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Investigation of the One-Flask Synthesis of Porphyrins Bearing *Meso*-linked Straps of Variable Length, Rigidity, and Redox Activity

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Abstract: The reactions of 18 dialdehydes have been examined in the two-step one-flask room temperature porphyrin synthesis. Efficient alkylation methods were established for the reaction of diols and diacids with *m*-bromomethylbenzaldehyde. Dialdehydes linked at the o,o'- or m,m'-positions were converted to strapped porphyrins in yields up to 25%, while the one p,p'-linked dialdehyde that was examined failed to give porphyrin. The resulting porphyrins bear straps joining adjacent *meso*-positions rather than across the face of the porphyrin. Dialdehydes incorporating rigid groups provided improved yields in some but not all cases. The yield of strapped porphyrin exhibited a maximum at 10^{-2} M reactant concentrations. The o,o'-strapped porphyrins exist as atropisomers that are sufficiently stable to interconversion at room temperature to be separable chromatographically. No atropisomers of m,m'-strapped porphyrins could be separated, though some could be observed by ^{1}H NMR spectroscopy. For two different m,m'-strapped porphyrins, the $\Delta G^{\ddagger}$ values for interconversion of the atropisomers were found to be 66 and 68 kJ/mol. The outer rings in these strapped porphyrins range in size from 14 to 24 atoms. Five porphyrins with bridging redox-active groups (ferrocene or anthraquinone) have been prepared in one-flask reactions, including a porphyrin bearing one ferrocene and one anthraquinone in straps across adjacent meta-substituted phenyl sites.

The design of porphyrin-based bioorganic model systems is contingent on the prevailing synthetic routes for access to various molecular architectures. A general challenge has been how to achieve a 3-dimensional organization of the porphyrin and non-porphyrin entities such as substrate binding sites, receptors, cofactors, sensitizing agents, protective cavities, and/or ligands. One recurring theme has been to prepare porphyrins with molecular straps fashioned between aryl groups, which in turn are attached to the *meso*-sites of the porphyrin. The model system architectures (I[1], II[1], III[2], IV[3], V[4], VI[5], VII[6]) progress in complexity depending on the number of different straps and the molecular topology, and have inspired various terms as shown in Chart 1. "Basket-handle" porphyrins (I, II) and "capped" porphyrins (VI) have found widespread use as models of heme proteins and cytochromes, because the strap spanning the face of the porphyrin can be functionalized with a ligand that binds to the metal. In photosynthetic light-harvesting, photosynthetic charge separation, or respiration, porphyrinic pigments serve as components of chains funneling energy or electrons. Thus the design of photochemical model systems or electron transport chains requires integration of the porphyrin in a network of sensitizing agents or redox-active units. Our goal is to place straps at the periphery of the porphyrin and exploit these architectures in the design of model systems. In a sense, the heme and cytochrome model systems require porphyrins bearing convergent groups while the photosynthetic or electron-transport model systems require porphyrins bearing divergent groups.

The terminology employed in this area of porphyrin chemistry often has relied on the geometrical resemblance between a particular porphyrin architecture and a macroscopic object. To avoid this abstraction and the cultural specificity of some of the macroscopic objects, we will use the generic term "strapped porphyrin" to denote any porphyrin with one or more intramolecular straps or linkers joining different peripheral sites. This general terminology encompasses the architectures shown in Chart 1.

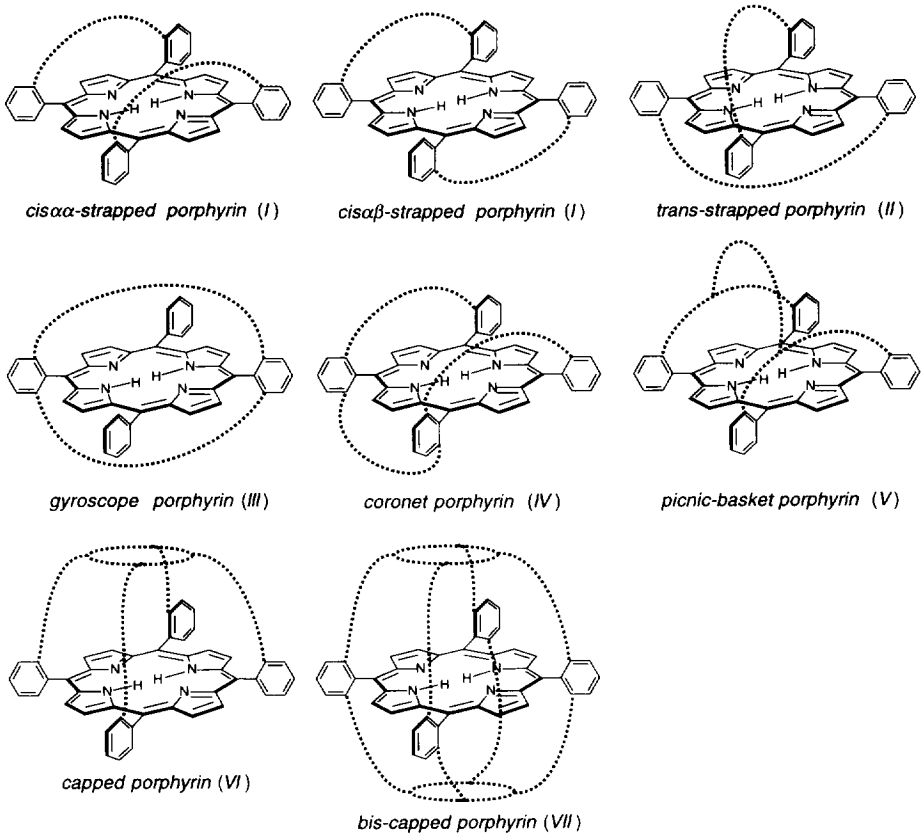
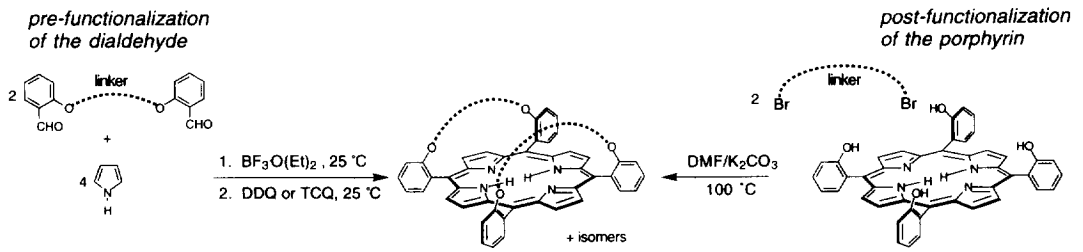


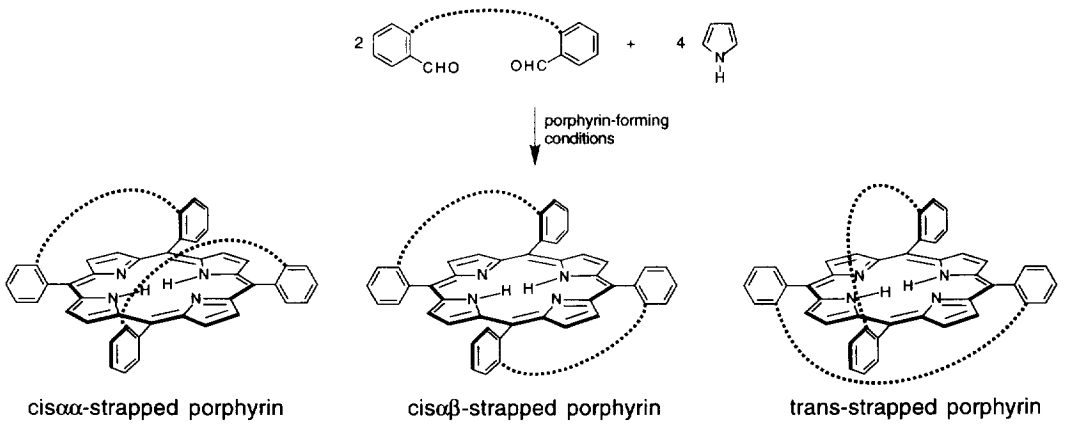
Chart 1. Porphyrins embedded in different macropolycyclic architectures.

The two prevailing routes for the synthesis of strapped tetraarylporphyrins have involved either the condensation of a dialdehyde with pyrrole, or the derivatization of functional groups on an existing porphyrin (Scheme 1). In the former route, the linker of the dialdehyde unit becomes the strap upon formation of the porphyrin, while in the latter route the reaction of a bifunctional alkylating agent with the porphyrin yields the strap.



Scheme 1. Distinct routes for the synthesis of strapped tetraarylporphyrins.

The direct synthesis of strapped porphyrins, developed by Momenteau et al.,[1] Weiser and Staab,[7] and Walker et al.,[8] has involved reaction of a dialdehyde (derived from salicylaldehyde) with pyrrole under Adler-Longo conditions. Three different architectures can be formed as shown in Scheme 2. The direct synthesis of strapped porphyrins as heme and cytochrome models has received little use because the desired porphyrin having straps across the faces (the trans-strapped porphyrin) is formed in low yield.[1,2,9-11] Consequently, most model systems using trans-strapped porphyrins have been prepared by functionalization of *meso*-tetrakis(2-hydroxyphenyl)porphyrin with a bifunctional alkylating agent.[9,12] More recently, the condensation of a dialdehyde with an unsubstituted dipyrromethane has been used to selectively prepare trans-strapped porphyrins.[13] Although the use of pre-functionalized dialdehydes to prepare porphyrin-based model systems has been demonstrated,[14-18] no detailed studies have been described concerning the dialdehyde and pyrrole condensations.



Scheme 2. Strapped porphyrin isomers. Cis refers to linkages at the 5,10- and 15,20-*meso*-positions, trans to linkages at the 5,15- and 10,20-*meso*-positions, and α and β to the faces of the porphyrin. Alternative names for the isomers have been employed.[1]

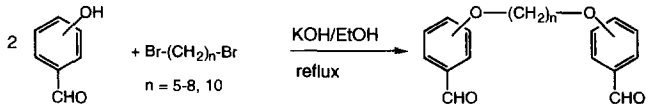
We investigated the synthesis of strapped porphyrins with two objectives. First, we wanted to understand how porphyrinogen self-assembly might vary with dialdehydes in contrast to mono-aldehydes.[19] Second, we sought to exploit the formation of strapped porphyrins as a means of creating well defined 3-dimensional architectures with redox groups situated at the periphery of the porphyrin macrocycle. In this paper we report a detailed study of the reactions of 18 dialdehydes with pyrrole in the room temperature synthesis of *meso*-substituted porphyrins. The effects of strap length have been surveyed in the reactions of o,o′-linked dialdehydes, strap length and rigidity have been surveyed in the reactions of m,m′-linked dialdehydes, and several porphyrins have been prepared that incorporate redox-active groups (ferrocene, anthraquinone) in the straps. In addition, ^{1}H NMR spectroscopy has been used to investigate the conformations of various strapped porphyrins. Preliminary accounts of this work have been published.[14,20,21] This work establishes the foundation for the use of pre-functionalized dialdehydes in the direct synthesis of a variety of strapped porphyrins.

RESULTS

Synthesis of Dialdehydes

A building block approach for creating straps derived from diols, bis-phenols, and dicarboxylic acids requires efficient reactions with benzaldehydes that can function as alkylating agents. Many alkylation methods employ the alkylating agent in large excess. We sought methods that employ stoichiometric quantities of aldehyde and linker, afford good yields of bis-alkylated product under mild reaction conditions, and can be readily scaled-up to multigram quantities.

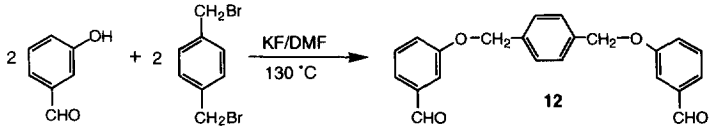
The KOH/ethanol method[8,9] was used to prepare alkoxy-linked dialdehydes as shown in Scheme 3. The alkoxy dialdehydes were recrystallized 2-3 times from ethanol to ensure high purity, with final yields in the range of 40-77%.



n	o,o′-dialdehyde	m,m′-dialdehyde	p,p′-dialdehyde
5	**1**	**6**	
6	**2**	**7**	
7	**3**	**8**	
8	**4**	**9**	
10	**5**	**10**	
12			**11**

Scheme 3. Synthesis of alkoxy-linked dialdehydes.

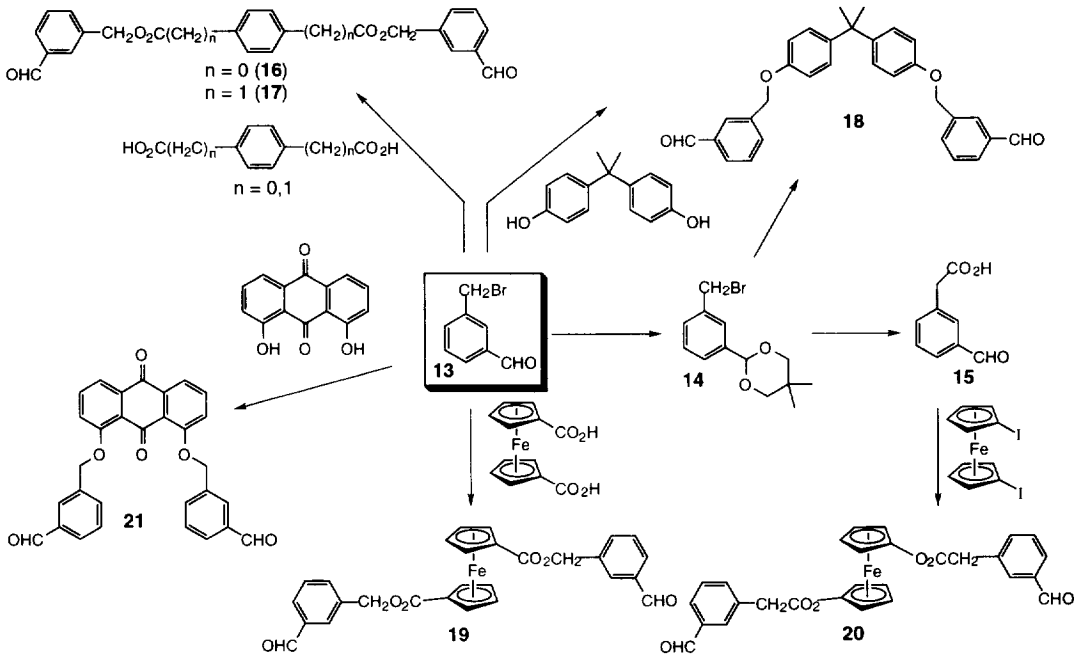
Similarly, reaction of 3-hydroxybenzaldehyde with α,α′-dibromo-*p*-xylene afforded the ether-linked dialdehyde **12** (Scheme 4).



Scheme 4. Synthesis of a dialdehyde bearing a rigid linker.

Treatment of α-bromo-*m*-tolunitrile with diisobutylaluminum hydride gave 3-(bromomethyl)-benzaldehyde **13**, which could be used directly or as the protected acetal **14**. Treatment of the acetal with NaCN[22] followed by base hydrolysis[23] gave *m*-formylphenylacetic acid (**15**). These compounds provided excellent building blocks for introducing straps at the meta-positions, as shown in Scheme 5. Several alkylation methods were examined for reaction of **13** with various linking units, including KOH/ethanol,[8,9] NaH/DMF, K_2CO_3/DMF,[4] KF/DMF,[24] and DBU/CH_3CN.[25] For terephthalic acid and 1,4-phenylenediacetic acid, ethanol was unsuited as a solvent, and the K_2CO_3/DMF method gave multiple products. However, reaction using KF in DMF at 130 °C for 1 h afforded the dialdehydes **16** and **17** in good yield. Ethanol also was an unsuitable solvent for alkylation of bisphenol A (4,4′-isopropylidenediphenol). Treatment of bisphenol A with NaH in DMF followed by reaction with **13** at 70 °C overnight resulted in multiple products, but the same conditions with acetal **14** gave **18** in 97% yield following acetal hydrolysis. Reaction of bisphenol A and **13** with K_2CO_3

at room temperature in DMF for 48 h gave **18** in 69% yield. The reaction of 1,8-dihydroxyanthraquinone with **13** via the K_2CO_3/DMF method at 80 °C for 8 h yielded the anthraquinone dialdehyde **21** in 86% yield. The reaction of 1,1′-ferrocenedicarboxylic acid with **13** in the presence of DBU at room temperature gave **19** in 48-66% yield. Ferrocene dialdehyde **20**, an isomer of **19**, was prepared by reaction of **15** with 1,1′-diiodoferrocene in the presence of Cu_2O.[26] Attempts to prepare ferrocene dialdehydes derived from 1,1′-bis(hydroxymethyl)ferrocene were abandoned due to their lability in the synthesis of ferrocenophanes.[27]



Scheme 5. Synthesis of m,m′-linked dialdehydes from the building block 3-(bromomethyl)benzaldehyde **13**.

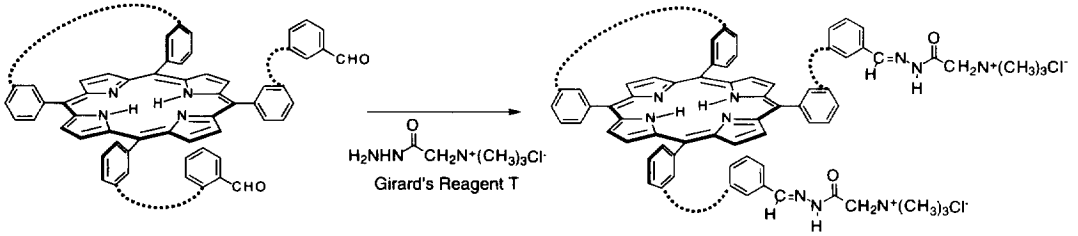
Condensations of dialdehydes with pyrrole

We performed a variety of studies of the condensation of dialdehydes and pyrrole in the two-step room temperature porphyrin synthesis. The distribution of porphyrin species was quantitated in the following manner:

1) Condensations were performed with equimolar (10 mM) pyrrole and aldehyde (5 mM dialdehyde; [CHO] = 10 mM) at room temperature. Several catalytic conditions known to give good results with mono-aldehydes were explored, including 3.3 mM $BF_3{\cdot}O(Et)_2$ in $CHCl_3$ (BF_3-ethanol cocatalysis) for o,o′-linked dialdehydes, 10 mM TFA in CH_2Cl_2 for all aldehydes, and 1.0 mM $BF_3{\cdot}O(Et)_2$ in CH_2Cl_2 for the m,m′- or p,p′-linked dialdehydes.[28,29]

2) The reaction mixture was treated with the oxidant DDQ or TCQ, neutralized with triethylamine, then examined by TLC in order to identify the number of porphyrin components. The dialdehyde-pyrrole reaction can yield porphyrins having zero or no straps; one example of such a porphyrin is shown in Scheme 6. In order to distinguish porphyrins bearing formyl groups from the intact strapped porphyrins, analytical samples from mixtures containing more than one porphyrin were treated with Girard's Reagent T (GT),[30] and re-examined by

TLC. Girard's Reagent T converts free formyl groups to polar semicarbazones that bind tightly on silica TLC, allowing their easy identification (Scheme 6).



Scheme 6. Reaction of a porphyrin bearing free formyl groups with Girard's Reagent T (GT).

3) The product mixture was carefully purified by column chromatography (silica, CH_2Cl_2) in order to retrieve all porphyrin components from unreacted starting material, quinone components, and polypyrromethenes. To avoid loss of any components during workup, chromatography columns were checked for complete elution by examination for porphyrin fluorescence under long wavelength UV illumination. Mixtures containing porphyrins with free formyl groups (identified analytically as GT-active porphyrins) were separated by centrifugal thin layer chromatography (CTLC) prior to determination of the isolated yield of all intact strapped porphyrins.

4) The isolated product, which generally consisted exclusively of the cis-strapped porphyrin(s), was examined by ^{1}H NMR spectroscopy for the existence of any trans-strapped porphyrins. The diagnostic test for the presence of trans-strapped porphyrins is the existence of ^{1}H NMR signals upfield from tetramethylsilane, which result from shielding of the protons in the strap by the porphyrin ring current.[8,9]

5) Further characterization was performed by absorption spectroscopy and mass spectrometry.

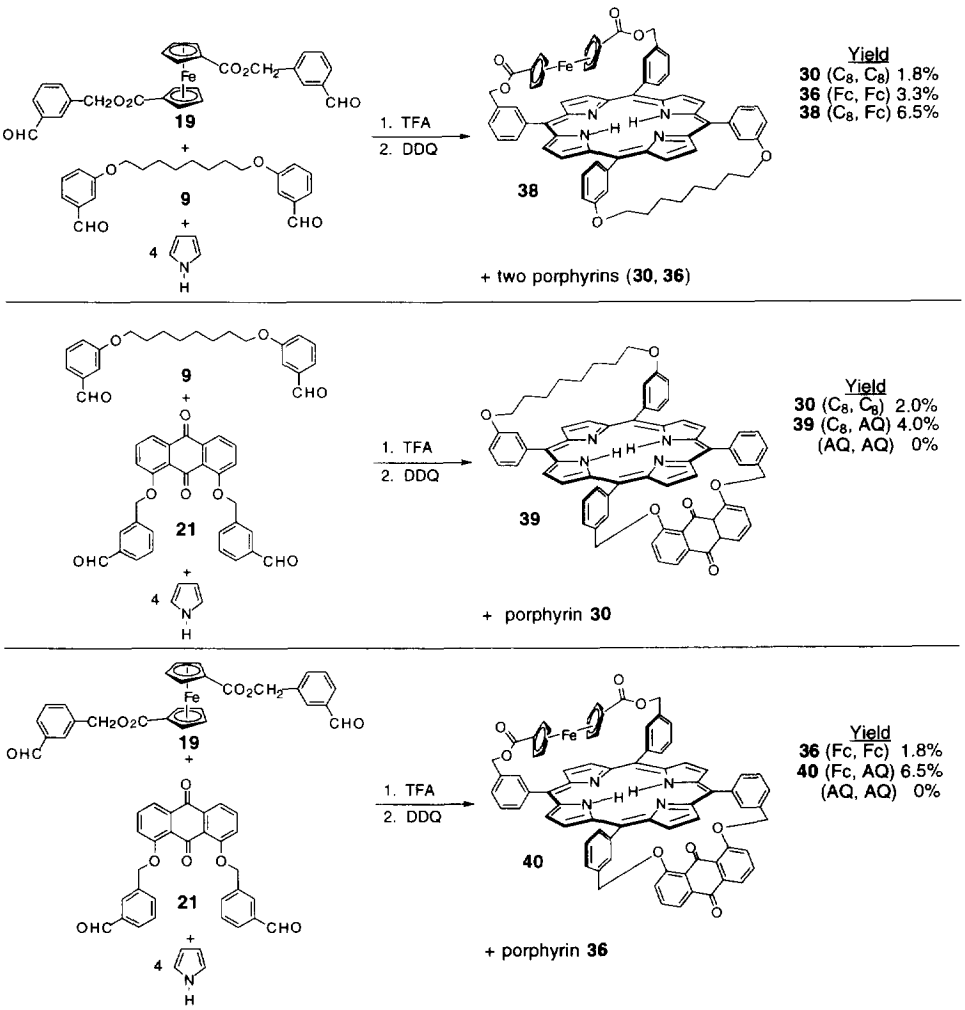
The results from these studies are summarized in Table 1. The reaction conditions have not been optimized for any of the dialdehydes, though some differences in catalytic conditions have been observed. For example, BF_3-ethanol cocatalysis[28] provided a two-fold improvement in yields with o,o′-alkoxy linked dialdehydes over catalysis with $BF_3{\cdot}O(Et)_2$ alone. TFA and $BF_3{\cdot}O(Et)_2$ catalysis gave roughly the same yields for the m,m′-linked dialdehydes, except for **16** which gave 8.1% with $BF_3{\cdot}O(Et)_2$ but 0% with TFA. In those cases where two porphyrin components (both GT-inactive) were observed (**22**-**26**), analytical HPLC was performed for quantitation purposes. Baseline resolution was achieved in each case. In the case of **22**, the two porphyrins were separated by semi-preparative HPLC, affording the cisαβ- and cisαα-strapped porphyrin isomers in yields of 2.0 and 4.4% (based on pyrrole), respectively. These isomers undergo interconversion at elevated temperatures (vide infra). Only with the o,o′-linked dialdehydes was evidence obtained for the existence of trans-strapped porphyrins. (In each case, the integrated intensity of the peaks upfield from TMS indicated an amount corresponding to 1% of the total porphyrins. While these results are consistent with their presence, no trans-strapped porphyrins have been isolated.) Furthermore, all m,m′-linked dialdehydes, including those with rigid linkers, gave only one porphyrin component. However, xylyl-strapped porphyrin **32** was isolated in <1% yield, which was insufficient for full analytical characterization. The yields observed with the ferrocene-strapped porphyrins (**36**,**37**) rival those of other dialdehydes bearing rigid linkers, indicating the compatibility of the reaction conditions with the ferrocene unit. The p,p′-substituted dialdehyde that was examined (**11**) failed to give any porphyrin.

Table 1. Synthesis and Product Distribution of Strapped Porphyrins

Dialdehyde	Strapped Porphyrin	Number of Porphyrins by TLC	GT-active components	^{1}H NMR evidence for trans-strapped porphyrins	Spectroscopic Yield (%)[a] BF_3	TFA	Isolated Yield (%)[b]
o,o′-alkoxy straps:							
1 (C_5)[c]	**22**	2	no	no	11	6	12
2 (C_6)	**23**	2	no	yes[d]	13	2.8	15
3 (C_7)	**24**	3	yes[e]	no	28	7.4	26[f]
4 (C_8)	**25**	3	yes[e]	yes[d]	26	11	23[f]
5 (C_{10})	**26**	2	no	yes[d]	19	12	33
m,m′-alkoxy straps:							
6 (C_5)	**27**	1	no[g]	no	3.2	6.4	5.4
7 (C_6)	**28**	1	no	no	3.4	6.7	5.2
8 (C_7)	**29**	1	no[g]	no	12	8.7	13
9 (C_8)	**30**	1	no	no	7.7	10	5.9
10 (C_{10})	**31**	1	no	no	7.9	13	5.0
p,p′-alkoxy straps:							
11 (C_{12})		0			0	0	0
rigid m,m′-linked straps:							
12 (xylyl)	**32**	1	no	NE[h]	3.7	3.7	<1[i]
16 (terephthalate)	**33**	1	no	no	8.1	0	0.8
17 (PDA)	**34**	1	no	no	20	30	15
18 (bisphenol)	**35**	1	no	no	31	27	25
19 (Fc)	**36**	1	NE	no	NE	NE	21
20 (Fc′)	**37**	1	NE	no	NE	NE	9

[a]The porphyrin yields were determined spectroscopically (assuming $\varepsilon = 5 \times 10^5\ M^{-1}\ cm^{-1}$) following removal of an aliquot and oxidation at 25 °C with DDQ. $BF_3{\cdot}O(Et)_2$ was 1 mM and TFA was 2×10^{-2} M in CH_2Cl_2. [b]Preparative reactions were performed on 50-100 mL scale at 10^{-2} M reactants in CH_2Cl_2 with 10^{-3} M $BF_3{\cdot}O(Et)_2$ ($CHCl_3$ was used for the o,o′-linked dialdehydes with 3.3 mM $BF_3{\cdot}O(Et)_2$). [c]Condensation of **1** in the presence of 5×10^{-2} M TFA gave **22** in 15% yield. [d]The ^{1}H NMR spectrum showed peaks upfield from TMS characteristic of the trans-strapped porphyrin with integrated intensity corresponding to <1% of the total porphyrins.[8,9] [e]The crude reaction mixture showed three porphyrin components with the most polar component (~5% of the total porphyrins) exhibiting GT-activity. These porphyrin impurities were removed by semi-preparative centrifugal TLC. [f]Determined after the removal of Girard's Reagent T-active material. [g]Monomeric porphyrin products bearing straps with free formyl groups were detected by plasma desorption mass spectrometry. [h]Not examined. [i]The preparative reaction was run with TFA-catalysis.

The condensation of two different dialdehydes (A,B) with pyrrole can yield three strapped porphyrins, the hybrid AB-strapped porphyrin, the A_2-strapped porphyrin, and the B_2-strapped porphyrin. We performed several reactions using two different dialdehydes as shown in Scheme 7. The product workup generally involved a flash column to isolate the porphyrins, followed by separation of the porphyrins via CTLC. These reaction mixtures were not treated with Girard's Reagent T. In this manner several hybrid-strapped porphyrins were obtained (Scheme 7), including the (C_8,Fc)-porphyrin **38**, the (C_8,AQ)-porphyrin **39**, and the (Fc,AQ)-porphyrin **40**. In general the AB-, A_2-, and B_2-strapped porphyrins are each obtained upon workup. However, in these condensations the putative (AQ,AQ)-porphyrin streaked on chromatographic media (silica gel, alumina) and proved difficult to isolate. Though the yields are low, these routes provide expedient syntheses of porphyrins bearing one or two redox-active groups. Other routes have yielded a tetraarylporphyrin with ferrocenes attached to the aryl groups,[31] or anthraquinone attached to the porphyrin *meso*-position.[32]



Scheme 7. One-flask synthesis of porphyrins bearing two different straps.

Concentration-dependence of strapped porphyrin formation

The concentration dependence in the synthesis of strapped porphyrins was examined using the reaction of bisphenol-dialdehyde **18** and pyrrole as a test case (Figure 1). The reactant concentrations (pyrrole and total aldehyde concentration) were varied from 10^{-1} M to 10^{-4} M with the concentration of trifluoroacetic acid fixed at 2 x 10^{-2} M. The porphyrin yields were determined spectroscopically at 1 h. TLC analysis of the reaction mixtures at 10^{-1} and 10^{-2} M showed that no porphyrinic species other than the strapped porphyrin **35** were formed. The yield profile resembles that found for tetramesitylporphyrin[28] and tetraphenylporphyrin[29] under fixed acid concentrations, with the maximum yield at 10^{-2} M reactants.

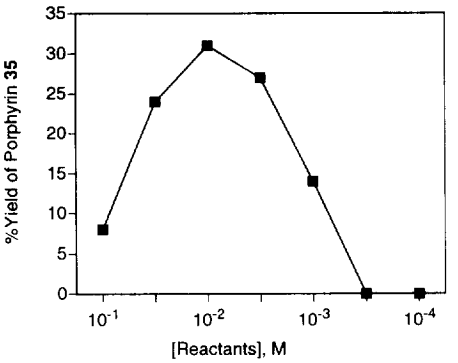


Figure 1. Yield of bisphenol-strapped porphyrin (**35**) as a function of concentration of reactants. The highest spectroscopic yield (31%) corresponds to a 25% isolated yield.

Physical properties of strapped porphyrins

Absorption and Emission Spectr The porphyrins bearing straps at the m,m'-positions (**27**-**29**, n = 5-7) exhibited red-shifted Soret and visible absorption bands relative to *meso*-tetrakis(3-methoxyphenyl)porphyrin (Table 2). The magnitude of the red-shift increased as the strap became shorter, reaching 12 nm for the shortest strap (n = 5). The porphyrins containing an anthraquinone strap (**39** and **40**) also exhibited red-shifted Soret and visible bands (~8-14 nm). In each of these compounds the (0-0) emission maximum was red-shifted and broadened. In contrast, porphyrins with longer straps at the m,m'-positions (n = 8, 10) showed no red-shifted spectral bands, nor did porphyrins bearing ferrocene straps (**36**-**38**). Thus neither the ferrocene nor the longer alkoxy-linked straps cause structural perturbations of the porphyrin macrocycle.

Table 2. m,m'-Alkoxy Strapped Porphyrin Absorption Data (in nm)

			absorption spectral bands			
Strapped Porphyrin	Soret B(0,0)	Soret fwhm (nm)	IV $Q_y(1,0)$	III $Q_y(0,0)$	II $Q_x(1,0)$	I $Q_x(0,0)$
27 (C_5)	430	19	528	568	606	666
28 (C_6)	428	17.5	526	564	600	660
29 (C_7)	424	15.6	522	560	596	654
30 (C_8)	422	11.7	518	554	594	648
31 (C_{10})	420	11.7	516	552	590	646
(m-OCH_3)$_4$TPP[b]	418	-----	514	548	590	646

[a]In CH_2Cl_2/ethanol (3:1). [b]*meso*-Tetrakis(*m*-methoxyphenyl)porphyrin.

The fluorescence emission spectra were collected for porphyrins **36** and **38-40** and their zinc chelates to examine the effects of redox-active groups on porphyrin photophysical properties (Table 3). The quantum yields of fluorescence in $CHCl_3$ were generally lowered by 1.5-2 fold, as compared with TPP, for the porphyrins containing either ferrocenyl straps (**36**, **38**), anthraquinone straps (**39**), or a combination of ferrocenyl and anthraquinone straps (**40**). In the polar solvents N,N-dimethylacetamide (DMAC)/ethanol or CH_3CN/ethanol, little change was observed for the free base porphyrins (**36**, **38-40**). However, significant decreases in fluorescence were observed for **Zn36**, **Zn39**, and **Zn40**.

Interpretation of the fluorescence data is aided by knowledge of the redox potentials of the components in the straps. The oxidation potentials for representative ferrocene compounds[33] bearing similar substituents as those in the straps were measured and the results are as follows: ferrocene, +0.45 V; $Fc(OAc)_2$, +0.55 V; $Fc(Ac)_2$, +0.90 V. The 1,8-di(benzyloxy)anthraquinone gave no oxidation wave, and gave an irreversible reduction wave with midpoint potential -0.95 V (for comparison, anthraquinone gave an oxidation potential of +0.44 V and a reduction potential of -0.85 V).

Table 3. Relative Fluorescence Yields in Several Solvents[a]

Compound	$CHCl_3$	DMAC[b]/ethanol	CH_3CN/ethanol
36 (Fc,Fc)	0.39	0.62	---
38 (C_8,Fc)	0.51	0.71	---
39 (C_8,AQ)	0.67	0.57	---
40 (Fc,AQ)	0.44	0.52	---
TPP	1.0	1.0	1.0
Zn30 (C_8,C_8)	0.79	0.58	1.1
Zn36 (Fc,Fc)	0.67	0.041	1.0
Zn38 (C_8,Fc)	0.79	0.84	1.2
Zn39 (C_8,AQ)	0.093	0.028	0.030
Zn40 (Fc,AQ)	0.13	0.041	0.053
ZnTPP	1.0	1.0	1.0

[a]The relative fluorescence yields for the free base porphyrins are ratioed to TPP (absolute $\phi_f = 0.11$),[34] and those for zinc porphyrins are ratioed to ZnTPP (absolute $\phi_f = 0.03$).[34] [b]N,N-dimethylacetamide.

Solubility. The strapped porphyrins generally exhibited good solubility in various organic solvents. The only exceptions are provided by the m,m′-alkoxy strapped porphyrins **27-31**, which are far less soluble than the o,o′-alkoxy strapped porphyrins (**22-26**) in solvents such as CH_2Cl_2 and $CHCl_3$, and are insoluble in DMSO. These porphyrins tend to deposit from solutions as a thin film on glassware.

Conformational properties of strapped porphyrins and atropisomerism

Each of the cis-strapped porphyrins (I, II, Chart 1) can in principle exhibit atropisomerism with the straps interconverting from one porphyrin face to the other. We examined a variety of the porphyrins by chromatography and ^1H NMR spectroscopy, in conjunction with thermal equilibration studies, in order to identify atropisomers and determine rates of interconversion between atropisomeric forms. In order to organize a large body of data, all evidence concerning atropisomerism in all of the strapped porphyrins is summarized in Table 4. The studies leading to these conclusions are described in detail below.

Table 4. Cisαβ- and Cisαα-Strapped Porphyrins

Porphyrin	separable by chromatography	detected by ^{1}H NMR at 25 °C	exchange observed by VT NMR experiments
o,o′-alkoxy straps:			
22-26	yes	yes	NE[a]
m,m′-linked straps:			
alkoxy-units:			
27-29	no	no	NE
30,31	no	yes	yes[b]
rigid units:			
32	no	NE	NE
33-35	no	yes	no
redox-active units			
36-38	no	yes	yes[c]
39,40	no	yes	no

[a]Not examined. [b]$\Delta G^{\ddagger}$ = 68 ± 1 kJ/mol for **30**. [c]$\Delta G^{\ddagger}$ = 66 ± 1 kJ/mol for **36**.

o,o′-Strapped porphyrins. One o,o′-strapped porphyrin (**23**) has been shown to exist as atropisomers that are separable at room temperature but can be interconverted at high temperature.[8] The β-pyrrole signals for the separate cisαβ- or cisαα-strapped porphyrins appear as two lines corresponding to four protons each due to the C_{2h} or C_{2v} symmetry of the porphyrin, respectively.[9,10] The H_6 (ortho) protons of the cisαα- and cisαβ-strapped porphyrins exhibit distinct resonances. For both isomers, the shorter the chain, the further downfield the H_6 resonance is observed. The chemical shift difference is not readily observable with the chain where n = 10 (**26**). Integration of the H_6 protons of the porphyrin mixture provides a convenient handle for determining the ratios of cisαβ:cisαα-strapped porphyrins.

We quantitated the amount of cisαα- and cisαβ-strapped porphyrin in each mixture (**22-25**) by ^{1}H NMR spectroscopy, and the ratios determined in this manner agreed with those measured by HPLC (Table 5). Treatment of porphyrins **22-25** in refluxing toluene (2-12 h) led, with exception of **22**, to changes in the ratios of the two ortho-aryl ^{1}H NMR multiplets, with corresponding changes in HPLC peak ratios. Thermal equilibration gives cisαβ:cisαα-strapped porphyrin ratios near the statistical expectation (1:1). Only the shortest chain (n = 5) o,o′-strapped porphyrin gave significant deviation (1:2.5) upon thermal equilibration. These results indicate the ratio of the cisαβ- and cisαα-strapped porphyrins formed synthetically is not identical to the thermally-equilibrated distribution. The product distribution obtained experimentally probably reflects the structures of the strapped porphyrinogens, which are conserved upon oxidation to the porphyrin.

Table 5. Atropisomers of o,o′-Alkoxy Strapped Porphyrins

	% cisαβ:% cisαα-strapped porphyrins			
	(before isomerization)[a]		(after isomerization)[b]	
Porphyrin	HPLC	NMR	HPLC	NMR
22 (C_5)	29:71	30:70	29:71	30:70
23 (C_6)	17:83	20:80	38:62	40:60
24 (C_7)	20:80	20:80	48:52	40:60
25 (C_8)	36:64	40:60	---[c]	60:40

[a]Ratio before isomerization in refluxing toluene. [b]Ratio after isomerization in refluxing toluene (see experimental). Products appear to be >99% cis-strapped porphyrins. The HPLC results assume equal molar absorptivities of the cisαα- and cisαβ-strapped porphyrins. [c]Not resolved by HPLC.

m,m′-Strapped porphyrins. In contrast to the o,o′-strapped porphyrins, which exist as atropisomers that are separable chromatographically, each m,m′-strapped porphyrin showed only one porphyrin component upon careful chromatographic analysis. Indeed, HPLC analysis of the ferrocenyl-strapped porphyrin **36** showed a single peak even with the protracted elution time of 112 min (void volume 3.2 min), and the bisphenol-strapped porphyrin **35** showed similar properties.

The observation that each m,m′-strapped porphyrin shows only one porphyrin component upon careful chromatographic analysis is consistent with several interpretations:

(1) Only one of the two cis-strapped porphyrin isomers was formed during the reaction.
(2) Both cisαα- and cisαβ-strapped porphyrin isomers were formed, but only one isomer was isolated.
(3) The isomers are stable to interconversion but possess identical chromatographic properties.
(4) The cisαα- and cisαβ-strapped porphyrin isomers rapidly interconvert during the time required for chromatography and cannot be separated.

The selective formation of a cisαβ- or cisαα-strapped porphyrin isomer seems unlikely, by analogy with the formation of both isomers with o,o′-linked dialdehydes. Selective isolation of one isomer seems unlikely, as both the crude reaction mixtures and the isolated products exhibited a single porphyrin component upon TLC analysis. In order to examine the stability of isomers toward interconversion, a toluene solution of **30** was refluxed overnight, but no new porphyrin components were produced. These observations tend to rule out the first three interpretations. In order to probe the dynamics of interconversion of the putative cisαβ- and cisαα-strapped porphyrin isomers, variable temperature ^{1}H NMR studies were performed (vide infra). These studies show that for the m,m′-strapped porphyrins examined here where the NMR spectra permit a clear conclusion to be drawn, the fourth interpretation is correct, that is, the cisαβ- and cisαα-strapped porphyrin isomers rapidly interconvert compared with the time required for chromatography and cannot be separated. The experiments leading to this conclusion are described below.

The aromatic and β-pyrrole regions of the ^{1}H NMR spectra for porphyrins **27-31** are shown in Figure 2. The H_6 proton peaks move downfield while the H_2 proton resonance moves upfield as the chain becomes shorter. In none of these m,m′-strapped porphyrins were distinct H_6 resonances observed that could be assigned to cisαβ- and cisαα-strapped porphyrins. However, three resonances in the β-pyrrole region (seen clearly for **30**, **31**, but coalesced for **27-29**) can be assigned (downfield to upfield) to the cisαβ(H_b), cisαα(H_b), and the coincident cisαβ(H_a) and cisαα(H_a) protons. (The *mixtures* of the cisαβ- and cisαα- o,o′-strapped porphyrins gave similar spectra in the β-pyrrole region.) The H_a protons are on the β-pyrrole under a strap while the H_b protons are not under a strap (Figure 2). Although this analysis is self-consistent and is made by analogy with the o,o′-strapped porphyrins (**22-26**), the HPLC, TLC, and ^{1}H NMR data do not afford an unambiguous assignment of the two cis-strapped porphyrin isomers. Based on these assignments, integration of the first two peaks gives the ratio of cisαβ- and cisαα-strapped porphyrin isomers. For **30** the ratio is 1:4, and for **31** the ratio is 1:2. Upon conversion of **30** to the zinc chelate (**Zn30**), the four β-pyrrole resonances were resolved, and the ratio of cisαβ and cisαα-strapped porphyrin isomers shifted from 1:4 to 1:2.5, based on integration of either the β-pyrrole region or the H_6 resonances.

The spectral features exhibited by **30** and **31** were exemplary for the phenylene-strapped porphyrins **33** and **34** and the ferrocene-strapped porphyrins (**36**, **37**). Bisphenol-strapped porphyrin **35** exhibited generally similar features although the broad resonances made interpretation difficult. Insufficient material was obtained for NMR analysis of porphyrin **32**. Porphyrins containing two different straps are discussed below.

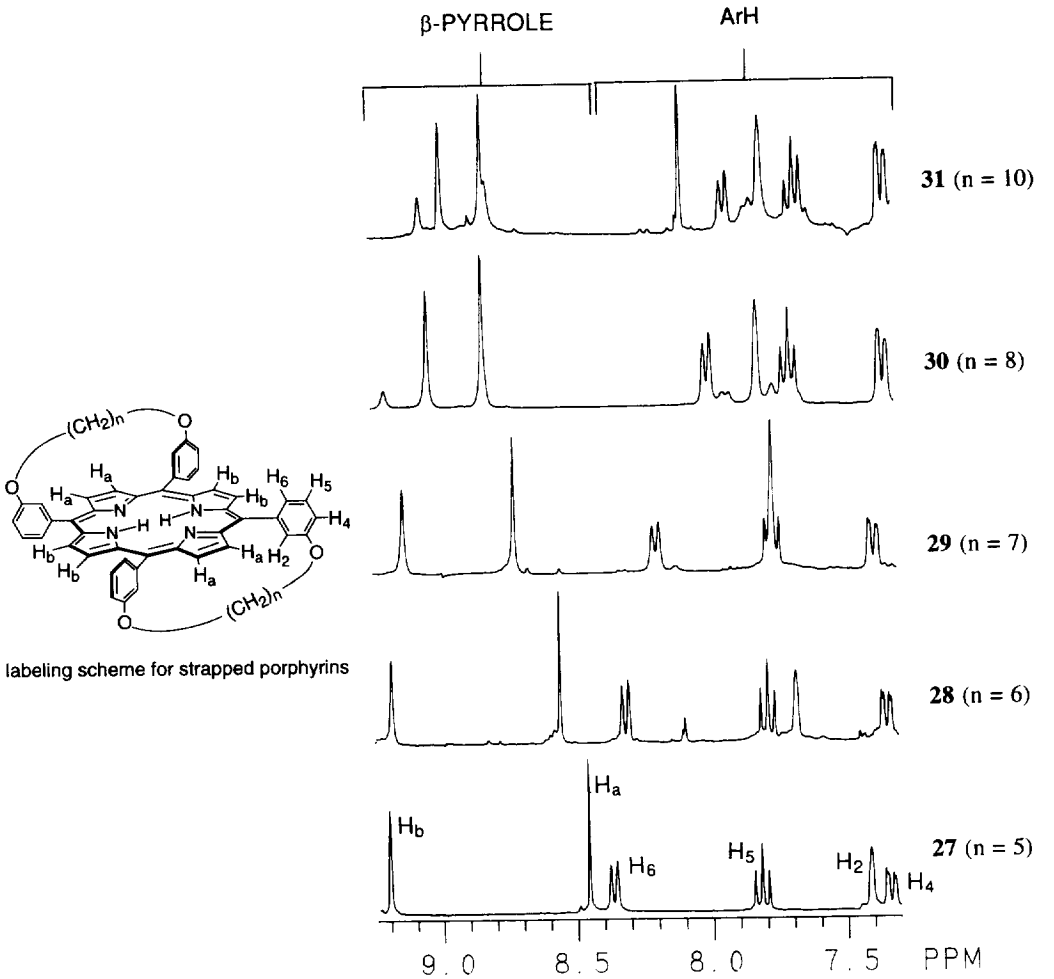


Figure 2. Aromatic region of the ^{1}H NMR spectra (300 MHz, $CDCl_3$) for m,m′-strapped porphyrins **27-31**.

Variable-temperature ^{1}H NMR experiments. Several m,m′-strapped porphyrins were examined by variable-temperature ^{1}H NMR spectroscopy in order to identify atropisomerization.

- For porphyrins **27-29**, the β-pyrrole region in each spectrum shows only two resonances. To determine whether atropisomers were interconverting rapidly at room temperature, low temperature ^{1}H NMR spectra were recorded of **Zn28** and **Zn29**. The zinc chelates were prepared to avoid freezing out the N-H tautomers, which causes splitting of the β-pyrrole resonances.[35] No spectral changes were observed at -40 °C, and at -50 °C **Zn28** and **Zn29** precipitated from both toluene-d_8 and CD_2Cl_2. Use of a chiral shift reagent (Eu(hfc)$_3$) at 620.2 MHz at room temperature failed to unveil any distinction among H_{b1} and H_{b2} protons of the putative cisαβ-strapped porphyrin **27**. In summary, atropisomers of porphyrins with short straps (**27-29**, n = 5-7) could not be detected by ^{1}H NMR spectroscopy.

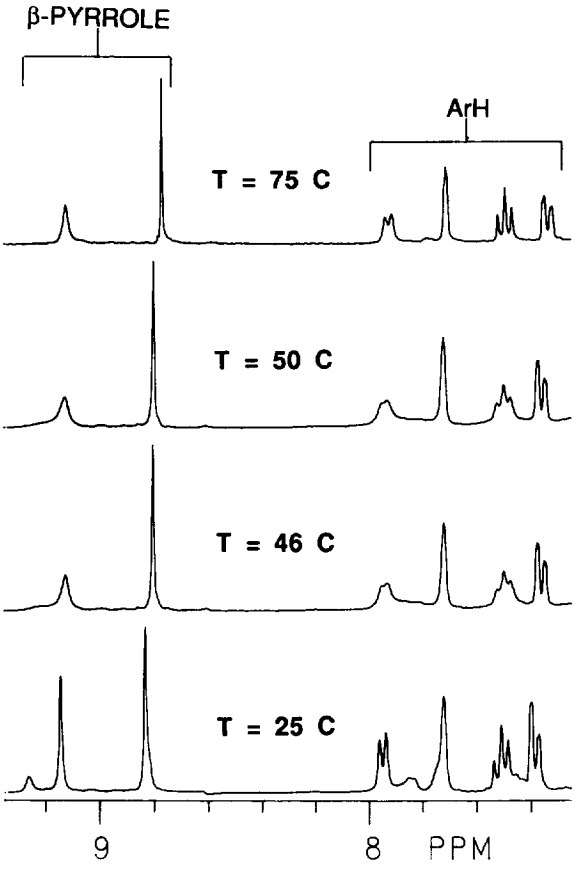


Figure 3. Variable-temperature ^1H NMR spectra at 300 MHz of porphyrin **30** in toluene-d_8.

- Porphyrin **30**, which shows three resonances in the β-pyrrole region, gave coalescence of the two downfield resonances at 50 °C (Figure 3), and a 1:1 ratio of the two resonances at 75 °C, indicating exchange between the cisαβ- and cisαα-strapped porphyrins. Upon return to 25 °C the original spectrum was obtained. The $\Delta G^{\ddagger}$ value for the interconversion of cisαβ- and cisαα-strapped porphyrins was calculated from the Eyring equation[36] to be 68 ± 1 kJ/mol (from Δ = 36 Hz and T_c = 323 K). The four β-pyrrole signals of **Zn30** also collapsed to two signals at 100 °C, indicative of rapid interconversion of the two isomers.

- Porphyrin **31** (n = 10) is very insoluble in solvents such as $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$, and toluene-d_8, and on the one occasion we were able to collect a ^1H NMR spectrum, the β-pyrrole region exhibited four resonances. At 75 °C the four resonances collapsed into two, indicating the limit of fast exchange was reached for the cisαβ- and cisαα-strapped porphyrin isomers.

- Phenylenediacetate-strapped porphyrin **34** exhibited three resonances in the β-pyrrole region, a feature similar to the spectra of the o,o'-strapped porphyrins (**22-26**) and consistent with cisαα- and cisαβ-strapped porphyrins. No significant spectral differences were observed at 25 and 75 °C. The sample decomposed at

temperatures above 75 °C. Bisphenol-strapped **35** exhibited numerous broad aryl resonances, making interpretation difficult. However, the β-pyrrole region exhibited four (broad) resonances, a feature consistent with cisαα- and cisαβ-strapped porphyrins. The β-pyrrole and aryl regions of the ^{1}H NMR spectrum of **Zn35** were identical at 25 and 75 °C. Thus for **34** and **35**, NMR evidence suggests the presence of atropisomers but no direct information is available concerning the rate of interconversion.

- Ferrocenyl-strapped porphyrin **36** exhibited four resonances with an integrated ratio of 1:5:5:1 (low to high field), consistent with a 1:5 ratio of cisαβ- and cisαα-strapped porphyrins. Coalescence of the β-pyrrole resonances occurred at temperatures above 50 °C, with a clearly resolved pair of singlets at 75 °C (Figure 4). Upon return to 25 °C the original spectrum was obtained. The $\Delta G^{\ddagger}$ value for the interconversion of atropisomers was calculated to be 66 ± 1 kJ/mol. The zinc chelate, **Zn36** in DMSO-d_6, gave the same features as **36**. Ferrocenyl-strapped porphyrin **37**, an isomer of **36**, also exhibited features similar to that of porphyrin **36**. The β-pyrrole protons indicate a 1:2 ratio of cisαβ-strapped porphyrin and cisαα-strapped porphyrins, and the limit of fast exchange was attained at 75 °C. The change in ratio of the two atropisomers in **36** and **37** must reflect the different conformations of the respective ferrocene straps.

m,m'-Strapped porphyrins bearing two different straps. For the (C_8,Fc)-strapped porphyrin **38**, the β-pyrrole protons give rise to 5 resonances in a 1:4:2:2:1 ratio, which could not be readily assigned. At 75 °C the β-pyrrole resonances collapse to three singlets in a 2:1:1 ratio, indicating the limit of fast exchange. The benzylic and cyclopentadienyl protons in porphyrin **38** exhibit behavior similar to that observed for porphyrin **36**.

For the (C_8,AQ)-strapped porphyrin **39**, the β-pyrrole region appeared very different from that of **38** or **30**, with two doublets and two singlets in ratio of 1:1:1:1 (low to high field). No change was observed in the ^{1}H NMR spectrum from 25-75 °C. Similar spectral features were observed in the ^{1}H NMR spectrum of porphyrin **40**, though some of the aryl resonances coincide with the β-pyrrole resonances. Thus, in neither **39** nor **40** was any evidence of atropisomers observed.

Conformational motion of the straps in strapped porphyrins. The formation of a strapped porphyrin entails some loss of conformational motion for the components of the strap. For example, all of the alkyl chain resonances of **27** are diastereotopic (resolved at both 300 and 620.2 MHz and assigned on the basis of ^{1}H NOE difference experiments at 620.2 MHz; see experimental). In contrast to porphyrin **27**, only the -$OC\underline{H}_2CH_2$- and -$OCH_2C\underline{H}_2$- protons of the alkyl straps for **28-31** were found to be diastereotopic, indicating that the remaining protons exchange rapidly on the NMR time scale. All dialdehydes derived from 3-bromomethylbenzaldehyde exhibited a singlet for the 3-methylene unit. However, each of the corresponding porphyrins exhibited a multiplet for the 3-methylene group, indicative of hindered rotation.

An excellent example of the loss of motional freedom in the strap is provided by porphyrin **36**. At room temperature the benzylic protons appear as a closely spaced pair of doublets in a 1:1 ratio (8 protons), which coalesce to a broad singlet above 55 °C, and appear as a sharp singlet at temperatures above 75 °C (Figure 4). The cyclopentadienyl protons of dialdehyde **19** appear as a pair of symmetrical triplets separated by 0.47 ppm, while the ring protons of porphyrin **36** appear as 4 singlets of equal intensity. The diastereotopic nature of the benzylic and cyclopentadienyl protons result from the rigidity of the strap which creates different local environments for these protons. At temperatures above 65 °C, the resonances at 4.40 and 4.50 ppm begin to coalesce as do those at 4.92 and 5.15 ppm. At temperatures above 95 °C, coalescence appears to be complete and two broad singlets remain at 4.43 and 5.06 ppm of equal intensity. The $\Delta G^{\ddagger}$ value for this interconversion was calculated to be 69 ± 1 kJ/mol, in agreement with the value of 66 ± 1 kJ/mol measured for atropisomerization by examination of the β-pyrrole protons. Similar spectroscopic features concerning limited motion of the strap were observed for ferrocenyl-strapped porphyrins **38** and **40**.

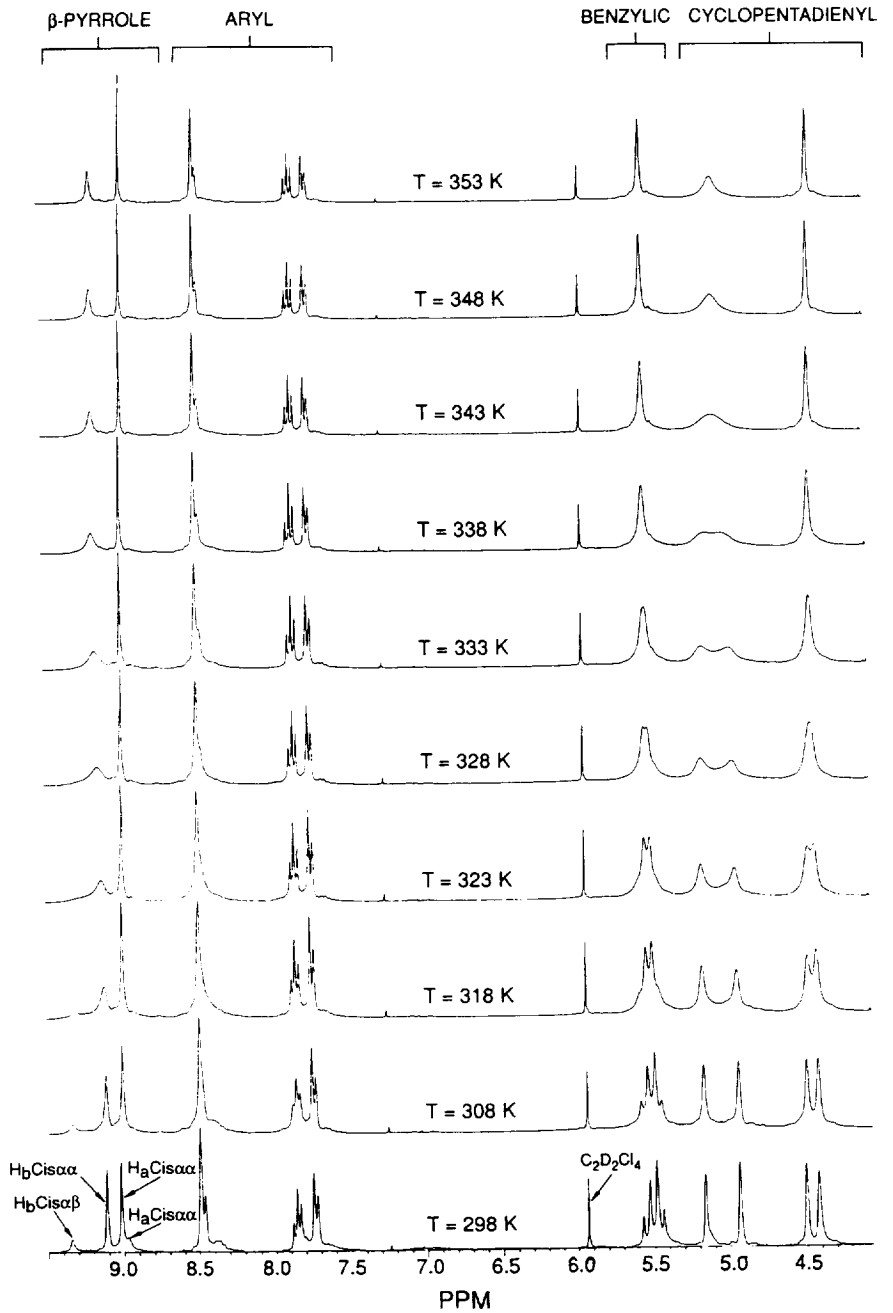


Figure 4. Variable-temperature ^1H NMR spectra of porphyrin **36** ($C_2D_2Cl_4$). Coalescence of the respective β-pyrrole, benzylic, and cyclopentadienyl protons is observed at elevated temperature.

DISCUSSION

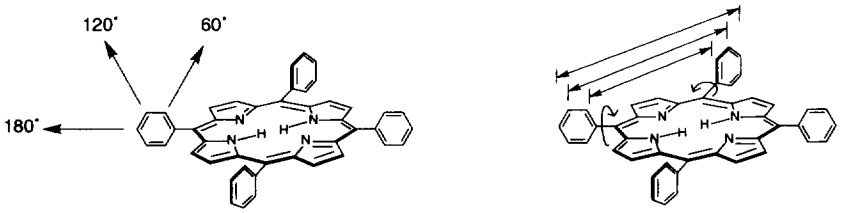
These results show that a wide variety of dialdehydes, having different length, position of substitution (o,o′-, m,m′-), structure, and redox activity can be converted to the corresponding porphyrins in an easily implemented one-flask process. This success occurs in spite of the complexity of the two reactions constituting the overall transformation. The first step involves a pyrrole-dialdehyde condensation, yielding a porphyrinogen with concomitant formation of eight C-C bonds. The second step involves the oxidative conversion of the porphyrinogen to the porphyrin, requiring removal of 6 electrons and 6 protons from the tetrapyrrolic macrocycle. Both reactions occur at room temperature, employing conditions identical to those used in reactions of mono-aldehydes. The reaction of a dialdehyde is somewhat different from that of a mono-aldehyde, however. With a mono-aldehyde, four aldehyde and four pyrrole molecules condense yielding the porphyrinogen macrocycle. With a dialdehyde, two dialdehyde and four pyrrole molecules condense in a combined macrocyclization and annulation process, yielding a total of three rings. Thus, the reaction of a dialdehyde is structurally more demanding due to the simultaneous formation of three rings, albeit less complicated stoichiometrically than that with a mono-aldehyde, as only 6 molecules undergo condensation.

Significant structural changes occur during conversion of pyrrole and any aldehyde (mono-, di-, or higher aldehyde) to the porphyrin. At the outset of this transformation, the aldehyde formyl carbon is sp^2-hybridized, upon condensation the resulting *meso*-carbon in the porphyrinogen is sp^3-hybridized, and following oxidation the *meso*-carbon in the porphyrin is sp^2-hybridized. Thus the porphyrinogen has a more 3-dimensional structure while the porphyrin is relatively planar. For the successful conversion of a dialdehyde to the strapped porphyrin, the linker in the dialdehyde must tolerate the structural requirements of the porphyrinogen and of the porphyrin, and be compatible with the acidic reaction conditions of the condensation process and the oxidative conditions of the aromatization process. Here we discuss the structural features (length, position of substitution, and rigidity) of a linked dialdehyde that lead to the corresponding strapped porphyrin, and the evidence concerning the conformations of the various strapped porphyrins.

Structural model for the formation of strapped porphyrins

Substituent position. The ortho-, meta-, and para-positions of the *meso*-aryl groups differ in the following ways. (1) The angle a substituent makes with respect to the plane of the porphyrin is 60° (ortho), 120° (meta), or 180° (para). Thus ortho-substituents project over the face of the porphyrin, but meta- and para-substituents have trajectories directed away from the porphyrin (Scheme 8). (2) Adjacent *meso*-positions diverge from each other by 90°, consequently the distances between two adjacent ortho-, meta-, or para-positions are different. (3) Rotation about the *meso*-carbon-aryl bond causes tilting of the *meso*-aryl group toward coplanarity with the porphyrin. Rotation of the aryl groups at adjacent *meso*-positions can tilt the respective substituents at opposite ends of the strap unit toward each other. Tilting decreases the distance between adjacent ortho-sites or the adjacent meta-sites, but no change occurs in the distance between adjacent para positions. Taken together, these structural and conformational features have significant implications for the tolerance for various straps located at the ortho-, meta-, or para-positions of the *meso*-aryl groups.

Successful formation of a strapped porphyrin first requires formation of the corresponding strapped porphyrinogen. Relatively little information is available concerning the structure of porphyrinogens, however the few available x-ray structures[37] as well as molecular models indicate the following. (1) The porphyrinogen has a puckered geometry with adjacent pyrroles perpendicular to each other and alternate pyrroles in nearly parallel planes. (2) The porphyrinogen has greater conformational flexibility than does the porphyrin. (3) The reaction of an aldehyde (or unsymmetrical ketone) and pyrrole can yield four isomeric porphyrinogens due to orientation of the two carbonyl substituents (about the *meso*-carbon) on the α- or β-face of the porphyrinogen. The resulting αααα-, ααaβ-, ααββ-, and αβαβ-isomers are expected in a 1:4:2:1 ratio.



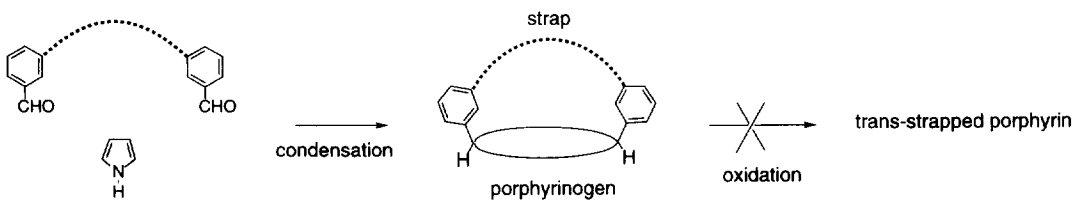
Scheme 8. Structural features with substituents at the *meso*-aryl groups.

The greater conformational pliability and isomeric variability of the porphyrinogen compared with the porphyrin suggests the possibility of forming strapped porphyrinogens, particularly trans-strapped porphyrinogens, that are incapable of conversion to the corresponding porphyrin (Scheme 9). We have built Corey-Pauling-Koltum (CPK) molecular models of a number of strapped porphyrinogens and strapped porphyrins in order to examine this possibility, and we make the following observations:

- Molecular models that appeared unstrained could be constructed of the trans-, cisαβ-, and cisαα-strapped porphyrinogens and porphyrins for each of the o,o′-linked dialdehydes (**1**-**5**). However, the observed yields of trans-strapped porphyrins were exquisitely low for these dialdehydes.

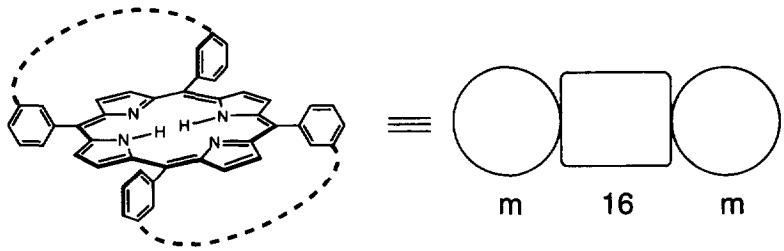
- Molecular models could be constructed of porphyrinogens derived from all of the m,m′-alkoxy-linked dialdehydes (**6**-**10**). However, none of the straps was long enough to build the model for the corresponding trans-strapped porphyrin, and in fact, no trans-strapped porphyrins were obtained in the reactions of **6**-**10** (Table 1). In the molecular models of the porphyrinogen, the *meso*-aryl groups stand upright and the meta-substituents (cis or trans) point toward each other (in contrast to the porphyrin where the meta-positions point 120° away from the porphyrin ring). This analysis suggests that dialdehydes **6**-**10** could yield trans-strapped porphyrinogens, but the oxidation would fail to yield the trans-strapped porphyrin.

- Molecular models could be constructed of a porphyrinogen and of the cis-strapped porphyrin derived from the p,p′-linked dialdehyde **11** (with full extension of the alkyl unit), however no porphyrin was observed experimentally. The perpendicular orientation of the adjacent para-positions makes incorporation of a strap at these sites the most demanding.



Scheme 9. Aborted conversion of a strapped porphyrinogen to the trans-strapped porphyrin.

Length of the strap. The strapped porphyrins can be grouped in terms of the length of the straps. An equivalent measure considers the size of the ring created by the strap. The number of atoms in each ring is counted by choosing the shortest path encompassing the strap, the *meso*-aryl rings, and the edge of the porphyrin. The sizes of the straps for porphyrins **22**-**40** are listed in Table 6.



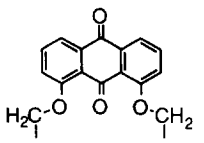
Linker	n		Porphyrin	m	Yield (%)
-O-(CH$_2$)$_n$-O-	5	C_5	**27**	16	5.4
	6	C_6	**28**	17	5.2
	7	C_7	**29**	18	13
	8	C_8	**30**	19	5.9
	10	C_{10}	**31**	20	5.0
-OCH$_2$-C$_6$H$_4$-CH$_2$O-		xylene	**32**	19	<1
-CH$_2$O$_2$C-C$_6$H$_4$-CO$_2$CH$_2$-		TPA	**33**	21	0.8
-CH$_2$O$_2$CCH$_2$-C$_6$H$_4$-CH$_2$CO$_2$CH$_2$-		PDA	**34**	23	15
-CH$_2$O-C$_6$H$_4$-C(CH$_3$)$_2$-C$_6$H$_4$-OCH$_2$-		bisphenol	**35**	24	25
Fe(C$_5$H$_4$CO$_2$CH$_2$-)$_2$		Fc	**36**	20	21
Fe(C$_5$H$_4$O$_2$CCH$_2$-)$_2$		Fc'	**37**	20	9
		AQ			
		C_8,Fc	**38**	21,20	6.5
		C_8,AQ	**39**	21,20	4.0
		Fc,AQ	**40**	20,20	3.7

Table 6. The topology of the strapped porphyrins and the ring size achieved with various linkers. The porphyrin ring size is 16. The term *m* denotes the number of atoms in the outer macrocycle.

Dialdehydes **1-10** were prepared to examine the effect of the length of the strap on porphyrin formation. The yield generally increases for the o,o'-alkoxy-linked dialdehydes with increasing strap length, ranging from 12% (**1**, n = 5), 15% (**2**), 26% (**3**), 23% (**4**), to 33% (**5**, n = 10) (Table 1). The porphyrin yield for *o*-anisaldehyde is 20%.[28] Therefore, shorter straps (**1**, **2**, n = 5, 6) lower the porphyrin yield and longer straps (**3**, **4**, **5**; n = 7, 8, 10) enhance yields. The latter examples are the only cases where a dialdehyde affords a higher yield of porphyrin than the corresponding mono-aldehyde. In contrast, the m,m'-alkoxy-linked dialdehydes (**6-10**) give constant yields at ~5% except for the linker with n = 7 (13%). These yields are much lower than with *m*-anisaldehyde (38%), which should have identical electronic effects as dialdehydes **6-10** and differ only in structural features.

Another comparison of linking unit length is provided by dialdehydes **12**, **16**, and **17**, each of which contains a para-phenylene moiety in the linker. The chain attaching the *meso*-phenyl group to the phenylene moiety increases from -OCH_2- (**12**), -CH_2-O-CO- (**16**), to -CH_2-O-CO-CH_2- (**17**). This progression of 2, 3, and 4 atom units (yielding macrocycles of m = 19, 21, and 23 atoms) is accompanied by yields of 3.7, 8.1, and 20%, respectively (BF_3·$O(Et)_2$ catalysis) (Table 1).

Another factor for a strap of a given length concerns the position of substitution. The o,o'-strapped porphyrins **22** and **23** (n = 5, 6) formed with ease, and their absorption spectra were not red-shifted as often occurs with distorted porphyrins. In contrast, the corresponding m,m'-strapped porphyrins **27** and **28** (n = 5, 6) exhibited distorted absorption spectra, indicative of conformational strain. Straps of identical length result in different conformations due to the greater distance that must be spanned between adjacent meta-positions compared with adjacent ortho-positions.

Rigidity of Linking Unit. The insertion of rigid groups in bifunctional chains often enhances macrocyclization yields.[38] We felt that the inclusion of rigid groups as linkers might impart some of the same advantages to porphyrin formation. The outer rings of the triple macrocycle range in size (m = total number of atoms in the ring as shown in Table 6) from 16 to 24. The inclusion of rigid groups in the linker backbone gives improved yields for **18** (bisphenol linker, 25%, m = 24) and **17** (phenylenediacetate linker, 15%, m = 23) compared to the flexible m,m'-alkoxy-linked dialdehyde **10** (decyl linker, 5.0%, m = 23). However, the rigid **16** (terephthalate linker, 0.8%, m = 21) and **12** (xylyl linker, <1%, m = 19) gave yields less than their flexible m,m'-alkoxy-substituted counterparts **9** (octyl linker, 5.0%, m = 21) and **7** (hexyl linker, 5.2%, m = 19), respectively, showing that rigid groups do not always enhance yields. Molecular models show that the porphyrinogens of these dialdehydes can be formed with ease. However, in the corresponding strapped porphyrins the phenylene group in the strap is sterically congested with the β-pyrrolic edge of the porphyrin, compared with the flexible alkyl chains in straps of similar length. One interpretation is that the inability of the rigid groups to flex out of the way of the pyrrole rings results in lower yields, while the additional two-atom linker (**17**) provides enough space for the rigid groups to escape interaction with the porphyrin macrocycle. This analysis illustrates the potential tradeoff between rigidity and flexibility in a macropolycyclization reaction.

Selectivity of Strapped Porphyrin Formation

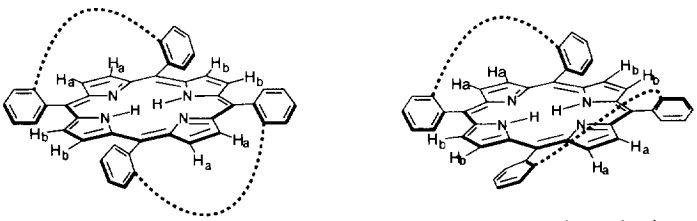
The condensation of a dialdehyde and pyrrole in principle can yield linked porphyrin dimers (and higher oligomers) in addition to the strapped porphyrins (I, II, III, Chart 1) and strapped porphyrins bearing free formyl groups (Scheme 6). In our studies using ^1H NMR spectroscopy, HPLC, and TLC we did not observe any dimers or oligomers. Examination by ^{252}Cf plasma desorption mass spectrometry[39] showed a peak of mass m/z = 2M (where M is the molecule ion mass of a monomeric strapped porphyrin) consistent with a porphyrin dimer for **24**, **25**, **27-31**, and **35**, and a peak consistent with a porphyrin trimer (m/z = 3M/2) for **24**, **25**, and **30**. In each case the intensity of the higher mass peak was <5% of that of the monomeric strapped porphyrin molecule ion. Non-covalent dimers occasionally are observed in mass spectrometric analysis of monomeric

porphyrins (lacking straps),[39] and these higher mass peaks tended to occur with the less soluble strapped porphyrins. Based on these observations, we believe the tiny quantities of dimers and trimers observed are mass spectrometric artifacts involving non-covalent aggregation, not synthetic by-products. Though we cannot absolutely rule out that trace amounts of covalently linked dimers and trimers are present in these samples, the pyrrole-dialdehyde condensation appears to be quite selective in forming the monomeric strapped porphyrin.

Conformations of Strapped Porphyrins

Cisαβ- and cisαα-strapped porphyrin isomers. In every case where cisαβ- and cisαα-strapped porphyrin isomers could be separated (**22-25**) or the ratios measured (various m,m′-strapped porphyrins), the cisαα-strapped porphyrin predominated. Thus the ratio of cisαβ:cisαα strapped porphyrin ranged from 20:80 to 40:60 for the o,o′-strapped porphyrins (**22-25**), was 20:80 for porphyrin **30**, 30:70 for **Zn30**, 33:67 for **31**, 17:83 for ferrocenyl-strapped porphyrin **36**, and 33:67 for ferrocenyl-strapped porphyrin **37**. The slight but persistent preference for both straps to be on the same face of the porphyrin (cisαα-strapped isomer) may reflect a subtle conformational effect with the porphyrin, such as slight doming that does not occur with the cisαβ-strapped porphyrin.

It is to be expected that as the straps become shorter, the phenyl rings will rotate toward coplanarity with the porphyrin to accommodate these straps. Markers for the conformational changes caused by short straps are red shifts in the absorption spectral bands of the porphyrin, and the displaced chemical shifts of the H_b and H_6 protons in the ^1H NMR spectra. This is clearly seen in the o,o′-alkoxy strapped porphyrins, where the H_6 protons shift downfield and the chemical shift difference of the H_b protons of the cisαβ- and cisαα-strapped porphyrin isomers increases (from ~0 for **25** to 0.35 for **22**) as the straps become shorter. A structural model which explains these shifts, proposed by Momenteau[1] and by Walker,[8] is shown in Scheme 10.



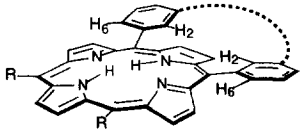
Scheme 10. Structural model for strained strapped porphyrins.

Rotation toward coplanarity thrusts the phenyl ring into close proximity of the β-pyrrole ring, causing deshielding of the H_6 protons and concomitant shifts downfield. In the cisαβ-strapped porphyrin the phenyl rings rotate in the same direction with respect to the H_b protons, and the coplanarity of the phenyl groups results in additive deshielding of the H_b protons. In contrast, in the cisαα-porphyrin isomer the adjacent phenyl rings rotate in opposite directions, causing cancellation of ring current effects on the H_b protons. Indeed, the H_b protons of the cisαα-strapped porphyrin isomers resonate at $\delta = 8.68$ ppm independent of strap length, similar to the β-pyrrole protons of *meso*-tetrakis(2-methoxyphenyl)porphyrin.[28] The H_a protons (under the strap) have adjacent phenyl groups rotated in opposite directions in both cisαβ- and cisαα-strapped porphyrin isomers, thus explaining the little difference observed in chemical shift for the cisαβ(H_a) and cisαα(H_a) protons.

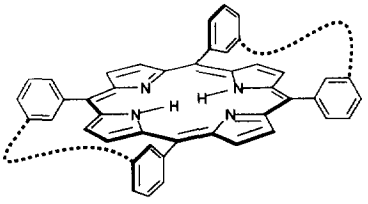
For the porphyrins with short straps (n = 5-7, **27-29**) across adjacent meta-positions, the progressive downfield shift of the H_6 protons with decreasing strap length, and the broadening and red-shifting in the absorption and fluorescence spectra, are attributed to rotation of the phenyl groups to accommodate the shorter

straps. However, unlike the o,o'-strapped porphyrins, no atropisomers were detected (Table 4). Space filling models of **27-29** show the phenyl rings to be essentially coplanar with the porphyrin macrocycle due to the short strap length. The models also show that a variant of a cis$\alpha\alpha$-strapped porphyrin conformer can be constructed that has all ortho (H_2 and H_6) protons and both straps on the same side of the porphyrin (Scheme 11). In this conformer the pyrrole rings point upward giving the porphyrin a domed structure, the *meso*-aryl rings are nearly coplanar with each other, and the ortho-protons of the phenyl rings project over the edges of the β-pyrrole units. A similar variant of the cis$\alpha\beta$-strapped porphyrin conformer can be constructed. It is not known if these conformers, which are hypothetical, could account for the failure to observe atropisomers of **27-29**.

Broadening and red-shifting in the absorption and fluorescence spectra, as observed with porphyrins **27-29**, indicates a distorted porphyrin macrocycle.[8,40] Distorted porphyrins are of interest for tuning the optical and redox properties of photosynthetic chromophores.[41,42] Far more severe distortions have been observed in the tetracycloalkenyl-*meso*-tetraphenylporphyrins,[40] which have substitution at all peripheral sites around the porphyrin macrocycle. Structural distortion due to short straps across the *meso*-positions is a mechanism complementary to the use of steric hindrance, though the magnitude of the structural distortions appears to be comparatively less even in the most strained of the strapped porphyrins (**27-29**) we have investigated.



Domed conformer due to short strap



S-strapped conformer with long straps

Scheme 11. Hypothetical conformers. The domed conformer has a short strap spanning adjacent meta-positions with ortho-hydrogens on one face, a proposed structure for porphyrins **27-29**. Only one of the straps is shown for clarity. The long straps in S-shaped conformations span opposite faces of the porphyrin, a proposed structure for porphyrins **30** and **31**.

The m,m'-strapped porphyrins with long alkoxy straps (n = 8,10; **30**, **31**) or rigid linkers (**34**, **35**, **36** (Fc,Fc), **37** (Fc',Fc'), **38** (C_8,Fc)) exhibit ^{1}H NMR spectral features characteristic of atropisomers (Table 4). However, the normal absorption spectrum in each case indicates the absence of strain in the porphyrin macrocycle. The $\Delta G^{\ddagger}$ value for **30** (68 ± 1 kJ/mol) or for **36** (66 ± 1 kJ/mol) is too low for separation of the atropisomers at room temperature. Indeed, the atropisomers of *meso*-tetrakis(2-fluoro-5-methoxyphenyl)-porphyrin exhibited $\Delta G^{\ddagger}$ = 93.1 kJ/mol and required chromatography at < 5 °C for isolation; the purity obtained was only 80%.[43] Similar $\Delta G^{\ddagger}$ values (60-78 kJ/mol) have been reported for rotation of phenyl rings in tetraphenylporphyrins.[44] Thus, substitution at the meta-position of the aryl group does not significantly hinder rotation at the *meso*-position. There have been no reports of atropisomerism in tetraarylporphyrins bearing bulky meta-substituents, and even the large cyclohexyl groups at the meta-positions of a molecular cleft porphyrin did not result in atropisomers.[45] In contrast, numerous substituents at the ortho-positions have given rise to atropisomers including the hydroxy,[46] methyl,[47] amino,[48] methoxy,[49] cyano and nitro,[50] pivalamido, hexadecylamido, and propionamido,[51] and fluoro, chloro, bromo, and iodo groups.[43]

Molecular models for the strapped porphyrins with long chains spanning adjacent meta-positions (**30** and **31**, n = 8, 10) revealed the possibility of forming a conformer where the strap takes on an S-shape in joining the two meta-sites on opposite sides of the porphyrin (Scheme 11). Such conformers, which at present are

hypothetical, could exist as stable entities or as intermediates in the interconversion of cis$\alpha\beta$- and cis$\alpha\alpha$-strapped porphyrin isomers.

The anthraquinone-strapped porphyrins **39** (C_8,AQ) and **40** (Fc,AQ) showed no evidence of atropisomers. Molecular models suggest that the anthraquinone, the two attached *meso*-aryl rings, and the porphyrin macrocycle are essentially coplanar. To accommodate a coplanar anthraquinone, the porphyrin macrocycle is forced to adopt a ruffled conformation. These observations are consistent with the red-shifted Soret and visible absorption bands. If these models are valid, the coplanarity of the anthraquinone and porphyrin would eliminate the possibility of atropisomerization.

Motion in the strap. The restricted motion of groups incorporated in the straps is most relevant for the porphyrins containing redox-active units (ferrocene and anthraquinone). A sizable literature exists concerning the synthesis and conformational properties of ferrocenophanes.[52] The effects of interannular bridging on the conformational geometries of the ferrocene nuclei have been extensively investigated through ^{1}H NMR spectroscopy.[53-56] Two pertinent effects include tilting of the cyclopentadienyl rings and ring-ring torsion. Ring tilting occurs in ferrocenophanes with conformationally-restricted bridges or bridges having fewer than four atoms between the two cyclopentadienyl moieties. This ring-tilting brings the ferrocene substituents closer to the iron atom, and in severe cases can create a differential shielding of up to 0.5 ppm of the protons on the C_1 and C_2 carbons attached to the cyclopentadienyl ring.[55] Ring-ring torsion occurs in ferrocenophanes when the bridge hinders the free rotation of the cyclopentadienyl rings. However, a ferrocene nucleus in a ferrocenophane can freely rotate if the bridge is sufficiently long.[53]

For each of the ferrocenyl-strapped porphyrins **36** (Fc,Fc), **37** (Fc′,Fc′), and **38** (C_8,Fc), multiple resonances are observed for the benzylic and cyclopentadienyl protons. Though atropisomers are present, these spectral features are a consequence of the restricted motion of the ferrocene strap. (Similar spectral features are observed for the benzylic and cyclopentadienyl protons in (Fc,AQ) strapped porphyrin **40**, which shows no evidence of atropisomers.) Molecular models suggest that the 3-atom linkers in the ferrocene straps in **36-38** and **40** are sufficiently long to prevent ring-tilt deformation of the cyclopentadienyl rings, but the interannular bridge composed of the porphyrin and the phenylmethoxycarbonyl chain is not sufficiently pliable to permit free rotation of the ferrocene nuclei. Lack of free rotation should cause inequivalence of the cyclopentadienyl protons, as is observed at room temperature. However, at elevated temperature the resonances from the ferrocene protons coalesce, implying motion of the ferrocene unit that places the protons in a time-averaged environment despite the lack of rotational freedom.

CONCLUSIONS

The two-step one-flask synthesis provides an expedient route to strapped porphyrins. The self-assembly of the porphyrinogen appears to be quite selective. First, scarcely any trans-strapped porphyrin was formed from o,o′-alkoxy-linked dialdehydes. Second, only a few of the fourteen porphyrins were contaminated with porphyrins bearing free formyl groups. Third, no multi-porphyrin structures (such as cofacial dimers) were isolated. The porphyrinogen self-assembly process also supports concomitant formation of two peripheral rings composed of widely differing structural entities. Flexible chains from 7-12 atoms are readily incorporated in the ortho- and the meta-positions, and the latter can tolerate rigid groups as integral constituents of the straps. A significant loss of motion of the strap unit occurs upon forming the porphyrin. The conditions of the condensation and oxidation are sufficiently mild to permit the direct incorporation of one or two redox-active substituents (ferrocene or anthraquinone) into a macropolycyclic architecture encompassing the porphyrin. This approach should enable rapid access to porphyrin model systems for study of electron transport processes.

EXPERIMENTAL

General. ^1H NMR spectra (300 MHz, General Electric GN 300NB and IBM FT-300), ^{13}C NMR spectra (75 MHz, General Electric GN 300NB), IR spectra (Nicolet 5DXB), absorption spectra (HP 8451A and IBM 9430), and fluorescence spectra (Gilford Fluoro IV) were collected routinely. Absorption and emission spectra were collected in CH_2Cl_2/ethanol (3:1) unless noted otherwise. K_2CO_3 and KF were dried at 140 °C *in vacuo* overnight. Pyrrole was distilled from CaH_2 and stored samples were discarded upon discoloration. 1,1′-bis(acetoxy)ferrocene was prepared according to the procedure of Akabori et al.[26] All other aldehydes were purchased from Aldrich and were used as received. Semi-preparative centrifugal thin layer chromatography (CTLC) was performed with a Harrison Research Chromatotron Model 7924T. Column chromatography was performed on silica (Merck, 70 - 230 mesh) or alumina (Fisher, 80 - 200 mesh). Flash chromatography was performed on Baker flash silica.[57] HPLC analysis was performed with an HP 1090 Liquid Chromatograph on silica (Waters μ-porasil 300 x 3.9 mm, 1 mL/min; 3 min void volume). Semi-preparative HPLC was performed on silica (IBM, 250 mm) with an IBM LC/9560. For yield determinations of small quantities of porphyrins, a solution of the porphyrin was passed through a 0.22 μm Nylon 66 filter (Micron Separations Inc.) to remove any residual silica gel. Melting points are uncorrected.

Solvents. CH_2Cl_2 (Fisher, reagent grade) and $CHCl_3$ (Fisher certified A.C.S.) were distilled from K_2CO_3 and were stored over 4-Å molecular sieves. 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.[28] CH_3CN was distilled from CaH_2. THF was distilled from a mixture of sodium in benzophenone. DMF, acetone, absolute ethanol, and DMSO (Aldrich, HPLC grade) were used as received.

Acid Catalysts. Stock solutions of $BF_3{\cdot}O(Et)_2$ were prepared by diluting $BF_3{\cdot}O(Et)_2$ (Aldrich, 8.1 M) to 2.5 M in CH_2Cl_2 or $CHCl_3$, depending on the solvent used in the reaction. Stock solutions remained viable for at least two weeks. Trifluoroacetic acid (TFA) was used as obtained from Aldrich.

Girard's Reagent T (GT).[30] All strapped porphyrin reaction mixtures were treated with GT to identify any porphyrins with unreacted formyl groups. Typically, 20 μL of a porphyrin solution was treated with 20 μL of an acidified methanolic solution of GT (0.12 M in GT, 1 M in trifluoroacetic acid). The resulting green solution was then subjected to TLC analysis (silica). GT proved effective for analytical identification of porphyrin-carboxaldehydes, but was awkward as a preparative separation method. Thus after purifying the crude reaction mixtures so that a mixture of the porphyrins was obtained (after removing quinone and polypyrromethene components), porphyrin-carboxaldehydes were removed by semi-preparative centrifugal TLC instead of with GT treatment.

Electrochemistry. The cyclic voltammetry measurements were recorded with Ag/AgCl reference and platinum wire counter electrodes under argon at room temperature. The samples were dissolved in acetonitrile (10^{-4} M) containing tetrabutylammonium hexafluorophosphate (0.8 M) as a supporting electrolyte. Half wave potentials were calculated using the equation $E_{1/2} = 1/2(E_{pc} + E_{pa})$. The symmetry of the voltammogram was considered as an indication of the reversibility of the redox reaction.

Analysis. Mass spectra were determined using ^{252}Cf plasma desorption mass spectrometry (PDMS)[39] or high-resolution fast atom bombardment mass spectrometry (JEOL HX110HF, ion source 40°C, polyethylene glycol standards, 10 ppm elemental compositional accuracy). The porphyrin spectroscopic yields were determined (assuming $\varepsilon = 5 \times 10^5$ M^{-1} cm^{-1}) following removal of an aliquot and oxidation at 25 °C with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[29,30] Reported absorption and emission spectra are in CH_2Cl_2/EtOH (3:1) unless noted otherwise.

Variable temperature NMR experiments. VT ^1H NMR experiments were performed using a General Electric GN 300NB and an IBM FT-300. We estimate the coalescence temperature to be accurate to ± 4 °C,

which gives an error range of ± 1 kJ/mol in the reported $\Delta G^{\ddagger}$ values.[31] In each case the original spectrum was obtained upon cooling to the starting temperature.

Synthesis of o,o′-linked dialdehydes. Dialdehydes (**1-5**) were prepared from salicylaldehyde (61.2 mmol) and the appropriate dibromoalkane (20.4 mmol).[8] Crude products were recrystallized twice from ethanol to give white compounds in all cases.

1,5-Bis(2-formylphenoxy)pentane (1).[8,58]

1,6-Bis(2-formylphenoxy)hexane (2).[8]

1,7-Bis(2-formylphenoxy)heptane (3). 3.8 g (55% yield); mp 47-48 °C; ^{1}H NMR ($CDCl_3$) δ 1.51, 1.57 (m, 6 H, $C_\gamma H_2$, $C_\delta H$), 1.85, 1.90 (m, 4 H, $C_\beta H$), 4.09 (t, 4 H, J = 6.3 Hz, $OC_\alpha H$), 6.96, 7.04 (m, 4 H, *m,m′* ArH), 7.51, 7.56 (m, 2 H, *p*-ArH), 7.82, 7.85 (m, 2 H, *o*-ArH); ^{13}C NMR ($CDCl_3$) δ 25.88, 28.86, 68.24, 112.35, 120.36, 124.75, 128.05, 135.81, 161.37, 189.70; Anal. calcd for $C_{21}H_{24}O_4$, C, 74.09; H, 7.11. Found: C, 73.84; H, 6.70.

1,8-Bis(2-formylphenoxy)octane (4). 5.4 g (75% yield); mp 63.5-64 °C; ^{1}H NMR ($CDCl_3$) δ 1.14, 1.27 (m, 4 H, $C_\delta H$), 1.42, 1.52 (m, 4 H, $C_\gamma H$), 1.82, 1.97 (m, 4 H, $C_\beta H$), 4.09 (t, J = 6.3 Hz, 4 H, $OC_\alpha H$), 6.97, 7.04 (m, 4 H, *m,m′*-ArH), 7.51, 7.57 (m, 2 H, *p*-ArH), 7.82, 7.85 (m, 2 H, *o*-ArH), 10.52 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 25.88, 28.95, 29.11, 68.31, 112.38, 120.36, 124.76, 128.09, 135.84, 161.43, 189.80; Anal. calcd for $C_{22}H_{26}O_4$, C, 74.55; H, 7.39. Found: C, 74.48; H, 7.28.

1,10-Bis(2-formylphenoxy)decane (5).[9]

Synthesis of m,m′-linked dialdehydes. Dialdehydes **6-10** were prepared using the KOH/ethanol method[8] and then recrystallized three times from ethanol to give tan colored compounds. Impurities in crude dialdehydes **9** and **10** gave one to two additional porphyrin components. These polar impurities were removed by flash chromatography (silica, CH_2Cl_2)[57] when recrystallization from ethanol did not yield pure products.

1,5-Bis(3-formylphenoxy)pentane (6). 3.7 g (58% yield); mp 55-56 °C; ^{1}H NMR ($CDCl_3$) δ 1.68, 1.72 (m, 2 H, $C_\gamma H$), 1.86, 1.95 (m, 4 H, $C_\beta H$), 4.06 (t, J = 6 Hz, 2 H, $OC_\alpha H$), 7.16, 7.20 (m, 2 H, ArH_3), 7.39 (m, 2 H, ArH_4) 7.44, 7.46 (m, 4 H, ArH_2, ArH_6), 9.97 (s, 2 H CHO); ^{13}C NMR ($CDCl_3$) δ 22.59, 28.72, 67.86, 112.61, 121.78, 123.30, 129.93, 137.68, 159.49, 192.06; Anal. calcd for $C_{19}H_{20}O_4$, C, 73.06; H, 6.45. Found: C, 73.05; H, 6.41.

1,6-Bis(3-formylphenoxy)hexane (7). 4.1 g (61% yield); mp 70.5-72.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.55, 1.59 (m, 4 H, $C_\gamma H$), 1.84, 1.88 (m, 4 H, $C_\beta H$), 4.04 (t, J = 6 Hz, 4 H, $OC_\alpha H$), 7.15, 7.19 (m, 2 H, ArH_3), 7.38, 7.39 (m, 2 H, ArH_4), (m, 4 H, ArH_2, ArH_6), 9.97 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 25.69, 28.92, 67.95, 112.61, 121.82, 123.27, 129.93, 137.65, 159.53, 192.10; Anal. calcd for $C_{20}H_{22}O_4$, C, 73.60; H, 6.79. Found: C, 73.54; H, 6.52.

1,7-Bis(3-formylphenoxy)heptane (8). 2.8 g (40% yield); mp 37-39 °C; ^{1}H NMR ($CDCl_3$) δ 1.48, 1.55 (m, 6 H, $C_\gamma H$, $C_\delta H$), 1.78, 1.88 (m, 4 H, $C_\beta H$), 4.03 (t, J = 6 Hz, 4 H, $OC_\alpha H$), 7.15, 7.19 (m, 2 H, ArH_3), 7.38, 7.39 (m, 2 H, ArH_4), 7.43, 7.45 (m, 4 H, ArH_2, ArH_6), 9.97 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ

25.85, 28.95, 68.08, 112.64, 121.85, 123.27, 129.93, 137.68, 159.59, 192.13; Anal. calcd for $C_{21}H_{24}O_4$, C, 74.09; H, 7.11. Found: C, 74.19; H, 7.06.

1,8-Bis(3-formylphenoxy)octane (9). 3.4 g (48% yield); mp 59-60 °C; ^{1}H NMR ($CDCl_3$) δ 1.41, 1.51 (m, 8 H, CγH, CδH), 1.77, 1.86 (m, 4 H, CβH), 4.02 (t, J = 6 Hz, 4 H, $OC_\alpha H$), 7.15, 7.19 (m, 2 H, ArH), 7.38, 7.45 (m, 6 H, ArH), 9.97 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 25.85, 29.02, 29.15, 68.11, 112.61, 121.85, 123.27, 129.93, 137.68, 159.59, 192.13; Anal. calcd for $C_{22}H_{26}O_4$, C, 74.55; H, 7.39. Found: C, 74.41; H, 7.41.

1,10-Bis(3-formylphenoxy)decane (10). 5.3 g (68% yield); mp 60-61 °C; ^{1}H NMR ($CDCl_3$) δ 1.34, 1.49 (m, 12 H, CγH, CδH, CεH), 1.76, 1.85 (m, 4 H, CβH) 4.01 (t, J = 6.6 Hz, 4 H, CαH), 7.15, 7.19 (m, 2 H, ArH_3), 7.38, 7.39 (m, 2 H, ArH_4), 7.43, 7.45 (m, 4 H, ArH_2, ArH_6), 9.97 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 25.88, 29.02, 29.24, 29.37, 68.18, 112.64, 121.85, 123.24, 129.90, 137.68, 159.62, 192.13; Anal. calcd for $C_{24}H_{30}O_4$, C, 75.36; H, 7.91. Found: C, 75.25; H, 7.63.

1,12-Bis(4-formylphenoxy)dodecane (11). 550 mg (55% yield); mp 70-72 °C; ^{1}H NMR ($CDCl_3$) δ 1.25, 1.49 (m, 16 H, $C_\gamma H_2$, $C_\delta H_2$, $C_e H_2$, $C_\zeta H_2$), 1.76, 1.86 (m, 4 H, $C_\beta H_2$), 4.04 (t, J = 6 Hz, 4 H, $OC_\alpha H$), 6.99 (AA'BB', 4 H, ArH), 7.82 (AA'BB', 4 H, ArH), 9.88 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 25.75, 28.86, 29.15, 29.34, 68.31, 114.55, 129.54, 131.77, 164.08, 190.61; $C_{26}H_{34}O_4$, calcd exact $(M+H)^+$ 411.2535, obsd m/z 411.2523 (FAB-MS).

1,4-Bis(3-formylphenoxy)xylene (12). Samples of 3-hydroxybenzaldehyde (778 mg, 6.37 mmol), α,α′-dibromo-*p*-xylene (7.85 mg, 297 mmol), 6 mL DMF, and KF (1.347 g, 23.2 mmol) were placed in a 25 mL one neck round bottom flask. The reaction mixture was placed in an oil bath preheated to 130 °C, yielding an orange reaction mixture. After 30 min 15 mL H_2O was added and the mixture was extracted with ether (2 x 20 mL). The combined ether extracts were dried (Na_2SO_4), and the solvent was evaporated to give an orange oil which yielded crystals upon standing. Recrystallization twice from ethanol gave an off-white powder. 325 mg (32% yield); mp 122-123 °C; ^{1}H NMR ($CDCl_3$) δ 5.14 (s, 4 H, CH_2), 7.23, 7.27 (m, 2 H, ArH), 7.43, 7.54 (m, 10 H, ArH), 9.98 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 69.73, 113.09, 122.08, 123.72, 127.73, 130.09, 136.26, 137.72, 159.11, 191.97; Anal. calcd for $C_{22}H_{18}O_4$, C, 76.29; H, 5.24. Found: C, 76.31; H, 5.30. This compound also was prepared by the method of Donahoe.[59]

m*-(Bromomethyl)benzaldehyde (13).** Into a dry 500 mL three neck round bottom flask was placed 75 mL CH_2Cl_2 (distilled from CaH_2) and 15.1 g α-bromo-*m*-tolunitrile (77 mmol). The flask was purged with a steady stream of N_2 and was immersed in an ice-water bath. A 100 mL solution of diisobutylaluminum hydride (1 M in hexanes, 100 mmol) was added dropwise over 3 h. After warming to room temperature the reaction mixture was poured slowly into a 600 mL beaker containing 400 g crushed ice and 75 mL 6 N HCl. After stirring for 1 h the phases were separated and the aqueous layer was extracted with ethyl acetate (2 x 75 mL). The organic extracts were combined, washed with 75 mL 5% $NaHCO_3$ and 75 mL brine, dried (Na_2SO_4), filtered, and concentrated. A clear liquid was obtained which solidified upon standing at 0 °C. 13.8 g (90% yield); mp 46-48 °C (lit mp, 36-37 °C);[60] ^{1}H NMR ($CDCl_3$) δ 4.54 (s, 2 H, CH_2), 7.5 , 7.6 (m, 1 H, ArH), 7.67 (d, J = 7.8 Hz, 1 H, ArH), 7.82 (d, J = 7.5 Hz, 1 H, ArH), 7.91 (s, 1 H, ArH), 10.02 (s, 1 H, CHO); IR (KBr) 2727 (m), 1700 (sh) cm^{-1}. ***Caution: **13** is a mild lachrymator in solid form, but a severe lachrymator when handled in volatile solvents. All manipulations of **13** should be performed in a well-ventilated hood.

(1,1-Dimethyl-3,5-dioxacyclohex-4-yl)-3-bromomethylbenzene (14). Samples of 3-(bromomethyl)benzaldehyde (**13**) (5.613 g, 28.2 mmol) and 2,2-dimethyl-1,3-propanediol (2.937 g, 28.2 mmol) were placed in a 250 mL one neck round bottom flask containing 140 mL CH_3CN and equipped with a distillation head. Upon dissolution of the starting materials, *p*-toluenesulfonic acid monohydrate (107 mg, 0.56 mmol) was added. The reaction vessel was placed in an oil bath at 120 °C. The solvent was distilled until a yellow oil remained in the vessel and no further distillate was obtained. After cooling to room temperature 50 mL 10% $NaHCO_3$ was added. The aqueous layer was decanted and the product was taken up in 75 mL CH_2Cl_2, which was subsequently washed with 50 mL brine, dried (Na_2SO_4), filtered, and concentrated. A yellow oil was obtained which gave an off-white solid upon standing at 0 °C. 6.88 g (86% yield); mp 70-72 °C; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 3.65 (d, J = 12 Hz, 2 H, OCH_2), 3.77 (d, J = 12 Hz, 2 H, OCH_2), 4.50 (s, 2 H, CH_2Br), 5.39 (s, 1 H, CH), 7.35, 7.54 (m, 4 H, ArH); IR (KBr) 3014 (m), 2854 (m) cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 21.78, 22.97, 30.15, 33.25, 101.10, 126.21, 126.66, 128.73, 129.48, 137.68, 139.04; Anal. calcd for $C_{13}H_{17}BrO_2$, C, 54.75; H, 6.01. Found: C, 55.07; H, 5.99. Note: This compound is not a lachrymatory agent.

***m*-Formylphenylacetic acid (15).**[61]

Bis(3-formylbenzyl)terephthalate (16). Terephthalic acid (831 mg, 5 mmol) was dissolved in 15 mL DMF at 130 °C. Anhydrous KF (2.556 g, 44 mmol), **13** (2.190 g, 11 mmol), and 5 mL DMF were added in succession. The mixture was stirred vigorously for 1 h at 130 °C, at which point the reaction was shown to be complete by TLC (silica, CH_2Cl_2/ethyl acetate 19:1). The mixture was diluted with 40 mL H_2O and extracted with ethyl acetate (3 x 25 mL). The combined extracts were washed with 40 mL brine, dried (Na_2SO_4), and concentrated to a white solid. 1.885 g (94% yield); mp 65-67 °C; ^1H NMR ($CDCl_3$) δ 5.46 (s, 4 H, OCH_2), 7.59 (m, 2 H, ArH), 7.73 (m, 2 H, ArH), 7.8 (m, 2 H, ArH), 7.97 (s, 2 H, ArH), 8.15 (s, 4 H, ArH), 10.05 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 66.21, 129.02, 129.38, 129.70, 129.80, 133.71, 134.00, 136.68, 136.81, 165.31, 191.84; Anal. calcd for $C_{24}H_{18}O_6$, C, 71.64; H, 4.51. Found: C, 71.23; H, 4.51.

1,4-Bis(3-formylbenzyl)phenylenediacetate (17). 1,4-Phenylenediacetic acid (971 mg, 5 mmol), **13** (2.190 g, 11 mmol), 20 mL DMF, and pulverized anhydrous KF (2.32 g, 40 mmol) were placed in a 25 mL round bottom flask and heated at 130 °C for 1 h. Then 25 mL H_2O was added and the solution was extracted with ethyl acetate (3 x 25 mL). The combined extracts were washed with 30 mL brine, dried (Na_2SO_4), and concentrated to an off-white solid. Recrystallization from pet ether/ethyl acetate gave a white powder. 1.722 g (80% yield); mp 74-77 °C; ^1H NMR ($CDCl_3$) δ 2.69 (s, 4 H, CH_2), 5.20 (s, 4 H, OCH_2), 7.26 (s, 4 H, ArH), 7.49, 7.58 (m, 4 H, ArH), 7.80, 7.84 (m, 4 H, ArH), 9.99 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 40.75, 65.59, 128.89, 129.05, 129.18, 129.35, 129.51, 132.58, 133.74, 136.94, 171.09, 191.94; Anal. calcd for $C_{26}H_{22}O_6$, C, 72.55; H, 5.15. Found: C, 72.52; H, 5.26.

2,2-Bis[4-(3-formylbenzyloxy)phenyl]propane (18). A sample of 4,4′-isopropylidenediphenol (2.5 g, 11 mmol) was dissolved in 35 mL DMF in a 50 mL one neck round bottom flask. The solution was cooled in an ice water bath and NaH (1.32 g, 33 mmol, 60% dispersion in white mineral oil, pre-washed with petroleum ether) was added in four portions over 30 min. Ten minutes after the final addition of NaH the reaction mixture was warmed to room temperature and then placed in an oil bath at 80 °C. This mixture was stirred at 80 °C for 45 min. (Initiation of the alkylation without heating the bisphenol alone in the presence of NaH consistently resulted in lower yields.) Then **14** (6.865 g, 24.1 mmol) was added in one portion and the mixture was stirred at 70 °C under a N_2 atmosphere overnight. The dark brown mixture was cooled to room temperature, poured into 50 mL H_2O, and extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with 75 mL

brine, dried (Na_2SO_4), and concentrated to a yellow oil. An off-white solid was obtained after drying *in vacuo*. 6.781 g (97% yield); mp 96-100 °C; ^1H NMR ($CDCl_3$) δ 0.81 (s, 6 H, CH_3), 1.30 (s, 6 H, CH_3), 1.63 (s, 6 H, $C(CH_3)_2$), 3.67 (d, J = 11 Hz, 4 H, CH_2), 3.76 (d, J = 11 Hz, 4 H, CH_2), 5.04 (s, 4 H, CH_2), 5.41 (s, 2 H, CH), 6.88 (AA'BB', 4 H, ArH), 7.12 (AA'BB', 4 H, ArH), 7.38, 7.48 (m, 6 H, ArH), 7.56 (s, 2 H, ArH).

The bis(acetal) from the previous step (6.73 g, 10.6 mmol) was dissolved in 30 mL CH_2Cl_2. A 30 mL solution of trifluoroacetic acid/H_2O (3:1) was added and the biphasic solution was stirred for two hours at room temperature. At this time TLC (silica, CH_2Cl_2/ethyl acetate 19:1) showed that no starting material remained. The mixture was diluted with 30 mL CH_2Cl_2, the phases were separated, and the aqueous layer was discarded. The organic layer was washed with 50 mL brine, 50 mL 5% $NaHCO_3$, dried (Na_2SO_4), and concentrated to a yellow oil. The solid obtained after drying *in vacuo* was recrystallized from pet ether/ethyl acetate, yielding 4.223 g (86% yield). mp 120-121 °C; ^1H NMR ($CDCl_3$) δ 1.64 (s, 6 H, $C(CH_3)_2$), 5.11 (s, 4 H, OCH_2), 6.90 (AA'BB', 4 H, ArH), 7.16 (AA'BB', 4 H, ArH), 7.53, 7.58 (m, 2H, ArH), 7.71 (m, 2 H, ArH) 7.84 (m, 2 H, ArH), 7.95 (s, 2 H, ArH), 10.04 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 30.92, 41.65, 69.05, 114.09, 127.76, 128.31, 129.22, 133.19, 136.55, 138.39, 143.60, 156.26, 192.06; Anal. calcd for $C_{31}H_{28}O_4$, C, 80.14; H, 6.09. Found: C, 79.97; H, 6.09.

Alternatively **18** was prepared directly by stirring **13** (4.817 g, 24.2 mmol, 2.2 equiv) and 4,4'-isopropylidenediphenol (2.5 g, 11 mmol) in the presence of K_2CO_3 (9.122 g, 66 mmol) in DMF at room temperature for 48 h. Flash chromatography (silica, CH_2Cl_2) gave 3.52 g (69% yield).

1,1'-Bis[(3-formylphenyl)methoxycarbonyl]ferrocene (19). Samples of 1,1'-ferrocenedicarboxylic acid (822 mg, 3 mmol) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (825 μL, 6 mmol) were added to 3 mL CH_3CN, giving a nearly homogeneous solution.[25] A solution of **13** (1.313 g, 6.6 mmol) in 5 mL of CH_3CN was added via a cannula. After stirring at room temperature under N_2 for 3 h, the reaction mixture was poured into 20 mL of H_2O and extracted with 3 x 10 mL CH_2Cl_2. The combined organic layers were washed with 2 x 20 mL of 10% Na_2CO_3 and 20 mL of brine. The organic layer was dried ($MgSO_4$), concentrated to dryness, and chromatographed on silica gel with a gradient from 4:1 CH_2Cl_2/hexanes to 50:1 CH_2Cl_2/methanol. Homogeneous product fractions were combined, concentrated to a thick oil and allowed to stand overnight in the freezer to solidify, affording 742 mg (48%) of a yellow-orange solid. mp 74-77 °C; ^1H NMR ($CDCl_3$) δ 4.35 (t, 4 H, *J* = 1.4 Hz, FcH), 4.82 (t, 4 H, *J* = 1.4 Hz, FcH), 5.32 (s, 4 H, CO_2CH_2Ar), 7.55 (t, *J* = 7.6 Hz, 2 H, ArH), 7.68 (d, *J* = 7.6 Hz, 2 H, ArH), 7.85 (d, *J* = 7.6 Hz, 2 H, ArH), 7.98 (s, 2 H, ArH), 10.0 (s, 2 H, CHO); ^{13}C NMR ($CDCl_3$) δ 65.14, 71.54, 72.83, 128.90, 129.22, 129.61, 133.97, 136.59, 137.46, 169.96, 191.90; IR 3114 (w), 2731 (w), 1720-1690 (br, s) cm^{-1}; Anal. calcd for $C_{28}H_{22}O_6Fe$, C, 65.89; H, 4.35. Found: C, 65.60; H, 4.21.

1,1'-Bis[(3-formylphenyl)acetoxy]ferrocene (20). 1,1'-Diiodoferrocene was prepared by suspending 1,1'-bis(chloromercuri)ferrocene[56] (2 g, 3.05 mmol) in 50 mL CH_2Cl_2 and cooled to 0 °C. A solution of *N*-iodosuccinimide (1.51 g, 6.71 mmol) in 150 mL CH_2Cl_2 was then added dropwise under N_2. The mixture was stirred overnight at room temperature, then quenched by the addition of 30 mL of 10% Na_2CO_3 and 30 mL of 10% $NaHSO_3$. The solids were removed via filtration through a pad of Celite. The layers were separated and the CH_2Cl_2 layer was washed with 50 mL of 10% Na_2CO_3, 50 mL H_2O, 50 mL brine, and dried ($MgSO_4$). Chromatography on silica gel (70-230 mesh, 10 x 2.5 cm) with hexanes afforded 479 mg (35%) of a red-brown oil. TLC (hexanes), R_f = 0.3. ^1H NMR δ 4.18 (A_2B_2, 4 H), 4.37 (A_2B_2, 4 H). This material was used without further purification. Following the method of Akabori,[26] samples of 1,1'-diiodoferrocene[62] (479 mg, 1.1 mmol), *m*-formylphenylacetic acid (430 mg, 2.6 mmol), and Cu_2O (189 mg, 1.32 mmol) were added to 10 mL of CH_3CN. The reaction mixture was refluxed 3 h under N_2. After cooling to room temperature, 20 mL diethyl ether was added and the solids were removed by filtration. The diethyl ether solution was washed with 2

x 20 mL of H_2O and dried over $MgSO_4$. The product was chromatographed by CTLC (2 mm, silica) with CH_2Cl_2 and 100:1 CH_2Cl_2/methanol, affording 115 mg (20%) of a light yellow oil. ^1H NMR ($CDCl_3$) δ 3.9 (s, 4 H, O_2CCH_2Ar), 4.0 (t, 4 H, FcH), 4.5 (t, 4 H, FcH), 7.6 (m, 4 H, ArH), 7.9 (m, 4 H, ArH), 10.0 (s, 2 H, CHO); IR 3100 (w), 2734 (m), 1757 (sh), 1700 (sh) cm^{-1}.

1,8-Bis(3-formylbenzoxy)-9,10-anthraquinone (21). A sample of 1,8-dihydroxyanthraquinone (0.913 g, 3.80 mmol) was dissolved in a minimal amount (5 mL) of DMF at 80 °C in a 25 mL flask. The flask was purged with nitrogen and immersed in an oil bath preheated to 80 °C. 6 equivalents of K_2CO_3 (3.13 g, 22.8 mmol) was added yielding a purple mixture. A solution of 0.190 g **13** (9.5 mmol) in 3 mL DMF was added. After 8 h at 80 °C, the red mixture was cooled to room temperature and 25 mL water was added. The aqueous layer was extracted with three 75 mL portions of ethyl acetate. The combined organic extracts were washed with 30 mL brine, dried (Na_2SO_4), and concentrated to a light brown solution. A small amount of silica gel 60 (70-230 mesh) was added and the resulting slurry was evaporated to dryness. The crude reaction material was placed on top of a silica column and chromatographed using CH_2Cl_2/ethyl acetate/hexane (10:1:1). Two yellow bands eluted with nearly complete resolution. The first band constituted only a small amount of the total product and was shown to be the mono-alkylated product by subsequent reaction with additional **13** and by ^1H NMR spectroscopy. Concentration of the second band afforded 1.60 g (86%) of a pale yellow solid. mp 195-200 °C; ^1H NMR ($CDCl_3$) δ 5.40 (s, 4 H, OCH_2), 7.39 (d, J = 8.1 Hz, 2 H, AQH), 7.55 (t, J = 7.6 Hz, 2 H, ArH), 7.65 (t, J = 8.1 Hz, 2 H, AQH), 7.86 (m, 4 H, AQH, ArH), 7.98 (d, J = 7.6, 2 H, AQH), 8.11 (s, 2 H, AQH), 10.0 (s, 2 H, CHO); Anal. calcd for $C_{30}H_{20}O_6$, C, 75.62; H, 4.23. Found: C, 75.36; H, 4.40.

Synthesis of alkoxy-linked o,o′-strapped porphyrins (22-26). Preparative reactions were run on 50 mL scale at room temperature in $CHCl_3$ with reactant concentrations (pyrrole, [CHO]) at 10^{-2} M and with 10^{-3} M $BF_3{\cdot}O(Et)_2$ catalysis. The synthesis of **22** is exemplary.

***o,o′*-C_5-strapped porphyrin (22).**[8] Samples of 1,5-bis(2-formylphenoxy)pentane **1** (78 mg, 0.25 mmol) and pyrrole (35 μL, 0.5 mmol, 10^{-2} M) were dissolved in 50 mL $CHCl_3$ in a 100 mL one neck round bottom flask. Then $BF_3{\cdot}O(Et)_2$ (66 μL of 2.5 M solution in $CHCl_3$, 0.165 mmol, 3.3 mM) was added to initiate the room temperature condensation forming the porphyrinogen. After 1 h DDQ (85 mg, 0.375 mmol, 3/4 equiv per pyrrole) was added in powder form to oxidize the porphyrinogen to the porphyrin. After 1 h at room temperature the solution was concentrated to half its original volume. TLC analysis (silica, CH_2Cl_2) showed two porphyrin components which were not GT-active. Then triethylamine (23 μL, 0.165 mmol, 1 equiv) and 750 mg Florisil were added and the mixture was concentrated to a dry powder. The powder was placed on top of a dry alumina column (1 x 15 cm) and chromatography was initiated with CH_2Cl_2. Three fractions were combined, giving 12 mg (12% yield) of a mixture of cisαβ- and cisαα-strapped porphyrins. Analytical HPLC (hexane/ethyl acetate 9:1) showed the cisαβ- (t_R, 13.7 min) and cisαα- (t_R, 16.4 min) strapped porphyrins with baseline resolution in a 1:2.5 ratio, respectively. Separation by semi-preparative HPLC (CH_2Cl_2) gave the cisαβ- and cisαα-strapped porphyrins in 2.0 and 4.4% yield (based on pyrrole), respectively. cisαβ-strapped porphyrin ^1H NMR ($CDCl_3$) δ -2.56 (s, 2 H, NH), 0.52, 0.69 (m, 8 H, CH_2), 0.93, 1.02 (m, 4 H, CH_2), 3.74, 3.92 (m, 8 H, CH_2), 7.16 (m, 4 H, ArH), 7.41, 7.46 (m, 4 H, ArH), 7.71, 7.76 (m, 4 H, ArH), 8.35 (m, 4 H, ArH), 8.67 (s, 4 H, β-pyrrole), 9.04 (s, 4 H, β-pyrrole). cisαα-strapped porphyrin ^1H NMR ($CDCl_3$) δ -2.52 (bs, 2 H, NH), 0.70, 0.94 (m, 8 H, CH_2), 1.03, 1.14 (m, 4 H, CH_2), 3.84, 3.98 (m, 8 H, CH_2), 7.20 (m, 4 H, ArH), 7.38, 7.43 (m, 4 H, ArH), 7.71, 7.76 (m, 4 H, ArH), 8.29, 8.32 (m, 4 H, ArH_6), 8.68 (s, 4 H, β-pyrrole), 8.69 (s, 4 H, β-pyrrole); $C_{54}H_{46}N_4O_4$, calcd exact mass 814.4, obsd m/z 814.4 (PDMS); combined λ_{abs} 424 (fwhm = 12 nm), 518, 558, 594, 648 nm; λ_{em} 657, 719 nm.

***o,o'*-C_6 Strapped porphyrin (23).**[8] A mixture of 16 mg (15% yield) cisαβ and cisαα isomers was obtained. There were no GT-active components. HPLC (hexane/ethyl acetate 19:1) showed cisαα- (t_R, 14.2 min) and cisαβ- (t_R, 19.7 min) strapped porphyrins with baseline resolution in a 1:5.0 ratio, respectively. The amount of trans product was estimated to be <1% of the total porphyrins by ^{1}H NMR. ^{1}H NMR (mixture of isomers; in $CDCl_3$) δ -2.59 (bs, NH), -2.54 (bs, NH), 0.19 (m, CH_2), 0.45, 0.56 (m, CH_2), 0.63, 0.71 (m, CH_2), 0.85, 0.97 (m, CH_2), 1.18, 1.23 (m, CH_2), 3.61, 3.66 (m, CH_2), 3.80, 3.84 (m, CH_2), 7.30, 7.44 (m, ArH), 7.70, 7.76 (m, ArH), 8.12, 8.15 (m, ArH_6, cisαα), 8.19, 8.22 (m, ArH_6, cisαβ), 8.68 (s, β-pyrrole), 8.78 (s, β-pyrrole), 8.91 (s, β-pyrrole); combined λ_{abs} 420, 516, 548, 592, 646 nm; λ_{em} 650, 715 nm.

***o,o'*-C_7 Strapped porphyrin (24).** After preliminary purification, TLC (silica, CH_2Cl_2) showed three porphyrins and the most polar (estimated 5% of the total porphyrins) was GT-active. Purification on centrifugal TLC (1 mm silica rotor, CH_2Cl_2) gave 28 mg (26% yield) of a mixture of cisαβ- and cisαα-strapped porphyrins. HPLC (hexane/ethyl acetate 19:1) showed partially-overlapping cisαβ- (t_R, 11.1 min) and cisαα- (t_R, 12.3 min) strapped porphyrins with an estimated ratio of 1:4.0, respectively. ^{1}H NMR (mixture of isomers; in $CDCl_3$) δ -2.68 (bs, NH), 0.41, 0.10 (m, CH_2), 0.10, 0.22 (m, CH_2), 0.40, 0.58 (m, CH_2), 0.71, 0.96 (m, CH_2), 1.04, 1.16 (m, CH_2), 3.83, 3.89 (m, CH_2), 4.01, 4.10 (m, CH_2), 7.24, 7.32 (m, ArH), 7.68, 7.32 (m, ArH), 7.87, 7.90 (m, ArH_6, cisαα), 7.97, 8.00 (m, ArH_6, cisαβ), 8.67 (s, β-pyrrole), 8.73 (s, β-pyrrole), 8.75 (s, β-pyrrole); $C_{58}H_{54}N_4O_4$, calcd exact mass 870.4, obsd m/z 870.5 (PDMS); calcd exact $(M+H)^+$ 871.4223, obsd m/z 871.4229 (FAB-MS); combined λ_{abs} 418, 514, 546, 588, 642 nm; λ_{em} 646, 712 nm.

***o,o'*-C_8 Strapped porphyrin (25).** After preliminary purification, TLC (silica, CH_2Cl_2) showed three well-resolved porphyrins; the most polar (estimated 5% of the total porphyrins) was GT-active. Purification on centrifugal TLC (1 mm silica rotor, CH_2Cl_2) gave 26 mg (23% yield) of a mixture of cisαβ- and cisαα-strapped porphyrins. HPLC (hexane/ethyl acetate 99:1) showed cisαβ- (t_R, 30.3 min) and cisαα- (t_R, 31.2 min) strapped porphyrins with partial resolution. The amount of trans-strapped porphyrin was estimated to be <1% of the total porphyrins by ^{1}H NMR. ^{1}H NMR (mixture of isomers; in $CDCl_3$) δ -2.66 (bs, NH), -2.63 (bs, NH), 0.10, 0.20 (m, CH_2), 0.35, 0.38 (m, CH_2), 0.46, 0.56 (m, CH_2), 0.90, 1.01 (m, CH_2), 1.22, 1.39 (m, CH_2), 3.89, 4.02 (m, CH_2), 4.02, 4.08 (m, CH_2), 7.24, 7.32 (m, ArH), 7.68, 7.73 (m, ArH), 7.84, 7.86 (m, ArH_6, cisαα), 7.89, 7.92 (m, ArH_6, cisαβ), 8.71 (s, β-pyrrole), 8.72 (s, β-pyrrole), 8.74 (s, β-pyrrole); $C_{60}H_{58}N_4O_4$, calcd exact mass 898.4, obsd m/z 898.6 (PDMS); calcd exact $(M+H)^+$ 899.4536, obsd m/z 899.4526 (FAB-MS); combined λ_{abs} 418, 514, 546, 588, 642 nm; λ_{em} 645, 712 nm.

***o,o'*-C_{10} Strapped porphyrin (26).**[1] A mixture of 39 mg (33% yield) of cisαβ- and cisαα-strapped porphyrins was isolated. The amount of trans isomer is <1% of the total porphyrins as estimated by ^{1}H NMR. ^{1}H NMR (mixture of isomers; in $CDCl_3$) δ -2.61 (bs, NH), -0.65, -0.61 (m, CH_2), -0.54, -0.53 (m, CH_2), -0.13 (m, CH_2), 0.05, 0.06 (m, CH_2), 0.18, 0.23 (m, CH_2), 0.90, 0.96 (m, CH_2), 1.05, 1.13 (m, CH_2), 3.87, 4.01 (m, CH_2), 7.27, 7.34 (m, ArH), 7.68, 7.74 (m, ArH), 7.90, 7.93 (m, ArH_6), 8.70 (s, β-pyrrole), 8.72 (s, β-pyrrole), 8.75 (s, β-pyrrole); $C_{64}H_{66}N_4O_4$ calcd exact mass 954.5, obsd m/z 955.4 (PDMS); combined λ_{abs} 418, 514, 548, 590, 644 nm; λ_{em} 650, 716 nm.

Thermal isomerization studies of o,o'-alkoxy strapped porphyrins. A small amount (5 mg) of porphyrin was placed in a 15 mL one-neck round bottom flask and dissolved in 5 mL of toluene under a nitrogen atmosphere. The flask was placed in an oil bath at 115 °C. The isomerization times for the strapped porphyrins were **22** (overnight); **23** (2 h); **24** and **25** (7 h). TLC analysis at the end of the reaction showed that no decomposition had occurred. The mixtures were then analyzed by HPLC and ^{1}H NMR spectroscopy (Table 5).

Synthesis of m,m'-Strapped Porphyrins (27-35). Preparative reactions were run on 100 mL scale at room temperature in CH_2Cl_2 with reactant concentrations (pyrrole, [CHO]) at 10^{-2} M and with 10^{-3} M $BF_3{\cdot}O(Et)_2$ catalysis. Chromatography on alumina gave porphyrins freed of black pigments and unreacted starting material, in contrast with chromatography on silica (CH_2Cl_2), which was unsuccessful and required recrystallization from CH_2Cl_2/methanol to remove these contaminants. In each synthesis the reaction vessel was coated with a thin black film that required treatment with a mixture of chromic and sulfuric acids for removal. The synthesis of **27** is exemplary.

***m,m'*-C_5 Strapped porphyrin (27).** Samples of 1,6-bis(3-formylphenoxy)pentane **6** (156 mg, 0.5 mmol) and pyrrole (69 μL, 1 mmol) were dissolved in 100 mL CH_2Cl_2 in a 250 mL round bottom flask. After the starting materials had dissolved $BF_3{\cdot}O(Et)_2$ (40 μL of a 2.5 M solution in CH_2Cl_2, 10^{-3} M) was added to initiate the room temperature condensation. After 1 h *p*-chloranil (184 mg, 0.75 mmol) was added and the reaction vessel was placed in an oil bath at 40 °C. Triethylamine (14 μl, 0.1 mmol, 1 equiv) was added after 1 h and the reaction mixture was concentrated to approximately 10 mL. The mixture was chromatographed on dry alumina (2.5 x 15 cm, CH_2Cl_2). The porphyrin eluted first as a broad band free of unreacted starting material and black pigments, affording 11 mg (5.4% yield). TLC analysis (silica with CH_2Cl_2, CH_2Cl_2/petroleum ether 2:1 and 3:1, CH_2Cl_2/ethyl acetate 19:1, CH_2Cl_2/toluene 2:1 and 3:1, CH_2Cl_2/benzene 2:1 and 3:1, toluene/cyclohexane 3:1, and toluene; alumina with CH_2Cl_2/toluene 1:1 and CH_2Cl_2/cyclohexane 1:1) of the purified product showed only one porphyrin component. No GT-active components were observed. HPLC (hexane/ethyl acetate 9:1) showed one porphyrin band (t_R, 13.4 min). ^{1}H NMR ($CDCl_3$, 620.2 MHz) δ 0.93, 1.05 (m, 2 H, $C_\gamma H_6$), 1.24, 1.38 (m, 2 H, $C_\gamma H_5$), 2.05, 2.18 (m, 4 H, $C_\beta H_3$), 2.63, 2.75 (m, 4 H, $C_\beta H_4$), 4.00, 4.10 (m, 4 H, $C_\alpha H_2$), 4.23, 4.33 (m, 4 H, $C_\alpha H_1$) 7.31, 7.35 (m 4 H, ArH_4), 7.40 (s, J_{26} = 1.4 Hz, J_{24} = 2.64 Hz, 4 H, ArH_2), 7.78, 7.83 (m, J_{56} = 7.20 Hz, J_{45} = 8.40 Hz, 4 H, ArH_5), 8.34, 8.37 (m, J_{46} = 0.97 Hz, 4 H, ArH_6), 8.45 (s, 4 H, β-pyrrole), 9.20 (s, 4 H, β-pyrrole); $C_{54}H_{46}N_4O_4$, calcd exact mass 814.4, obsd m/z 814.4 (PDMS); calcd exact $(M+H)^+$ 815.3597, obsd m/z 815.3605 (FAB-MS); λ_{abs} 430, 528, 568, 606, 666 nm; λ_{em} 678, 725-758 nm.

***m,m'*-C_6 Strapped porphyrin (28).** 11 mg (5.2% yield). HPLC (hexane/ethyl acetate 9:1) showed one porphyrin band (t_R, 9.0 min). ^{1}H NMR ($CDCl_3$) δ -2.50 (s, 2 H, NH), 1.54, 1.64 (m, 8 H , $C_\gamma H_{5,6}$), 1.85, 1.90 (m, 4 H, $C_\beta H_3$), 2,41, 2.43 (m, 4 H, $C_\beta H_4$), 4.08, 4.17 (m, 4 H, $C_\alpha H_2$), 4.32, 4.41 (m, 4 H, $C_\alpha H_1$), 7.32, 7.35 (m, 4 H, ArH_4), 7.67 (s, 4 H, ArH_2), 7.75, 7.80 (m, 4 H, ArH_5), 8.29, 8.32 (m, 4 H, ArH_6), 8.55 (s, 4 H, β-pyrrole), 9.18 (s, 4 H, β-pyrrole); $C_{56}H_{50}N_4O_4$, calcd exact mass 842.4; obsd m/z 842.4 (PDMS); calcd exact $(M+H)^+$ 843.3910, obsd m/z 843.3959 (FAB-MS); λ_{abs} 428, 526, 564, 600, 660 nm; λ_{em} 672, 719-750 nm.

***m,m'*-C_7 Strapped porphyrin (29).** 28 mg (13% yield). HPLC (hexane/ethyl acetate 9:1) showed one porphyrin band (t_R, 7.4 min). ^{1}H NMR ($CDCl_3$) δ -2.63 (bs, 2 H, NH), 1.26, 1.62 (m, 12 H, $C_\gamma H_{5,6}$, $C_\delta H_{7,8}$), 2.00, 2.03 (m, 4 H, $C_\beta H_3$), 2.12, 2.19 (m, 4 H, $C_\beta H_4$), 4.13, 4.21 (m, 4 H, $C_\alpha H_2$), 4.31, 4.39 (m 4 H, $C_\alpha H_1$), 7.36, 7.40 (m, 4 H, ArH_4), 7.73, 7.78 (m, 8 H, $ArH_{2,5}$), 8.18, 8.20 (m, 4 H, ArH_6), 8.72 (s, 4 H, β-pyrrole), 9.14 (s, 4 H, β-pyrrole); $C_{58}H_{54}N_4O_4$ calcd exact mass 870.4, obsd m/z 870.4 (PDMS); calcd exact $(M+H)^+$ 871.4223, obsd m/z 871.4235 (FAB-MS); λ_{abs} 424, 522, 560, 596, 654 nm; λ_{em} 664, 725 nm.

***m,m'*-C_8 Strapped porphyrin (30).** 26 mg (12% yield). Scaling up to a 1 L reaction gave 133 mg porphyrin (5.9% yield) after chromatography (alumina, CH_2Cl_2). HPLC (hexane/ethyl acetate 19:1) showed one porphyrin band (t_R, 5.6 min). ^{1}H NMR ($CDCl_3$) δ -2.79 (bs, NH), -2.76 (bs, NH), 1.39, 1.58 (m, 16 H, $C_\gamma H_{5,6}$, $C_\delta H_{7,8}$), 1.79, 1.89 (m, 4 H, $C_\beta H_3$), 2.12, 2.18 (m, 4 H, $C_\beta H_4$), 4.11, 4.20 (m, 4 H, $C_\alpha H_2$), 4.34,

4.43 (m, 4 H, $C_{\alpha}H_1$), 7.33, 7.35 (m, ArH_4), 7.66, 7.71 (m, ArH_5), 7.75 (s, ArH_2), 7.81 (s, ArH_6), 7.91, 7.93 (m, ArH_6), 7.98, 8.01 (m, ArH_6), 8.83 (s, β-pyrrole), 9.04 (s, β-pyrrole), 9.20 (s, β-pyrrole); $C_{60}H_{58}N_4O_4$, calcd exact mass 898.4, obsd m/z 898.4 (PDMS); calcd exact $(M+H)^+$ 899.4536, obsd m/z 899.4538 (FAB-MS); λ_{abs} 422, 518, 554, 594, 648 nm; λ_{em} 652, 717 nm.

***m,m'*-C_{10} Strapped porphyrin (31).** 12 mg (5.0% yield). HPLC (hexane/ethyl acetate 19:1) showed one porphyrin band (t_R, 7.4 min). ^1H NMR ($CDCl_3$) δ -2.78 (bs, 2 H, NH), 1.25, 1.47 (m, 24 H, CH_2), 1.83, 1.92 (m, 4 H, CH_2) 1.95, 2.02 (m, 4 H, CH_2), 4.08, 4.16 (m, 4 H, CH_2), 4.26, 4.36 (m, 4 H, CH_2), 7.30, 7.35 (m, 4 H, ArH), 7.64, 7.69 (m, 4 H, ArH), 7.79 (s, 4 H, ArH), 8.81 (s, 4 H, β-pyrrole), 8.98 (s, 2 H, β-pyrrole), 9.06 (s, 2 H, β-pyrrole); $C_{64}H_{66}N_4O_4$ calcd exact mass 954.5, obsd m/z 954.6 (PDMS); calcd exact $(M+H)^+$ 955.5162, obsd m/z 955.5140 (FAB-MS); λ_{abs} 420, 516, 552,590, 646 nm; λ_{em} 650, 718 nm.

1,4-Xylyl strapped porphyrin (32). From dialdehyde **12**. The spectroscopic yield using TFA catalysis was 3.7%. TLC analysis showed only one porphyrin component. No GT-active components were observed. Two silica columns were required for preliminary purification. Insufficient material was obtained for characterization.

Terephthalate strapped porphyrin (33). The reaction of **16** (325 mg, 0.81 mmol) and pyrrole (112 μL, 1.62 mmol) in 132 mL $CHCl_3$ was initiated by addition of $BF_3{\cdot}O(Et)_2$ (211 μL of 2.5 M solution in $CHCl_3$, 3.3 mM). After 1 h DDQ (276 mg, 1.22 mmol) was added, and after oxidation for 1 h at room temperature, the volume was reduced to 25 mL and then passed through a plug of silica on a fritted funnel under aspirator vacuum (3.5 x 6.5 cm, CH_2Cl_2/ethyl acetate 19:1). Column chromatography on silica (2 x 10 cm, CH_2Cl_2 enriched with ethyl acetate) gave the porphyrin as a tight band (3 mg, 0.8% yield). ^1H NMR ($CDCl_3$) δ -3.00 (bs, 2 H, NH), 7.05 (s, 8 H, CH_2), 7.70, 7.75 (m, 8 H, ArH), 8.09, 8.32 (m, 16 H, ArH), 8.70, 9.00 (m, 8 H, β-pyrrole); $C_{64}H_{42}N_4O_8$ calcd exact mass 994.3, obsd m/z 994.8 (PDMS); calcd exact $(M+H)^+$ 995.3081, obsd m/z 995.3061 (FAB-MS); λ_{abs} 420, 516, 544, 596, 650 nm; λ_{em} 650, 715 nm.

1,4-Phenylenediacetic acid strapped porphyrin (34). The reaction of dialdehyde **17** at 100 mL scale afforded 39 mg (15% yield) following chromatography (alumina, CH_2Cl_2/ethyl acetate 19:1). ^1H NMR ($CDCl_3$) δ -2.76 (bs, 2 H, NH), 3.67 (s, 8 H, CH_2), 5.19 (s, 8 H, CH_2), 7.28, 7.29 (m, 4 H, ArH), 7.46, 7.56 (m, 8 H, ArH), 7.75, 7.82 (m, 12 H, ArH), 8.85, 8.95 (m, 8 H, β-pyrrole); $C_{68}H_{50}N_4O_8$ calcd exact mass 1050.4, obsd m/z 1050.5 (PDMS); calcd exact $(M+H)^+$ 1051.3707, obsd m/z 1051.3696 (FAB-MS); λ_{abs} 420, 514, 544, 594, 648 nm; λ_{em} 650, 714 nm.

Bisphenol-strapped porphyrin (35). The reaction of 2,2-bis[4-(3-formylbenzyloxy)phenyl]propane (**18**) (232 mg, 0.5 mmol) and pyrrole (69 μL, 1 mmol) in 100 mL CH_2Cl_2 was initiated by addition of $BF_3{\cdot}O(Et)_2$ (40 μL of 2.5 M solution in CH_2Cl_2, 10^{-3} M). After 1 h *p*-chloranil (184 mg, 0.75 mmol) was added, and after oxidation for 1 h at 45 °C, the mixture was concentrated to a damp powder and then chromatographed on silica (2.5 x 20 cm, CH_2Cl_2). The porphyrin eluted as a tight band with CH_2Cl_2 (70 mg, 25% yield). ^1H NMR ($CDCl_3$) δ -2.93, -2.85 (m, 2 NH), 1.63, 1.71 (m, 12 H, CH_3), 5.39, 5.58 (m, 8 H, CH_2), 6.97, 7.30 (m, 16 H, ArH), 7.67, 7.91 (m, 8 H, ArH), 8.14, 8.45 (m, 8 H, ArH), 8.81, 8.90 (m, 8 H, β-pyrrole); $C_{78}H_{62}N_4O_4$ calcd avg mass 1119.3, obsd m/z 1119.6 (PDMS); calcd exact $(M+H)^+$ 1119.4849, obsd m/z 1119.4851 (FAB-MS); λ_{abs} 419, 516, 550, 590, 646 nm; λ_{em} 650, 714 nm. The zinc chelate $C_{78}H_{60}N_4O_4Zn$ gave calcd avg mass 1182.7, obsd m/z 1182.4.

Ferrocenyl (Fc)-strapped porphyrin (36). Samples of ferrocene dialdehyde **19** (128 mg, 0.25 mmol, 5 mM) and pyrrole (35 μL, 0.5 mmol) were added to 20 mL CH_2Cl_2. TFA (77 μL, 1.0 mmol) was added and the solution was stirred at room temperature under nitrogen for 45 min. *p*-Chloranil (92 mg, 0.38 mmol) was then added and stirring was continued for 1 h. The reaction mixture was neutralized with 150 μL triethylamine and the porphyrin was isolated by column chromatography on silica gel with a gradient of CH_2Cl_2 to CH_2Cl_2/ethyl acetate (10:1). The fractions containing product were concentrated to dryness and washed with methanol. The purple solid was collected by filtration and chromatographed by CTLC (2 mm silica, 10:1 CH_2Cl_2/ethyl acetate). The purple solid was washed with methanol and collected by filtration, yielding 31 mg (21%). ^1H NMR ($CDCl_3$) δ -2.64 (s, 2 H, NH), 4.44-4.55 (m, 8 H, FcH), 4.95-5.05 (m, 4 H, FcH), 5.15-5.25 (m, 4 H, FcH), 5.47 (d, J = 13 Hz, 4 H, $ArCH_2O$), 5.60 (d, J = 13 Hz, 4 H, $ArCH_2O$), 7.75 (d, J = 8 Hz, 4 H, ArH), 7.88 (t, J = 8 Hz, 4 H, ArH), 8.40 (d, J = 8 Hz, 2 H, ArH), 8.50 (d, J = 8 Hz, 2 H, ArH), 8.56 (s, 4 H, ArH), 8.95-9.40 (m, 8 H, β-pyrrole); $C_{72}H_{50}Fe_2N_4O_8$, calcd avg mass 1210.8, obsd m/z 1211.7 (PDMS); calcd exact $(M+H)^+$ 1211.2406, obsd m/z 1211.2361 (FAB-MS); λ_{abs} (n-PrCN) 420, 518, 552, 594, 650 nm.

Ferrocenyl (Fc')-strapped porphyrin (37). Samples of ferrocene dialdehyde **20** (115 mg, 0.225 mmol) and pyrrole (31 μL, 0.45 mmol) in 45 mL CH_2Cl_2 were reacted following the procedure for porphyrin **36**. Column chromatography with 20:1 CH_2Cl_2/ethyl acetate afforded 13 mg (9%) porphyrin. ^1H NMR δ -2.70 (m, 1 H, NH), 3.80-4.20 (m, 16 H, CH_2Ar, FcH), 4.30-4.50 (m, 4 H, FcH), 4.60-4.80 (m, 4 H, FcH), 7.65-7.90 (m, 8 H, ArH), 8.10-8.50 (m, 8 H, ArH), 8.90-9.10 (m, 8 H, β-pyrrole); $C_{72}H_{50}Fe_2N_4O_8$, calcd avg mass 1210.8, obsd m/z 1211.8 (PDMS); calcd exact $(M+H)^+$ 1211.2406, obsd m/z 1211.2374 (FAB-MS); λ_{abs} 418, 516, 550, 590, 646 nm.

(C_8,Fc)-strapped porphyrin (38). Samples of 1,8-bis(3-formylphenoxy) octane (**9**) (443 mg, 1.25 mmol), 1,1′-bis[(3-formylphenyl)methoxycarbonyl]ferrocene (**19**) (603 mg, 1.25 mmol), and pyrrole (347 μL, 5 mmol) were condensed in 500 mL of CH_2Cl_2 with trifluoroacetic acid (770 μL, 10 mmol). After 1 h (32% spectroscopic yield) DDQ (851 mg, 3.75 mmol) was added and the oxidation was allowed to proceed for 30 min. Triethylamine (1.40 mL, 10 mmol) was added to neutralize the solution, the solvent was removed, and the residue was dissolved in 25 mL CH_2Cl_2 and chromatographed on silica gel. The porphyrin components eluted quickly with CH_2Cl_2/ethyl acetate (20:1). TLC analysis showed three porphyrin components which were purified by CTLC (4 mm rotor, silica). Chromatography with CH_2Cl_2 cleanly eluted **30** (19.8 mg, 1.8%) from all other components which were bound at the origin. Subsequent gradients (50:1 and 20:1 CH_2Cl_2/ethyl acetate) separated porphyrins **38** (85.8 mg, 6.5%) and **36** (50.3 mg, 3.3%), respectively. ^1H NMR ($CDCl_3$) δ -2.35 (s, 2 H, NH), 1.35, 1.60 (m, 8 H, $C_\gamma H_2$, $C_\delta H_2$), 1.80, 1.90 (m, 2 H, $C_\beta H_2$), 2.15 (m, 2 H, $C_\beta H_2$), 4.15 (m, 2 H, OCH_2R), 4.40, 4.60 (m, 6 H, FcH, OCH_2R), 5.00 (s, 2 H, FcH), 5.20 (s, 2 H, FcH), 5.55 (q, 4 H, OCH_2), 7.35 (m, 2 H, ArH), 7.68, 7.88 (m, 6 H, ArH), 8.02 (d, J = 7.3, 2 H, ArH), 8.46 (d, J = 7.5 Hz, 2 H, ArH), 8.56 (s, 2 H, ArH), 8.85, 9.08 (m, 8 H, β-pyrrole H); $C_{66}H_{54}FeN_4O_6$, calcd avg mass 1054.9, obsd m/z 1055.0 (PDMS); calcd exact $(M+H)^+$ 1055.3471, obsd m/z 1055.3467 (FAB-MS); λ_{abs} ($CHCl_3$), 424 (fwhm 12 nm), 520, 556, 596, 652 nm.

(C_8,AQ)-strapped porphyrin (39). Samples of 1,8-bis(3-formylphenoxy)octane (**9**) (443 mg, 1.25 mmol), 1,8-bis(3-formylbenzoxy)-9,10-anthraquinone (**21**) (596 mg, 1.25 mmol), and pyrrole (347 μL, 5 mmol) were dissolved in 500 mL of CH_2Cl_2 with trifluoroacetic acid (770 μL, 10 mmol). After 1 h (26% spectroscopic yield) DDQ (851 mg, 3.75 mmol) was added and the oxidation was allowed to proceed for 30 min. Triethylamine (1.40 mL, 10 mmol) was added to neutralize the solution, the solvent was removed, and the residue was dissolved in 25 mL CH_2Cl_2 and chromatographed on silica gel. The C_8-strapped porphyrin (**30**) and the (AQ-C_8)-strapped porphyrin eluted quickly with CH_2Cl_2/ethyl acetate (10:1). TLC analysis showed two

major porphyrin components which were purified by CTLC (2 mm silica rotor). Chromatography with CH_2Cl_2/hexane (50:1) eluted **30**, leaving the (AQ,C_8)-strapped porphyrin bound at the origin. After **30** eluted (22.5 mg, 2.0% yield), several other species were eluted with CH_2Cl_2/hexane (50:1), then CH_2Cl_2/ethyl acetate (20:1) was used to elute **39** (51.0 mg, 4.0% yield). ^{1}H NMR ($CDCl_3$) δ -2.25 (s, 2 H, NH), 1.40, 1.60 (m, 8 H, $C_\gamma H_2$, $C_\delta H_2$), 1.90 (m, 2 H, $C_\beta H_2$), 2.15 (m, 2 H, $C_{\beta'} H_2$), 4.15 (m, 2 H, OCH_2R), 4.40 (m, 2 H, OCH_2R), 5.85 (q, 4 H, OCH_2Ar), 7.32 (m, 2 H, ArH), 7.46, 7.51 (m, 4 H, ArH), 7.62, 7.79 (m, 6 H, ArH), 7.90, 7.98 (m, 4 H, ArH), 8.27 (bs, 2 H, β-pyrrole H), 8.40 (bs, 2 H, β-pyrrole H), 8.70 (d, J = 7.7 Hz, 2 H, ArH), 8.74 (s, 2 H, ArH), 8.91 (d, J = 4.6 Hz, 2 H, β-pyrrole), 9.05 (d, J = 4.6 Hz, 2 H, β-pyrrole); $C_{68}H_{52}N_4O_6$, calcd exact mass 1020.4, obsd m/z 1020.5 (PDMS); calcd exact $(M+H)^+$ 1021.3965, obsd m/z 1021.3962 (FAB-MS); λ_{abs} ($CHCl_3$) 428 (fwhm 15 nm), 526, 564, 600, 656 nm.

(Fc,AQ)-strapped porphyrin (40). Samples of 328 mg 1,8-bis(3-formylbenzoxy)-9,10-anthraquinone (**21**) (0.688 mmol, 2.5 mM), 332 mg 1,1′-bis[(3-formylphenyl)methoxycarbonyl]ferrocene (**19**) (0.688 mmol, 2.5 mM), and pyrrole (191 μL, 2.75 mmol, 10^{-2} M) were dissolved in 275 mL CH_2Cl_2 in a 500 mL round bottom flask. Trifluoroacetic acid (424 μL, 5.5 mmol, 2 x 10^{-2} M) was added to initiate porphyrinogen formation and the reaction was allowed to proceed at room temperature. After 1 h (31% spectroscopic yield), 469 mg DDQ (2.06 mmol, 7.5 x 10^{-3} M) was added and the oxidation was allowed to proceed for 30 min. Triethylamine (767 μL, 5.5 mmol) was added to neutralize the solution, the solvent was removed, and the residue was dissolved in 20 mL CH_2Cl_2 and chromatographed on silica gel. The porphyrin components eluted quickly with CH_2Cl_2/ethyl acetate (5:1). Purification by CTLC (2 mm silica rotor, CH_2Cl_2/ethyl acetate (15:1)) gave 35.6 mg (4.3%) of **36** and 29.7 mg (3.7%) of **40**. ^{1}H NMR ($CDCl_3$) δ -2.35 (s, 2H, NH), 4.40 (s, 2 H, FcH), 4.50 (s, 2 H, FcH), 4.90 (s, 2 H, FcH), 5.15 (s, 2 H, FcH), 5.50 (q, 4 H, OCH_2), 5.75 (s, 4 H, OCH_2), 7.49, 7.55 (m, 4 H, ArH), 7.66 (d, J = 6.6 Hz, 2 H, ArH), 7.73 (d, J = 7.1 Hz, 2 H, ArH), 7.80, 7.88 (m, 4 H, ArH), 7.94 (t, J = 7.6 Hz, 2 H, ArH), 8.33 (s, 2 H, β-pyrrole), 8.43 (d, J = 7.6 Hz, 2 H, ArH), 8.50 (m, 4 H, β-pyrrole, ArH), 8.74 (d, J = 7.2 Hz, 2 H, ArH), 8.93 (m, 4 H, β-pyrrole, ArH), 9.09 (d, 2 H, β-pyrrole); $C_{74}H_{48}FeN_4O_8$, calcd avg mass 1177.0, obsd m/z 1177.3 (PDMS); calcd exact $(M+H)^+$ 1177.2900, obsd m/z 1177.2880 (FAB-MS); λ_{abs} ($CHCl_3$) 428 (fwhm 15 nm), 526, 564, 600, 658 nm.

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