) and benzyl bromide (1.57 mL, 13.2 mmol) were added and the red reaction mixture was placed in an oil bath at 80 °C. Vigorous stirring for 1 h yielded a yellow mixture, which was cooled to room temperature, 50 mL H_2O was added, and the aqueous layer was extracted with ethyl acetate (3 x 25 mL). The combined extracts were washed with 50 mL brine, dried (Na_2SO_4), and rotary evaporated to an oil. Flash chromatography (silica gel, CH_2Cl_2) yielded fifteen 30 mL fractions. Fractions 8-12 contained the product, and these were concentrated to give 1.09 g of a white solid (57% yield). Attempts to purify the product by recrystallization gave lesser purity than flash chromatography. mp 76-77 °C (lit. mp 76-77 °C);[24] ^1H NMR ($CDCl_3$) δ 5.18 (s, 4 H, OCH_2), 6.62 (d, 2 H, J = 8.7 Hz, ArH), 7.48-7.29 (m, 11 H, PhH, ArH), 10.66 (s, 1 H, CHO); Anal. ($C_{21}H_{18}O_3$) C, H.

Methyl 2,6-dibenzyloxybenzoate (3): 30 mmol (5.04 g) of methyl 2,6-dihydroxybenzoate[42] and 66 mmol of benzyl bromide were reacted using the K_2CO_3 method, affording 5.33 g (61% yield) of a white solid following flash chromatography (silica, CH_2Cl_2). mp 72-73 °C (lit bp 242-246 °C/0.5 mm);[43] ^1H NMR ($CDCl_3$) δ 3.90 (s, 3 H, CH_3), 5.12 (s, 4 H, OCH_2), 6.58 (d, 2 H, J = 8.4 Hz, ArH), 7.20 (t, 1 H, J = 8.4 Hz, ArH), 7.40-7.25 (m, 10 H, PhH); Anal. ($C_{22}H_{20}O_4$) C, H. **3** can also be prepared by benzylation of methyl 2,6-dihydroxybenzoate.[24]

Conversion of **3** to **2**: A sample of 5.33 g **3** (15.3 mmol) was dissolved in 43 mL toluene in a dry 200 mL three neck round bottom flask. Diisobutylaluminum hydride (DIBAL-H) (23 mL of 1.5 M solution in toluene) was added slowly under nitrogen via syringe. Then the reaction vessel was placed in an oil bath at 45 °C. After 1 h the adduct was decomposed at 0 °C by the addition of 100 mL methanol and 100 mL H_2O. After stirring for 10 min the white gelatinous mixture was filtered through Celite 545 (Fisher). The filtrate was extracted with ethyl acetate (2 x 150 mL). The combined extracts were washed with 150 mL brine, dried (Na_2SO_4), and rotary evaporated to an oil. Drying in vacuo gave 3.48 g 2,6-dibenzyloxybenzyl alcohol as a white oily solid (71% yield). ^1H NMR ($CDCl_3$) δ 2.57 (t, 1 H, J = 6.9 Hz, OH), 4.89 (d, 2 H, J = 6.6 Hz, CH_2), 5.10 (s, 4 H, OCH_2), 6.63 (d, 2 H, J = 8.4 Hz, ArH), 7.18 (t, 1 H, J = 8.4 Hz, ArH), 7.44-7.32 (m, 10 H, PhH); Anal. ($C_{21}H_{20}O_3$) C, H. (Note: Attempts to reduce **3** with DIBAL-H at -78 °C failed to give direct conversion to the aldehyde.) A solution of 3.36 g 2,6-dibenzyloxybenzylalcohol (10.5 mmol) in 40 mL CH_2Cl_2 was oxidized at room temperature by addition in one portion of 4.53 g pyridinium chlorochromate (21 mmol). After stirring for 1 h, 50 mL diethyl ether was added and the mixture was decanted. The remaining black precipitate was washed with four 100 mL portions of diethyl ether. The organic fractions were combined and vacuum filtered through Florisil (12 x 2.5 cm) in a Buchner funnel. The light-yellow filtrate was concentrated to give 2.87 g yellow crystals (86% yield). Recrystallization from diethyl ether afforded **2** as white crystals.

2,6-Bis(4-bromobenzyloxy)benzaldehyde (4): 6 mmol of **1** and 13.2 mmol 4-bromobenzyl bromide were reacted using the K_2CO_3 method. Flash chromatography (silica, CH_2Cl_2) afforded 2.12 g (74% yield).

mp 142-143 °C; ^{1}H NMR ($CDCl_3$) δ 5.13 (s, 4 H), 6.61 (d, 2 H, J = 8.7 Hz), 7.42, 7.34 (m, 5 H), 7.52 (AA'BB', 4 H), 10.62 (s, 1 H); Anal. ($C_{21}H_{16}Br_2O_3$) C, H.

2,6-Bis(4-methylbenzyloxy)benzaldehyde (5): 6 mmol of **1** and 13.2 mmol α-bromo-*p*-xylene were reacted using the K_2CO_3 method. Flash chromatography (silica gel, CH_2Cl_2) afforded 1.25 g (60% yield). mp 120-121 °C; ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 6 H, CH_3), 5.14 (s, 4 H, CH_2), 6.61 (d, 2 H, J = 8.7 Hz, *m*-ArH), 7.19 (AA'BB', 4 H, ArH), 7.36, 7.33 (m, 5 H, ArH), 10.62 (s, 1 H, CHO); Anal. ($C_{23}H_{22}O_3$) C, H.

2,6-Bis(2,3,4,5,6-pentafluorobenzyloxy)benzaldehyde (6): 6 mmol of **1** and 13.2 mmol α-bromo-2,3,4,5,6-pentafluorotoluene were reacted using the K_2CO_3 method. Flash chromatography (silica gel, CH_2Cl_2) afforded 1.92 g (64% yield) of an off-white solid: mp 125-126 °C; ^{1}H NMR ($CDCl_3$) δ 5.21 (s, 4 H, CH_2), 6.78 (d, 2 H, J = 8.4 Hz, *m*-ArH), 7.52 (t, 1 H, J = 8.4 Hz, *p*-ArH), 10.34 (s, 1 H, CHO); Anal. ($C_{21}H_8F_{10}O_3$) C, H.

2,6-Bis(4-methoxycarbonylbenzyloxy)benzaldehyde (7): 6 mmol of **1** and 24 mmol (5.5 g) methyl α-bromo-*p*-toluate were dissolved in 20 mL DMF, 2.79 g KF (48 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. Then 50 mL H_2O was added, the aqueous layer was extracted with ethyl acetate (3 x 30 mL), and the combined extracts were washed with 50 mL brine and dried (Na_2SO_4). Removal of the solvent via rotary evaporation gave a gummy yellow solid. Flash chromatography (silica gel, CH_2Cl_2) afforded 647 mg (25% yield) of an off-white solid. mp 208-209 °C; ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 6 H, CH_3), 5.24 (s, 4 H, CH_2), 6.61 (d, 2 H, J = 8.4 Hz, *m*-ArH), 7.39 (t, 1 H, J = 8.4 Hz, *p*-ArH), 7.55 (AA'BB', 4 H, ArH), 8.07 (AA'BB', 4 H, ArH), 10.68 (s, 1 H, CHO); Anal. ($C_{25}H_{22}O_7$) C, H.

3,5-Dibenzyloxybenzaldehyde (8): 6 mmol of 3,5-dihydroxybenzaldehyde and 13.2 mmol benzyl bromide were reacted using the K_2CO_3 method. Flash chromatography (silica gel, CH_2Cl_2) afforded 596 mg (31% yield) of white flakes. mp 72-73 °C; ^{1}H NMR ($CDCl_3$) δ 5.08 (s, 4 H, CH_2), 6.87 (t, 1 H, J = 2.1 Hz, *p*-ArH), 7.11 (d, 2 H, J = 2.1 Hz, *o*-ArH), 7.44, 7.34 (m, 10 H, ArH), 8.89 (s, 1 H, CHO); Anal. ($C_{21}H_{18}O_3$) C, H.

3,5-Bis(4-methoxycarbonylbenzyloxy)benzaldehyde (9): 6 mmol of 3,5-dihydroxybenzaldehyde and 24 mmol of methyl α-bromo-*p*-toluate were reacted using the K_2CO_3 method. Flash chromatography (silica gel, CH_2Cl_2/ethyl acetate 19:1) afforded 1.868 g (72% yield) of a white solid. mp 101-102 °C; ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 6 H, CH_3), 5.16 (s, 4 H, CH_2), 6.85 (t, 1 H, J = 2.2 Hz, *p*-ArH), 7.11 (d, 2 H, J = 2.2 Hz, *o*-ArH), 7.50 (AA'BB', 4 H, ArH), 8.07 (AA'BB', 4 H, ArH), 9.90 (s, 1 H, CHO); HRMS calcd for $C_{25}H_{22}O_7$ 434.1365, found 434.1362.

2,4,6-Tribenzyloxybenzaldehyde (10): Following the Mitsunobu reaction, a flame dried 50 mL three neck round bottom flask was charged with 500 mg 2,4,6-trihydroxybenzaldehyde (3.24 mmol), 3.824 g triphenylphosphine (14.58 mmol), 1.51 mL benzyl alcohol (14.58 mmol), and 10 mL THF. A solution of 2.30 mL diethyl azodicarboxylate (14.58 mmol) in 10 mL THF was added dropwise over 1 h. The reaction mixture turned red-orange and became warm during the addition. After 24 h the mixture was concentrated to a gum and triturated with cold diethyl ether. The mother liquor was separated from the precipitate by filtration. The filtrate was concentrated to a solid, and flash chromatography (silica gel, CH_2Cl_2/ethyl acetate 19:1) afforded 522 mg (38% yield) of a white solid. mp 131-132 °C; ^{1}H NMR ($CDCl_3$) δ 5.03 (s, 2 H, CH_2), 5.14 (s, 4 H, CH_2), 6.22 (s, 2 H, ArH), 7.50-7.31 (m, 15 H, ArH), 10.51 (s, 1 H, CHO); Anal. ($C_{28}H_{24}O_4$) C, H.

2,4,6-Tri(2,3,4,5,6-pentafluorobenzyloxy)benzaldehyde (11): 3.24 mmol of 2,4,6-trihydroxybenzaldehyde was reacted with pentafluorobenzyl alcohol according to the procedure for **10**. Flash

chromatography (silica gel, CH_2Cl_2) afforded 900 mg (40% yield). mp 92-93 °C; ^1H NMR ($CDCl_3$) δ 5.19 (s, 4 H, CH_2), 5.22 (s, 2 H, CH_2), 6.36 (s, 2 H, ArH), 10.20 (s, 1 H, CHO); Anal. ($C_{28}H_9F_{15}O_4$) C, H.

***meso*-Tetrakis(2,6-dibenzyloxyphenyl)porphyrin (12)**: Samples of 2,6-dibenzyloxybenzaldehyde (**2**, 1.592 g, 5 mmol, 10^{-2} M) and pyrrole (347 μL, 5 mmol, 10^{-2} M) were dissolved in 500 mL of $CHCl_3$ at room temperature, then $BF_3{\cdot}O(Et)_2$ (660 μL of 2.5 M solution, 3.3 mM) was added to initiate the condensation. After 1 h with stirring at room temperature, DDQ (851 mg, 3.75 mmol) was added. After a further 1 h at room temperature, 230 μL of triethylamine was added and the reaction mixture was concentrated to a damp powder. This residue was dissolved in a minimum amount of CH_2Cl_2 and placed on top of a silica column (silica 60, 70 - 230 mesh, 5 x 7 cm, CH_2Cl_2/petroleum ether 2:1). The porphyrin was eluted quickly with CH_2Cl_2. Five 75 mL fractions were collected, yielding 367 mg porphyrin (20% yield). ^1H NMR ($CDCl_3$) δ -2.22 (s, 2 H, NH), 4.89 (s, 16 H, CH_2), 6.64, 6.98 (m, 40 H, ArH), 6.97 (d, 8 H, J = 8.4 Hz, *m*-ArH) 7.56 (t, 4 H, J = 8.4 Hz, *p*-ArH), 8.85 (s, 8 H, β-pyrrole); $C_{100}H_{78}N_4O_8$ calcd avg mass 1463.7, obsd 1464.1; absorption and emission spectra (in $CHCl_3$), λ_{abs}(log ε) 420 (5.50, fwhm 10 nm), 514 (4.20), 546 (3.56), 590 (3.68), 644 nm (2.99); λ_{em} 648, 714 nm; $\phi_f = 0.073$.

The remaining porphyrins were prepared in the same fashion as **12**:

***meso*-Tetrakis(2,6-dimethoxyphenyl)porphyrin (13)**: A 100 mL reaction of 2,6-dimethoxybenzaldehyde (166 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 55 mg (26%) of porphyrin following chromatography (silica gel, CH_2Cl_2-ethyl acetate 19:1). ^1H NMR ($CDCl_3$) δ -2.50 (s, 2 H, NH), 3.49 (s, 24 H, OCH_3), 6.96 (d, 8 H, J = 8.4 Hz, ArH), 7.67 (t, 4 H, J = 8.4 Hz, ArH), 8.66 (s, 8 H, β-pyrrole); $C_{52}H_{46}N_4O_8$ calcd mass 854.3, obsd 854.4; λ_{abs} 418, 512, 544, 586, 642 nm; λ_{em} 644, 710 nm; $\phi_f = 0.076$. Porphyrin **13** has been prepared via the Adler method in yields of 7.1%[13] and 15%.[14]

***meso*-Tetrakis[2,6-bis(4-bromobenzyloxy)phenyl]porphyrin (14)**: A 175 mL reaction of **4** (833 mg, 1.75 mmol) and pyrrole (121 μL, 1.75 mmol) afforded 84.7 mg (9.3%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -2.27 (s, 2 H, NH), 4.86 (s, 16 H, CH_2), 6.50 (AA'BB', 16 H, ArH), 6.86 (AA'BB', 8 H, ArH), 6.94 (d, 16 H, J = 8.4 Hz, *m*-ArH), 7.57 (t, 4 H, J = 8.4 Hz, *p*-ArH), 8.77 (s, 8 H, β-pyrrole); $C_{100}H_{70}Br_8N_4O_8$ calcd avg mass 2094.9, obsd 2094.9; λ_{abs} 420, 514, 546, 590, 644 nm; λ_{em} 648, 714 nm; $\phi_f = 0.070$.

***meso*-Tetrakis[2,6-bis(4-methylbenzyloxy)phenyl]porphyrin (15)**: A 100 mL reaction of **5** (346 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 67 mg (17%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -2.26 (bs, 2 H, NH), 1.91 (s, 24 H, CH_3), 4.83 (s, 16 H, CH_2), 6.58 (AA'BB', 16 H, ArH), 6.79 (AA'BB', 16 H, ArH), 6.94 (d, 8 H, J = 8.4 Hz, *m*-ArH), 7.52 (t, 4 H, J = 8.4 Hz, *p*-ArH), 8.82 (s, 8 H, β-pyrrole); $C_{108}H_{94}N_4O_8$ calcd avg mass 1576.0, obsd 1575.7; λ_{abs} 420, 514, 548, 590, 644 nm; λ_{em} 650, 716 nm; $\phi_f = 0.081$.

***meso*-Tetrakis[2,6-bis(2,3,4,5,6-pentafluorobenzyloxy)phenyl]porphyrin (16)**: A 100 mL reaction of **6** (498 mg, 1.0 mmol) and pyrrole (1.0 mmol) afforded 285 mg (52%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -2.99 (s, 2 H, NH), 4.79 (s, 16 H, CH_2), 7.10 (d, 8 H, J = 8.4 Hz, *m*-ArH), 7.72 (t, 4 H, J = 8.4 Hz, *p*-ArH), 8.54 (s, 8 H, β-pyrrole); $C_{100}H_{38}F_{40}N_4O_8$ calcd avg mass 2183.4, obsd 2183.0; λ_{abs} 418, 512, 544, 588, 644 nm; λ_{em} 646, 712 nm; $\phi_f = 0.068$.

***meso*-Tetrakis[2,6-bis(4-methoxycarbonylbenzyloxy)phenyl]porphyrin (17)**: A 100 mL reaction of **7** (434 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 43 mg (11%) of porphyrin following chromatography (silica gel, CH_2Cl_2-ethyl acetate 19:1). ^1H NMR ($CDCl_3$) δ -2.16 (s, 2 H, NH), 3.65 (s, 24

H, CH_3), 4.96 (s, 16 H, CH_2), 6.81 (AA'BB', 16 H, ArH), 6.90 (d, 8 H, J = 8.4 Hz, *m*-ArH), 7.49 (AA'BB', 16 H, ArH), 7.54 (t, 4 H, J = 8.4 Hz, *p*-ArH), 8.89 (s, 8 H, β-pyrrole); $C_{116}H_{94}N_4O_{24}$ calcd avg mass 1928.0, obsd 1928.1; λ_{abs} 420, 514, 546, 590, 646 nm; λ_{em} 650, 715 nm; $\phi_f = 0.065$.

***meso*-Tetrakis[3,5-dibenzyloxyphenyl]porphyrin (18)**: A 100 mL reaction of **8** (318 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 151 mg (41%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -2.86 (s, 2 H, NH), 5.24 (s, 16 H, CH_2), 7.54, 7.34 (m, 52 H, ArH), 8.89 (s, 8 H, β-pyrrole); $C_{100}H_{78}N_4O_8$ calcd avg mass 1463.7, obsd 1463.6; λ_{abs} 422, 516, 550, 588, 644 nm; λ_{em} 650, 715 nm.

***meso*-Tetrakis[3,5-bis(4-methoxycarbonylbenzyloxy)phenyl]porphyrin (19)**: A 100 mL reaction of **9** (434 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 73 mg (15%) of porphyrin following chromatography (silica gel, CH_2Cl_2-ethyl acetate 19:1). ^1H NMR ($CDCl_3$) δ -2.90 (s, 2 H, NH), 3.90 (s, 24 H, CH_3), 5.30 (s, 16 H, CH_2), 7.06 (t, 4 H, J = 1.5 Hz, *p*-ArH), 7.48 (d, 8 H, J = 2.1 Hz, *o*-ArH), 7.57 (AA'BB', 16 H, ArH), 8.07 (AA'BB', 16 H, ArH), 8.83 (s, 8 H, β-pyrrole); $C_{116}H_{94}N_4O_{24}$ calcd avg mass 1928.0, obsd 1927.8; λ_{abs} 420, 516, 548, 590, 644 nm; λ_{em} 648, 714 nm.

***meso*-Tetrakis(2,4,6-tribenzyloxyphenyl)porphyrin (20)**: A 100 mL reaction of **10** (424 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 72 mg (15%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -2.36 (s, 2 H, NH), 4.84 (s, 16 H, CH_2), 5.18 (s, 8 H, CH_2), 6.62-6.73 (m, 38 H, ArH), 7.14-7.57 (m, 30 H, ArH), 8.89 (s, 8 H, β-pyrrole); $C_{128}H_{102}N_4O_{12}$ calcd avg mass 1888.2, obsd 1887.8; λ_{abs} 424, 516, 550, 592, 648 nm; λ_{em} 650, 717 nm; $\phi_f = 0.080$.

***meso*-Tetrakis[2,4,6-tri(2,3,4,5,6-pentafluorobenzyloxy)phenyl]porphyrin (21)**: A 100 mL reaction of **11** (694 mg, 1.0 mmol) and pyrrole (69 μL, 1.0 mmol) afforded 325 mg (44%) of porphyrin following chromatography (silica gel, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ -3.06 (s, 2 H, NH), 4.78 (s, 16 H, CH_2), 5.42 (s, 8 H, CH_2), 6.77 (s, 8 H, ArH), 8.56 (s, 8 H, β-pyrrole); $C_{128}H_{42}F_{60}N_4O_{12}$ calcd avg mass 2967.7, obsd 2968.1; λ_{abs} 420, 514, 546, 590, 644 nm; λ_{em} 648, 713 nm; $\phi_f = 0.080$.

***meso*-Tetrakis(2,4,6-trimethoxyphenyl)porphyrin (22)**: Prepared previously in 11% yield[8] and also by the Adler method.[15]

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