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Synthesis and Characterization of β-Trifluoromethyl-*meso*-tetraphenylporphyrins

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β-Trifluoromethyl-*meso*-tetraphenylporphyrins were synthesized to investigate the electronic and steric effects of the trifluoromethyl groups on the macrocycle. Preparation of these novel porphyrins was carried out by copper-assisted trifluoromethylation of β-tetrabromo-*meso*-tetraphenylporphyrin metal complexes and in situ generated CF_3Cu. For comparison, the β-methyl analogues were also prepared. Analysis of β-trifluoromethylporphyrins by UV−vis, NMR, and cyclic voltammetry (CV) showed that the electron-withdrawing effects of the trifluoromethyl groups on the antipodal pyrroles required the macrocycle to take a fixed 18π-electron pathway. UV−vis, CV, and molecular modeling studies suggest that the novel porphyrins are distorted following introduction of trifluoromethyl groups onto the pyrrolic β-position of *meso*-tetraphenylporphyrin. The pK_a difference of β-tetrakis-(trifluoromethyl)-*meso*-tetraphenylporphyrin from that of DBU in CH_2Cl_2, obtained by spectrophotometric titration, affirms that it is one of the most electron-deficient porphyrins so far prepared.

Introduction

Electronically modified porphyrins incorporating strong electron-withdrawing substituents at the pyrrolic β-positions and *meso*-positions form a class of so-called "electron-deficient porphyrins".[1−6] Many electron-deficient porphyrins have been reported, largely as a result of studies directed toward the determination of the ability of their metal complexes (such as Cr(III), Mn(III), or Fe(III)) to mimic the activity of cytochrome P-450 enzymes.[7−9] It has been shown and generally accepted that electron-deficiency is essential for P-450 mimics to improve their efficiency and robustness as catalytic oxidants.[10−12] However, it also has been shown that pursuing extremely electron-deficient porphyrins may not be the best route for the development of catalysts with P-450-like activities.[13−16] Thus, a moderate electron-withdrawing effect could be ideal for P-450 mimics. To stabilize the catalysts, steric effects should also be considered as an important factor for stabilizing the active species which are metal oxo complexes.[17] So far, there are no reports regarding β-trifluoromethyl-TPPs despite the fact that *meso*-tetraphenylporphyrin (TPP) is the most easily synthesized porphyrin unit. However, numerous other electron-deficient porphyrins such as β-halogeno-TPP, β-cyano-TPP, or β-nitro-TPPs have been synthesized.

The trifluoromethyl group is strongly electron-withdrawing[18] and bulky (with a van der Waals radius of 2.2 Å[19] or more[20]). Thus, it was expected that introduction of trifluoromethyl groups onto the porphyrin periphery

(1) Usually the term "electron-deficient" refers to compounds for which full octets are not achieved in the Lewis structure (Shriver, D. F.; Atkins, P. *Inorganic Chemistry*, 3rd ed.; W. H. Freeman and Company: New York, 1999). However, the term is often and arbitrarily used in the literature to refer to porphyrins in which the electron density of the macrocycle has been lowered by the presence of strong electron-withdrawing substituents.

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would impact the electronic and steric properties of the macrocycle. In addition, the porphyrin macrocycle could be protected by peripheral trifluoromethyl groups consisting of thermodynamically stable C−F bonds (e.g. $F-CF_2CH_3$ 522.2 ± 8 kJ/mol, cf. $H-CH_3$ 438.9 ± 0.4 kJ/mol).[21,22] This paper documents multiple trifluoromethylations of TPP at the pyrrolic β-positions and characterization of β-trifluoromethyl-TPPs.

Results and Discussion

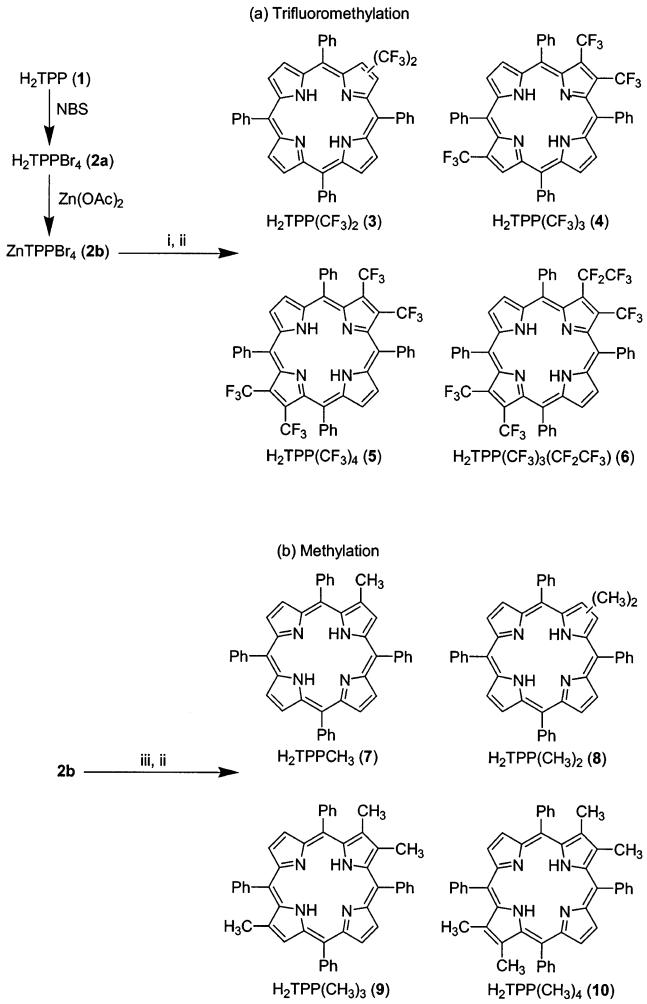
To prepare β-trifluoromethyl-TPP, we attempted direct β-trifluoromethylation of β-brominated TPP. Although 3,4-bis(trifluoromethyl)pyrrole is available,[23,24] no successful cyclization of this pyrrole with aldehydes to give β-trifluoromethylporphyrins has yet been reported. Presumably, cyclization with aldehydes is unlikely due to the low electron density at the α positions of the pyrrole[25] and subsequent destabilization of reaction intermediates. In our experiments we attempted to prepare β-tetrakis-(trifluoromethyl)-TPP by copper-assisted nucleophilic substitution of β-tetrabromo-TPP with the trifluoromethyl anion.

The synthetic route for β-tetrakis(trifluoromethyl)-TPP is shown in Scheme 1a. Free-base TPP was partially brominated to obtain β-tetrabromo-TPP (H_2TPPBr_4: **2a**).[26] After **2a** was metalated to give $ZnTPPBr_4$ (**2b**), it was treated with in situ generated CF_3Cu from the metathesis of trifluoromethyl cadmium ($(CF_3)_2Cd$ and CF_3CdBr) with CuBr.[27,28] Trifluoromethylation was attempted in DMF in the presence of HMPA at 70 °C for several hours; under these conditions trifluoromethylation of aromatic compounds such as bromobenzene is normally complete.[29] However, with zinc porphyrin (**2b**) under the same conditions $H_2TPP(CF_3)_4$ (**5**) was obtained in only an 11% yield, partially trifluoromethylated $H_2TPP(CF_3)_2$ (**3**) and $H_2TPP(CF_3)_3$ (**4**) in 2 and 8% yields, respectively, and a significant amount (~70%) of partially brominated and trifluoromethylated TPPs was found in the reaction mixture by mass spectral and TLC analysis. Isolation of β-trifluoromethyl-TPPs in freebase form was possible from this reaction. However, isolation of the partially brominated and trifluoromethylated TPPs was not attempted due to the difficulty in separating them by chromatography. It was, nevertheless, possible to improve the yield of **5** up to about 40% by increasing the reaction temperature. Results of trifluoromethylation with $ZnTPPBr_4$ (**2b**) are summarized in Table 1.

The structure of **5** was confirmed by standard analytical methods and by X-ray crystallography of its Zn complex.[30] Compound **3** was characterized as a mixture of regioisomers. It is known that copper-assisted trifluoromethylation[28,29] can lead to extension of the perfluoroalkyl chain. Several porphyrins with extended perfluoroalkyl chains were detected by mass spectral analysis. One such porphyrin, β-tris(trifluoromethyl)(pentafluoroethyl)-TPP ($H_2TPP(CF_3)_3(CF_2CF_3)$, **6**), was successfully isolated (Table 1).

Copper and nickel complexes of β-tetrabromo-TPP were also tested under similar conditions. However, these metalloporphyrins were not very soluble in the reaction

SCHEME 1. Synthetic Routes[a]



[a] Conditions: (i) CF_3^-/CuBr/HMPA, (ii) TFA/CH_2Cl_2, (iii) CuBr/CH_3Li.

TABLE 1. Isolated β-Perfluoroalkyl-*meso*-tetraphenylporphyrins

		isolated porphyrin (%)			
temp (°C)	time (h)	**3**	**4**	**5**	**6**
70	88		5.6	13	22
	5	2	8	11	
90	7	9	21	38	10
	5	11	24	42	8
110	21	13	12	17	
	8	16	13	20	

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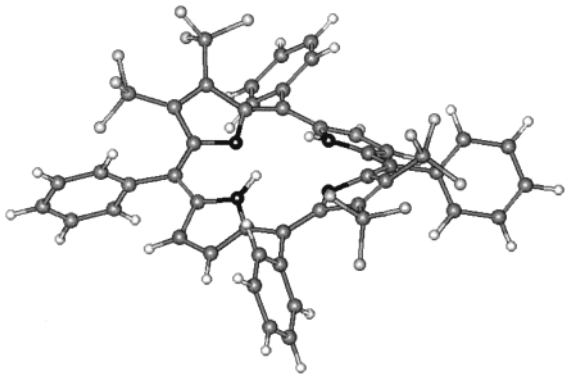

FIGURE 1. Molecular structure of $H_2TPP(CF_3)_4$ (**5**) modeled by HyperChem[34] geometry optimization (MM+).

mixture and only a small amount of **3** and **4** (~1−5%) and 70−80% of the starting porphyrins were recovered; formation of **5** was not observed.

The β-bis- and β-tris(trifluoromethyl) species (**3** and **4**) were reasonably soluble in chlorinated solvents such as chloroform or methylenechloride, but **5** and **6** were barely soluble in such solvents. The best solvent for **5** and **6** was benzene where they were only sparingly soluble.

For comparison purposes, β-methyl-*meso*-tetraphenylporphyrins were also synthesized. Although the palladium-catalyzed cross-coupling reaction is known as a useful method for methylation of pyrrolic β-positions of porphyrins,[31,32] we attempted an alternative method utilizing dimethyllithiumcopper, $Li(CH_3)_2Cu$.[33] As shown in Scheme 1b, $ZnTPPBr_4$ (**2b**) was treated with excess $Li(CH_3)_2Cu$ in dry ether for 24 h. The products from this reaction were then refluxed in DMF in the presence of CuBr for 2 h to bring about debromination (C−Br → C−H). After demetalation, the final products were chromatographed to yield H_2TPP (**1**) (32%), β-methyl-*meso*-tetraphenylporphyrin (H_2TPPCH_3: **7**) (0.5%), β-dimethyl-*meso*-tetraphenylporphyrin ($H_2TPP(CH_3)_2$: **8**) (19%), β-trimethyl-*meso*-tetraphenylporphyrin ($H_2TPP(CH_3)_3$: **9**) (17%), and β-tetramethyl-*meso*-tetraphenylporphyrin ($H_2TPP(CH_3)_4$: **10**) (15%). The structures of **7**, **9**, and **10** were confirmed by MS, NMR spectroscopy, and/or CHN analysis. Compound **8** was a mixture of regioisomers; **7**, **9**, and **10** were soluble in chloroform or methylene chloride.

Molecular modeling[34] shows that compound **5** is severely distorted and not surprisingly takes up a saddle-shaped conformation[35] (Figure 1). These distortions result from the interactions of the trifluoromethyl groups (van der Waals radii of 2.2 Å[19]) and the π-cloud of the phenyl groups (with a thickness of 3.70 Å[36]). Significant red-shifts of their absorption maxima, from those of H_2TPP (**1**), are observed for the series of β-trifluoromethylporphyrins (Figure 1a−c). The spectrum of **6** is very similar to that of **5**. On the other hand, the series of β-methyl species (Figure 2d−f) shows insignificant red-shifts, and the spectra of these porphyrins are quite similar to that of H_2TPP (**1**). These observations indicate that the electronic structures of the β-trifluoromethyl species are significantly changed from that of H_2TPP(**1**). There are two points of interest: (1) the spectral pattern of β-tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin (**5**) is quite different from that of *meso*-tetrakis(trifluoromethyl)-porphyrin,[37] which shows H_2TPP (**1**)-like Q-bands and blue-shifted or unchanged peaks from those of H_2TPP (**1**), and (2) the spectra of compounds **4**, **5**, and **6** look surprisingly like that of a bacteriochlorin,[38] especially in terms of the pattern of the Q-bands. This suggests that a dramatic change in the electronic structure of the macrocycle causes the 18π-electron pathway to be locked in place due to the electron-withdrawing effects of the substitiuents.

A similar, but less pronounced, effect was seen on the optical spectrum of the tetra bromo derivative **2a**. Crossley[39] and his colleagues note that even in 2,3-dibromo-5,10,15,20-tetraphenylporphyrin "the substituents fix the aromatic delocalization pathway" such that the NH groups do not tautomerize and subsequent electrophile attack occurs on the antipodal pyrrolenic ring.

We initially focused on elucidation of the molecular and electronic structures of β-trifluoromethylporphyrins by ^1H NMR spectroscopy. We first examined the β-tris-(trifluoromethyl) compound **4**. Compound **4** is very soluble in $CDCl_3$ and the H^5 proton is unique. Figure 3a shows the 400-MHz ^1H NMR spectrum of **4**. The spectrum consists of one singlet for H^5, two AB quartets for H^1, H^2, H^3 and H^4, multiplets for the phenyl protons, and two broad singlets for the N-*H* groups. The 188-MHz ^{19}F NMR spectrum of **4** consisting of a multiplet (6F) at −49.1 ppm and a singlet at −53.1 ppm (vs $CFCl_3$) is shown in Figure 3b. A 400-MHz $^1H-^1H$ COZY experiment (Figure 4) showed couplings between pyrrolic β-*H* and N-*H* protons. As seen in the expansion, couplings were observed only between H^1-H^4 and N-*H* protons, and no connectivity was shown between H^5 and N-*H* groups. It should be noted that the couplings between the pyrrolic β-*H*s and N-*H*s could be observed only when residual water was removed. The proton exchange between residual water and N−H resulted in more intensified signals for H^1-H^4 and a very broad singlet for N-*H*s.[40] These NMR experiments not only confirm the structure of compound **4** as shown in Scheme 2 but also show that the N-*H* protons reside exclusively on N^1 and N^3, at room temperature, which indicates a fixed 18π-electron pathway as shown in Figure 5. This agrees with the observations that conjugated electron pathways of the

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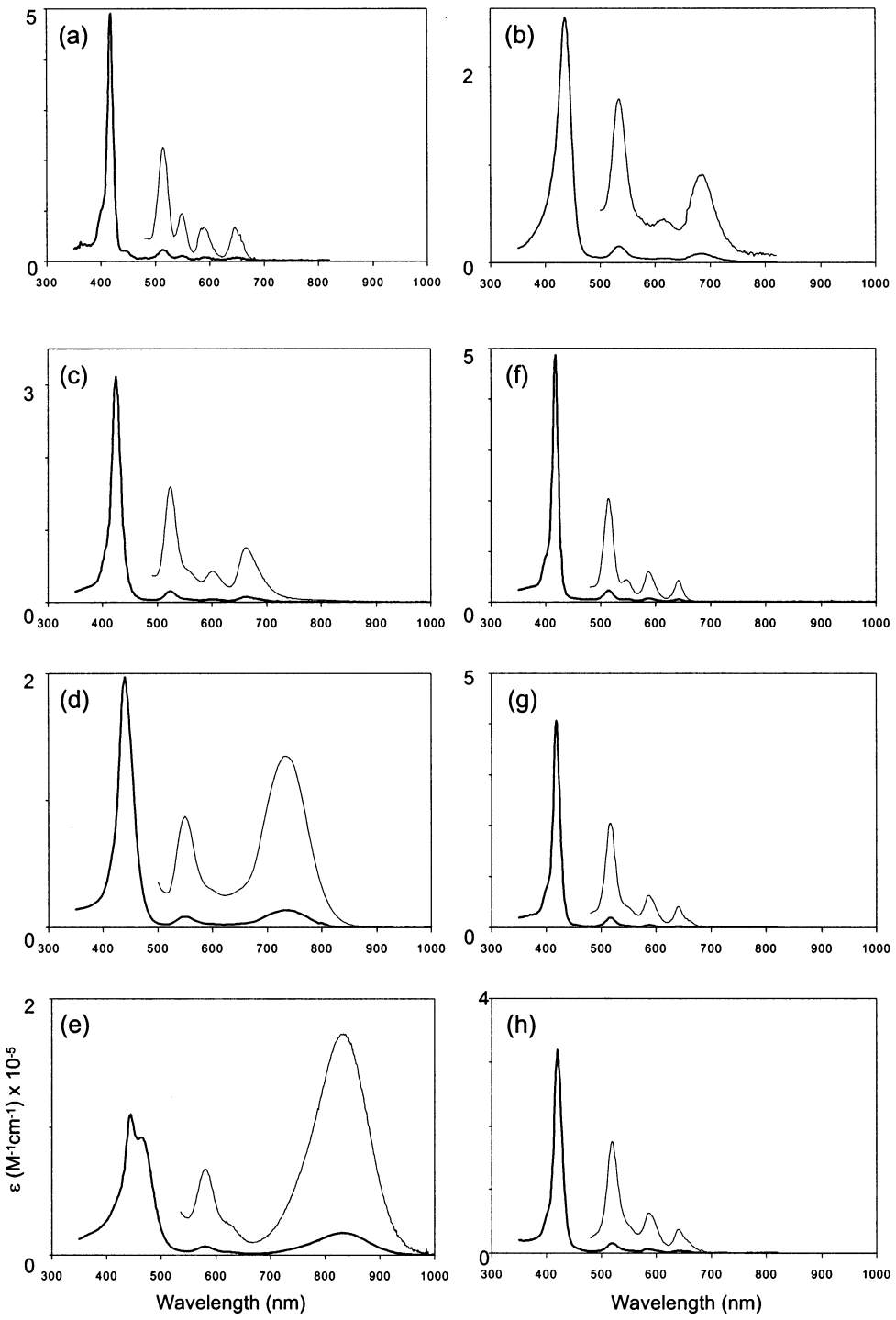

FIGURE 2. UV−visible spectra of H_2TPP (**1**) and β-trifluorormethyl- and β-methyl-TPPs: (a) H_2TPP (**1**), (b) H_2TPPBr_4 (**2a**), (c) $H_2TPP(CF_3)_2$ (**3**), (d) $H_2TPP(CF_3)_3$ (**4**), (e) $H_2TPP(CF_3)_4$ (**5**), (f) $H_2TPP(CH_3)_2$ (**8**), (g) $H_2TPP(CH_3)_3$ (**9**), and (h) $H_2TPP(CH_3)_4$ (**10**) in CH_2Cl_2. The narrow lines show 10 times magnification of the corresponding regions of thick lines.

porphyrin macrocycle tend to avoid electron-withdrawing substituents on the pyrrolic β-positions.[39,41]

The methyl groups are electron-donating and the opposite effect is expected in terms of fixing of the electronic pathway of the porphyrin macrocycle,[41] and a similar COSY experiment at room temperature using $H_2TPP(CH_3)_3$ (**9**) did not show any couplings between pyrrolic β-*H*s and N-*H*s. Presumably the N−H tautomerization for **9** is similar to that for H_2TPP (**1**) on the NMR time scale.[42]

Figure 6 shows the atypical upfield shift of the β-protons of compound **5**. Aggregation is common with porphyrins[43,44] and this phenomenon has been extensively studied by NMR.[45−47] However, the chemical shift of the β-protons remains unchanged over a wide range of

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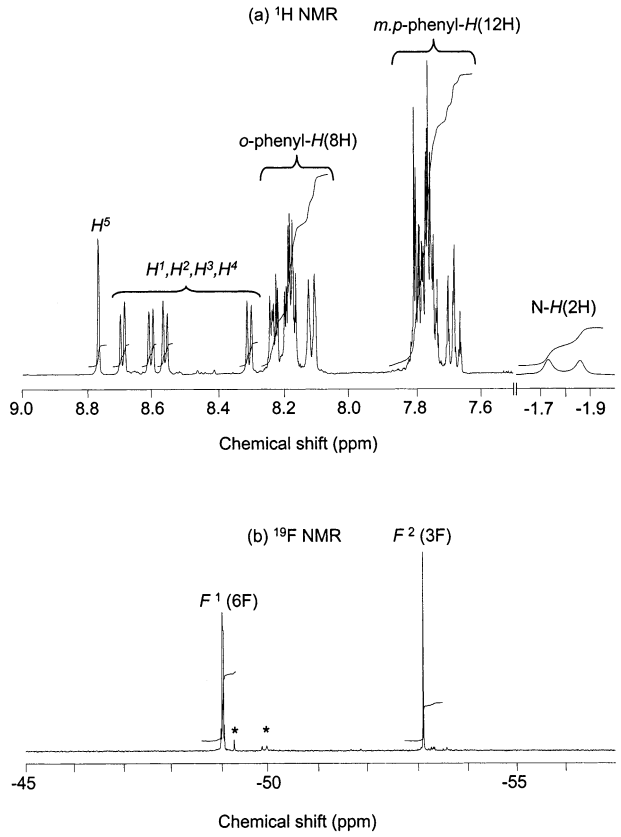


FIGURE 3. The (a) 400-MHz ^{1}H and (b) 188-MHz ^{19}F NMR spectra of $H_2TPP(CF_3)_3$ (**4**) in $CDCl_3$ at room temperature. An asterisk indicates impurities.

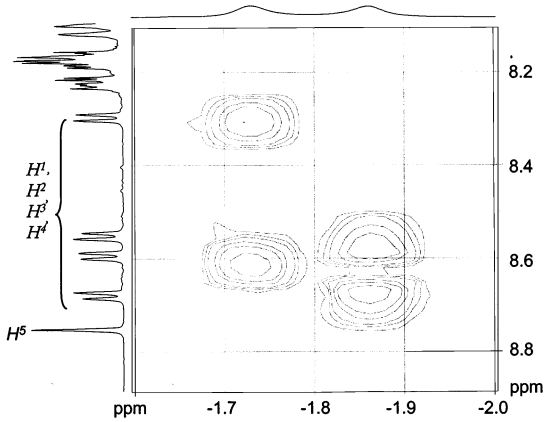
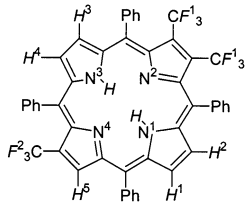


FIGURE 4. The 400-MHz ^{1}H COSY spectra of $H_2TPP(CF_3)_3$ (**4**).

SCHEME 2. Designation for Protons of $H_2TPP(CF_3)_3$ (4)



concentration when measured in TFA. One might anticipate that this shift is due to the unusual conformation of the macrocycle. However, these changes are clearly in

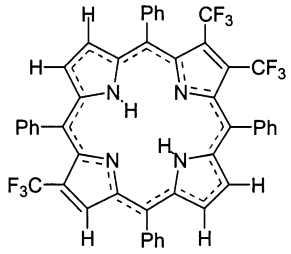


FIGURE 5. The 18π-electron pathway of **4**.

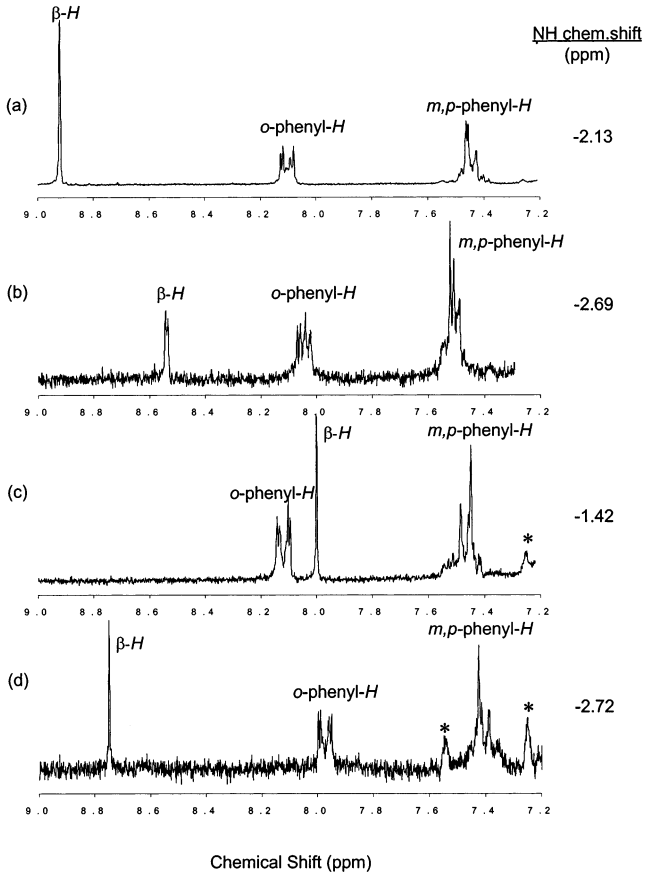


FIGURE 6. The 200-MHz ^{1}H NMR spectra of (a) H_2TPP (**1**), (b) H_2TPPBr_4 (**2a**), (c) $H_2TPP(CF_3)_4$ (**5**), and (d) $H_2TPP(CH_3)_4$ (**10**) in C_6D_6 at room temperature. An asterisk indicates the ^{13}C satellite of benzene.

line with the decreased ring current and fixing of the aromatic pathway. Indeed *meso*-tetraphenylbacteriochlorin exhibits a signal at 7.85 ppm (d, J = 2 Hz) for the aromatic β-protons.[48] This is paralleled by NH groups

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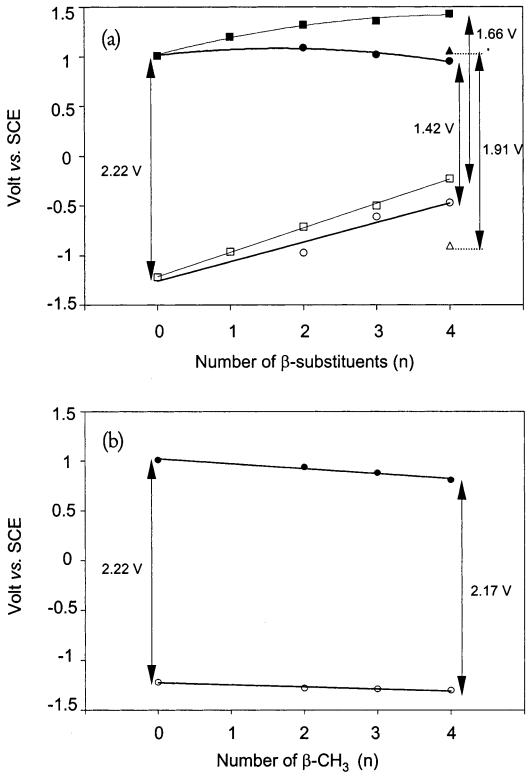

FIGURE 7. Redox potentials of (a) $H_2TPP(CF_3)_n$ (n = 0 (**1**), 2 (**3**), 3 (**4**), and 4 (**5**)) (●, ○), H_2TPPBr_4 (**2a**) (▲, △), and $H_2TPP(CN)_n$ (n = 0 (**1**), 1 (**11**), 2 (**12**), 3 (**13**), 4 (**14**))[52] (■, □) and (b) $H_2TPP(CH_3)_n$ (n = 0 (**1**), 2 (**8**), 3 (**9**), and 4 (**10**)). Solid and open symbols indicate the first oxidation and first reduction, respectively.

which resonate at only −1.3 ppm, similar to the NH groups of **5** which appear at −1.42 ppm.

The redox potentials for **3**−**5** and **8**−**10** are plotted against the number of β-substituents as shown in Figure 7. A simple model predicts that increasing the number of electron-withdrawing groups should make oxidation more difficult and reduction easier.[49−52] On the other hand, macrocyclic distortion can result in low oxidation potentials even in electron-deficient porphyrins.[53−56]

As would be expected the methyl groups on **8**−**10** have only a small influence on the redox chemistry when compared to TPP. Surprisingly, the additional CF_3 groups make oxidation easier, due, we suggest, to both the distortion of the macrocycle and, principally, locking of the conjugated system. Reduction, on the other hand, shows a linear relationship with CF_3 substitution.

An interesting observation is that the redox potential gap (the HOMO-LUMO gap)[49] for β-trifluoromethylporphyrins progressively decreases as the number of substituents increases, on the other hand, the gap for β-methylporphyrins parallels to that for H_2TPP (**1**). The gap for **1** by our observation was 2.22 V, which agrees well with the literature values.[49,51] The observed gap for $H_2TPP(CF_3)_4$ (**5**) is 1.42 V. A similar gap contraction was observed in β-tetracyano-TPPs in which cyano groups were introduced on the antipodal pyrroles.[52] This phenomenon can be rationalized by the unique electronic structures of these porphyrins with strongly electron-withdrawing β-substituents on the antipodal pyrroles where the π-electrons take up a bacteriochlorins-like pathway. It is well-known that the HOMO-LUMO gap of the porphyrin macrocycle progressively contracts as the macrocycle is reduced to chlorins or bacteriochrorins.[38,57] According to a theoretical study,[58] the gap of bacteriochlorin, in which the 18π-electron pathway is fixed due to the reduced pyrroles in antipodal positions, is about 60% of that calculated for porphyrin. Thus, the dramatic gap contraction to 1.42 V observed for β-trifluoromethylporphyrins is likely due to the bacteriochlorin-like electronic structure of the macrocycle.

A simple comparison of ring redox potentials of porphyrins does not necessarily give a good estimation of their electron-deficiency since this may be greatly affected by the molecular and electronic structure as shown above. We describe here an estimation of the pK_a of $H_2TPP(CF_3)_4$ (**5**) obtained by spectrophotometric titration with DBU. This method for pK_a estimation was previously carried out on β-octafluoro-*meso*-tetraarylporphyrins by Woller and DiMagno.[4]

Figure 8 shows the results of the titration of **5** with DBU in CH_2Cl_2. The color of the solution changed from golden-yellow for the free-base to weak orange for the first deprotonated species. When excess DBU was added no further deprotonation occurred but with time the chromophore was destroyed (even in the absence of O_2 and H_2O). The spectrophotometric results were analyzed based on the absorbance changes at 463 and 513 nm. As shown in Figure 8b, the logarithmic analysis of the first colorimetric change gave a straight line with a slope of 1.1 and the y intercept of 2.9 as the ΔpK_a value for the following reaction: H_2P + DBU ⇄ HP^- + $DBUH^+$ (H_2P,: porphyrin free-base; HP^-, porphyrin monoanion; $DBUH^+$, protonated DBU). The ΔpK_a value of 2.9 is the difference between the pK_a of **5** and the pK_a of DBU in CH_2Cl_2. Woller and DiMagno found that the N−H in H_2TPPF_8[59] (**15**) and $H_2TPFPPF_8$[59] (**16**)[4] were less acidic than protonated DBU by 3.9 and −0.2 pK_a units, respectively, and H_2TPPF_8 was at least 1000 times more acidic than H_2TPP (**1**).[4] Thus **5** is more acidic than **15**; however,

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(52) H_2TPPCN (**11**): 7-cyano-*meso*-tetraphenylporphyrin. $H_2TPP(CN)_2$ (**12**): 7,17- (or 7,18- or 7,8-)dicyano-*meso*-tetraphenylporphyrin. $H_2TPP(CN)_3$ (**13**): 7,8,17-tricyano-*meso*-tetraphenylporphyrin. $H_2TPP(CN)_4$ (**14**): 7,8,17,18-tetracyano-*meso*-tetraphenylporphyrin. (Giraudeau, A.; Callot, H. J.; Gross, M. *Inorg. Chem.* **1979**, *18*, 201.)

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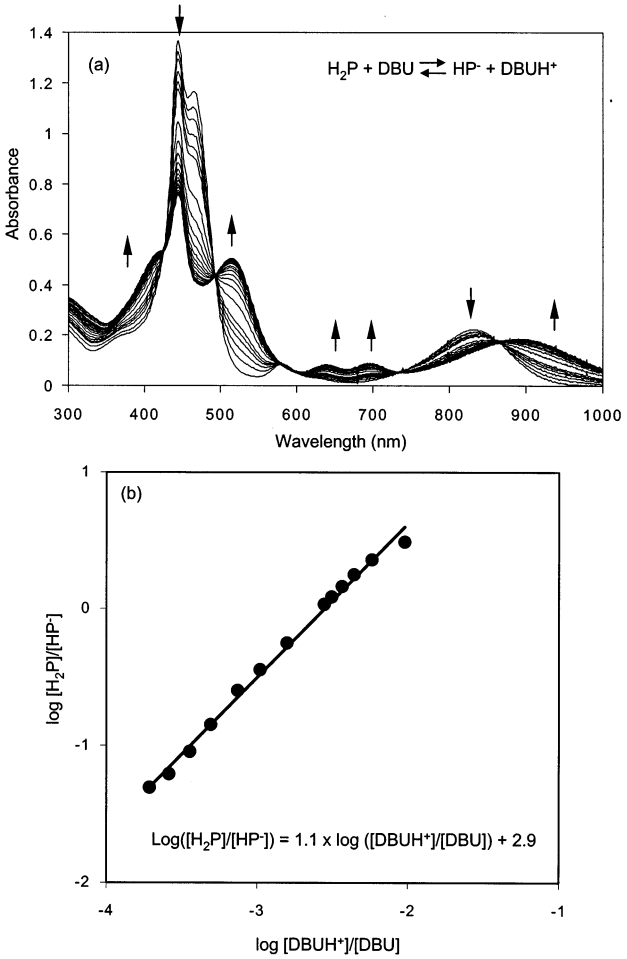

FIGURE 8. Spectrophotometric titration of $H_2TPP(CF_3)_4$ (**5**) with DBU in CH_2Cl_2. (a) UV−visible spectral change for the first deprotonation at [**5**] = 1.24×10^{-5} M [DBU] = 0−5.4×10^{-2} M. No spectral change between [DBU] = 4.5×10^{-2} and 5.4×10^{-2} M. (b) Logarithmic analysis of the spectral data. H_2P is porphyrin and $DBUH^+$ is protonated DBU.

under the same conditions we find that H_2TPPBr_8[59] and $H_2TDCPPCl_8$[59] are more acidic with ΔpK_a values (in CH_2Cl_2 vs DBU) of 0.8 and 1.2, respectively.

Experimental Section

Instrumentation and Materials. All chemicals were purchased and purified by published procedures.[60] Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories or Aldrich. Chlorinated solvents were filtered using *N*-alumina (activity I) to remove trace acid (HCl or DCl). Methylene chloride for cyclic voltammetric measurements was distilled from CaH_2, degassed by three cycles of freeze−pump−thawing, and kept over activated molecular sieves (4). Column chromatography was performed with use of 70−230 or 230−400 mesh silica gel. Analytical thin-layer chromatography was performed with precoated silica gel on aluminum plates containing a fluorescent indicator. NMR spectra were recorded at 200, 300, or 400 MHz (^{1}H) and 188 or 282 MHz (^{19}F). Cyclic voltammetric measurements were performed with a single-compartment electrochemical cell and a bipotentiostat. The titration was carried out by adding aliquots of DBU into a porphyrin solution in a UV−visible cell, using microsyringes. Concentrations of the species at each titrating point were determined based on absorbances. The equilibrium constants K_5 and K_{DBU} for deprotonation of **5** (H_2P) and protonated DBU ($DBUH^+$) derive from eqs 1 and 2.

$$H_2P \leftrightarrows HP^- + H^+ \qquad K_a^{H_2P} = \frac{[HP^-][H^+]}{[H_2P]} \tag{1}$$

$$DBUH^+ \leftrightarrows DBU + H^+ \qquad K_a^{DBUH^+} = \frac{[DBU][H^+]}{[DBUH^+]} \tag{2}$$

The equilibrium constant for the H_2P-DBU reaction can be rearranged as (eq 3).

$$H_2P + DBU \leftrightarrows HP^- + DBUH^+$$

$$K = \frac{[HP^-][DBUH^+]}{[H_2P][DBU]} = K_a^{H_2P}/K_a^{DBUH^+} \tag{3}$$

$$-\log k = -\log K_a^{H_2P} + \log K_a^{DBUH^+} \text{ or } \Delta pK_a = pK_a^{H_2P} - pK_a^{DBUH^+}$$

Thus

$$\log \frac{[H_2P]}{[HP^-]} = \Delta pK_a + \log \frac{[DBUH^+]}{[DBU]} \tag{4}$$

7,8,17,18-Tetrabromo-*meso*-tetraphenylporphyrin (H_2-TPPBr$_4$) (2a). The porphyrin was synthesized by published procedures.[26] UV−vis (CH_2Cl_2): λ_{max} (nm) 436 (Soret), 534, 616, 686. ^{1}H NMR ($CDCl_3$): δ −2.83 (s, 2H, N*H*), 7.78 (m, 12H), 8.18 (m, 8H), 8.68 (d, 4H, J_4 = 1.4 Hz). ^{1}H NMR (C_6D_6): δ −2.69 (s, 2H), 7.50 (m, 12H), 8.04 (m, 8H), 8.54 (d, 4H, J_4 = 1.4 Hz). ^{1}H NMR (CF_3CO_2D): δ 8.37 (m, 12H), 8.68 (m, 4H), 8.92 (m, 4H), 8.75 (s, 4H),. The spectroscopic characteristics of this compound compare well to those reported in the literature.[26,41]

2,3,12,13-Tetrabromo-*meso*-tetraphenylporphyrinatozinc(II) (Zn(TPPBr$_4$)) (2b). Zn(II) was inserted into **2a** by a published procedure.[61] LR-MS (EI, 300 °C): M^+(*m*/*z*) 993, calcd for $C_{44}H_{24}Br_4N_4Br$ 993.7. UV−vis (CH_2Cl_2): λ_{max} (nm) 430 (Soret), 560, 598. ^{1}H NMR (DMSO-d_6): δ 8.61 (s, 4H), 8.02 (m, 8H), 7.80 (m, 12H). The spectroscopic characteristics of this compound compare well to those reported in the literature.[62]

Trifluoromethylcadmium ($CF_3CdBr + (CF_3)_2Cd$)). This reagent was synthesized by the published procedure.[27] Trifluoromethylcadmium reagent was obtained as ca. 1 M solution of trifluoromethyl anion in DMF. ^{19}F NMR (DMSO-d_6): δ (vs $CFCl_3$) −33.2 (3F) and −33.9 (6F), each of which was accompanied by the satellite peaks by ^{111}Cd and ^{113}Cd. The concentration of CF_3^- was determined by the ratio of the peak integration to the internal reference, 3-fluorotoluene.

***β*-Trifluoromethyl-*meso*-tetraphenylporphyrins.** A typical example of this reaction is given. The trifluoromethylcadmium reagent (14 mL, ca. 1 M) and dry HMPA (14 mL) were transferred to a two-neck 100-mL round-bottom flask and the mixture was cooled to 0 °C and stirred for 3 min under N_2. To this brown solution was added CuBr (1 g, 7 mmol) at room temperature and the mixture was stirred until the CuBr was dissolved. Zn(TPPBr$_4$) (**2b**) (0.5 g, 0.5 mmol) was then added

(59) H_2TPPF_8: 2,3,7,8,12,13,17,18-octafluoro-*meso*-tetraphenylporphyrin. $H_2TPFPPF_8$: 2,3,7,8,12,13,17,18-octafluoro-*meso*-tetrakis(pentafluorophenyl)porphyrin. H_2TPPBr_8: 2,3,7,8,12,13,17,18-octabromo-*meso*-tetraphenylporphyrin. $H_2TDCPPCl_8$: 2,3,7,8,12,13,17,18-octachloro-*meso*-tetrakis(2,6-dichlorophenyl)porphyrin.

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and the mixture was heated at 90 °C for 7 h under N_2. After the mixture was cooled to room temperature, DMF was removed by a rotary evaporator at 100 °C. A small amount of HMPA was removed at 2−3 mmHg at 100 °C[63] but most of it could not be removed by heating even at temperatures above 110 °C. The green residue was mixed with methylene chloride (100 mL). Green porphyrin products were dissolved but some inorganic residues remained undissolved. Approximately the same volume of silica gel (230−400 mesh) was added to this mixture. The preadsorbed silica gel was dried for several hours at room temperature, packed in a short column without additional silica gel, and eluted with methylene chloride to obtain green porphyrin products. After methylene chloride was evaporated from the green eluate, HMPA was distilled off at 100−110 °C at 2−3 mmHg. If HMPA could not be removed completely, the preadsorption−elution process was repeated. The final green solid was dissolved in methylene chloride (50 mL) and the solution was filtered to remove inorganic residue. Trifluoracetic acid (10 mL) was then added to the green solution. The mixture was refluxed over a steam bath for 30 min until the color became dark orange. The mixture was diluted with methylene chloride, washed with distilled water, 10% aq $NaHCO_3$, and then distilled water. The mixture of free-base porphyrins was dissolved in a minimum amount of benzene and adsorbed on silica gel (230−400 mesh, same volume as the benzene solution). After the benzene was removed by evaporation, the preadsorbed silica gel was loaded on top of a wet silica gel bed prepared by using 5 times the amount used for preadsorption and eluted with methylene chloride/hexane (30/70−50/50 (v/v)) to give $H_2TPP(CF_3)_2$ (**3**) (34 mg, 9%) and $H_2TPP(CF_3)_3$ (**4**) (86 mg, 21%). The remaining porphyrins were eluted with benzene/acetone (90/10 (v/v)). The solvent was removed and the porphyrins were dissolved in benzene and preadsorbed on a minimum amount of silica gel (230−400 mesh). Preabsorbed silica gel was place on top of a wet silica gel bed prepared by using 7−8 times the volume of silica gel to the amount used for preadsorption and flash-chromatographed with benzene/cyclohexane/acetone (20/80/2 (v/v/v)−50/50/2−90/0/10)). Yield: $H_2TPP(CF_3)_4$ (**5**) (140 mg, 38%), $H_2TPP(CF_3)_3(CF_2CF_3)$ (**6**) (47 mg, 10%).

Compound **3a** showed a single mass corresponding to β-bis-(trifluoromethyl)-TPP by mass spectroscopy. However, ^{1}H NMR of **3** did not show a clear spectrum corresponding to a specific regioisomer. Two very close bands that could not be separated were observed by TLC analysis of **3** on a silica gel plate, using CH_2Cl_2/hexane (10/90 (v/v)) as a solvent. ^{19}F NMR of **3** showed two singlets whose chemical shifts were very close. Thus, **3** is most probably a mixture of regioisomers.[64] The mixture of these regioisomers was used throughout subsequent experiments.

β-Bis(trifluoromethyl)-*meso*-tetraphenylporphyrin (H_2-TPP(CF_3)$_2$) (3). LR-MS (EI, 250 °C): M^+(*m*/*z*) 750, calcd for $C_{46}H_{28}F_6N_4$ 750.7448. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 424 (5.49), 524 (4.19), 601 (3.62), 661 (3.86). ^{19}F NMR ($CDCl_3$): δ (vs $CFCl_3$) −52.7 (s), −52.8 (s). CHN Anal. (%) Calcd for $C_{46}H_{28}F_6N_4$: C, 73.59; H, 3.76; N, 7.46. Found: C, 73.53; H, 3.78; N, 7.54.

7,8,17-Tris(trifluoromethyl)-5,10,15,20-tetraphenylporphyrin (H_2TPP(CF_3)$_3$) (4). LR-MS (EI, 250 °C): M^+(*m*/*z*) 818, calcd for $C_{47}H_{27}F_9N_4$ 818.7. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 440 (5.29), 550 (3.94), 590 sh (3.51), 735 (4.13). ^{1}H NMR ($CDCl_3$): δ −1.73 (s, 1H), −1.85 (s, 1H), 7.77 (m, 12H), 8.17 (m, 8H), 8.70 and 8.57, 8.61 and 8.31 (2 AB q, J_{AB} = 5.06, 5.11 Hz, 4H), 8.76 (s, 1H). ^{19}F NMR ($CDCl_3$): δ (vs $CFCl_3$) −49.1 (m, 6F), −53.1 (s, 3F). CHN Anal. (%) Calcd for $C_{47}H_{27}F_9N_4$: C, 68.95; H, 3.32; N, 6.84, found: C, 68.71; H, 3.38; N, 6.54.

7,8,17,18-Tetrakis(trifluoromethyl)-*meso*-tetraphenylporphyrin (H_2TPP(CF_3)$_4$) (5). LR-MS (EI, 250 °C): M^+(*m*/*z*)=887, calcd for $C_{48}H_{26}F_{12}N_4$ 886.7. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 444 (5.04), 463 (4.96), 580 (3.81), 620sh (3.38), 832 (4.23). UV−vis (C_6H_6): λ_{max} (nm) (log ϵ) 446 (5.11), 466 (5.03), 577 (3.94), 616 sh (3.48), 822 (4.32). ^{1}H NMR (C_6D_6): δ −1.42 (s, 2H), 7.45 (m, 12H), 8.00 (s, 4H), 8.11 (m, 4H), 8.13 (m, 4H). ^{1}H NMR (CF_3CO_2D): δ 8.16 (m, 12H), 8.28 (s, 4H), 8.55 (s, 8H). ^{19}F NMR (C_6D_6): δ (vs $CFCl_3$) −49.6 (s). CHN Anal. (%) Calcd for $C_{48}H_{26}F_{12}N_4$: C, 65.02; H, 2.96; N, 6.32. Found: C, 65.00; H, 2.86; N, 6.17.

7,8,17-Tris(trifluoromethyl)-18-pentafluoroethyl-*meso*-tetraphenylporphyrin ($H_2TPP(CF_3)_3(CF_2CF_3)$) (6). LR-MS (EI, 250 °C): M^+(*m*/*z*) 936, calcd for $C_{49}H_{26}F_{14}N_4$ 936.7458. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 444 (5.03), 468 (5.01), 586 (3.90), 628 (3.55), 844 (4.36). ^{1}H NMR (C_6D_6): δ −1.27 (s, 1H), −1.03 (s, 1H), 7.44 (m, 12H), 7.92 (d, 1H), 7.96 (d, 1H), 8.03 (m, 8H), 8.22 (br d (maybe overlapped two doublets), 2H), in addition to these porphyrin peaks there were two sharp peaks at 1.40 (s, 2H) and 1.60 (s, 2H). These peaks diminish when D_2O was added. So possibly these peaks are due to water. A residual water peak also appears at 0.4 ppm as usual for the ^{1}H NMR spectrum for C_6D_6. ^{19}F NMR (C_6D_6): δ (vs $CFCl_3$) −47.7 (m, 3F), −49.6 (m, 6F), −82.3 (m, 3F), −98.2 (m, 2F). CHN Anal. (%) Calcd for $C_{49}H_{26}F_{14}N_4 \cdot 0.75C_6H_6$: C, 53.18; H, 2.43; N, 5.64. Found: C, 53.25; H, 2.54; N, 5.42.

β-Methyl-*meso*-tetraphenylporphyrins. CuBr (1.00 g, 7 mmol) and CH_3Li (10 mL of a 1.4 M solution in diethyl ether, 14 mmol) were mixed at −80 °C under N_2 in a flame-dried 50-mL one-neck round-bottomed flask with a stopcock sidearm, which was sealed with a rubber septum. The mixture was stirred at −80 °C under N_2 until the CuBr was completely dissolved. Zn(TPPBr$_4$) (**2b**) (233 mg, 0.235 mmol) was added under a N_2 stream to the solution. The color of the mixture became green instantly. The solution was kept in an oil bath at 32 °C. A small amount of the mixture was withdrawn with a syringe to monitor the UV−vis spectrum during the reaction. The solids that built up at the edge of the solution were dissolved with a sonicator. The reaction was run for 24 h. There was no difference in UV−vis spectra between 6 and 24 h. After the reaction was complete, dilute HCl (5 mL) was carefully added to the reaction mixture. The mixture was diluted with methylene chloride (100 mL) and washed with H_2O (100 mL). The organic layer was collected and a red powder was obtained by removing CH_2Cl_2. To remove any remaining bromine groups on the pyrrolic β-positions, the Zn-(II) porphyrins were refluxed in DMF (not dried) in the presence of CuBr for 2 h. After removal of DMF, Zn(II) porphyrins were dissolved in methylene chloride and CuBr was removed by filtration. A red powder was obtained after removing solvent. The red powder (140 mg) was dissolved in TFA (3 mL) and refluxed for 1.5 h. The mixture was cooled to room temperature and diluted with chloroform (100 mL). The green solution was washed with H_2O (100 mL) twice, with 7.5% aq $NaHCO_3$ (100 mL), and with H_2O (100 mL). The volume was reduced to ca. 5 mL. Free-base porphyrins were mixed with approximately the same amount of silica gel (70−230 mesh). The silica gel was dried in air at room temperature in the fume hood. The porphyrin-preadsorbed silica gel was placed on top of the silica gel column prepared in chloroform. Two fractions were obtained upon eluting with chloroform. Each fraction contained two compounds. The compounds in the first fraction were chromatographed on a silica gel column with methylene chloride/petroleum ether and the separation yielded H_2TPP (**1**) (46 mg, 32%), H_2TPPCH_3 (**7**) (<0.5 mg), and $H_2TPP(CH_3)_2$ (**8**) (29 mg, 19%). The remaining mixture was chromatographed on a silica gel column with methylene chloride containing 2 vol % of acetone and the separation yielded $H_2TPP(CH_3)_3$ (**9**) (26 mg, 17%) and $H_2TPP(CH_3)_4$ (**10**) (24 mg, 15%).

β-Methyl-*meso*-tetraphenylporphyrin (H_2TPPCH_3) (7). LR-MS (EI, 250 °C): M^+(*m*/*z*) 628, calcd for $C_{45}H_{32}N_4$ 628.7778. UV−vis (CH_2Cl_2): λ_{max} (nm) 417 (Soret), 514, 548, 588, 644.

β-Dimethyl-*meso*-tetraphenylporphyrin ($H_2TPP(CH_3)_2$)

(63) **Caution!** HMPA is a highly toxic carcinogen. Handling of this material must be performed in a fume hood.

(64) The possible regioisomers are 7,17-bis(trifluoromethyl)-TPP, 7,-18-bis(trifluoromethl)-TPP, and 7,8-bis(trifluoromethl)-TPP.

(8). LR-MS (EI, 250 °C): $M^+(m/z)$ 642, calcd for $C_{46}H_{34}N_4$ 642.8048. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 418 (5.69), 514 (4.35), 546 (3.76), 587 (3.87), 640 (3.75).

2,3,12-Trimethyl-*meso*-tetraphenylporphyrin (H_2TPP-$(CH_3)_3$) (9). LR-MS (EI, 250 °C): $M^+(m/z)$ 656, calcd for $C_{47}H_{34}N_4$ 656.8318. UV−vis (CH_2Cl_2): λ_{max} (nm) (log ϵ) 419 (5.60), 516 (4.29), 584 (3.66), 644 (3.24). ^{1}H NMR ($CDCl_3$): δ -2.67 (s, 1H), −2.94 (s, 1H), 2.42 (s, 3H), 2.44 (s, 3H), 2.59 (s, 3H), 7.70 (m, 12H), 8.06 (m, 6H), 8.17 (m, 2H), 8.63, 8.56 (ABq, 2H), 8.54 (m, 2H), 8.59 (s, 1H). CHN Anal. (%) Calcd for $C_{47}H_{36}N_4 \cdot 0.5H_2O$: C, 84.78; H, 5.68; N, 8.41. Found: C, 84.79; H, 5.43; N, 8.48.

2,3,12,13-Tetramethyl-*meso*-tetraphenylporphyrin (H_2-TPP$(CH_3)_4$) (10). LR-MS (EI, 250 °C): $M^+(m/z)$ =670, calcd for $C_{48}H_{38}N_4$ 670.8588. UV−vis (CH_2Cl_2): λ_{max} (nm) 420 (5.50), 520 (4.19), 588 (3.76), 640 (3.55). ^{1}H NMR ($CDCl_3$): δ −2.77 (s, 2H), 2.39 (s, 12H), 7.71 (m, 12H), 8.07 (m, 8H), 8.44 (s, 4H). ^{1}H NMR (C_6D_6): δ 2.38 (s, 12H), 7.40 (m, 12H), 7.97 (m, 8H), 8.75 (s, 4H). ^{1}H NMR (CF_3CO_2D): δ 2.57 (s, 12H), 8.40 (m, 12H), 8.66 (s, 4H), 9.01 (s, 4H), 8.80 (s, 4H). CHN Anal. (%) Calcd for $C_{48}H_{38}N_4 \cdot 0.5CHCl_3$: C, 79.73; H, 5.31; N, 7.67. Found: C, 79.35; H, 5.31; N, 7.41.

Conclusions

As previously reported for 7,8,17,18-tetrabromo-*meso*-tetraphenylporphyrin (**2a**),[39] the 18π-electron pathway is fixed by the strong electron-withdrawing effect of pyrrolic β-trifluoromethyl groups in antipodal pyrroles. Detailed analysis by cyclic voltammetric measurements revealed that the HOMO-LUMO gap contracts progressively as the number of trifluoromethyl groups increases. Despite the effects of macrocycle distortion, the gap contraction is prominent. Calculations have shown that the HOMO-LUMO gap for a non-β-substituted *meso*-tetraarylporphyrin should be retained for the corresponding β-octahalo derivatives if there is no macrocycle distortion. Although nonlinear change of oxidation potentials against the number of bromine atoms for some series of β-bromoporphyrins has been thought to be due to the macrocycle distortion, our results show that distortion is not the only reason for the HOMO-LUMO gap contraction along with peripheral substitution. Thus, the HOMO-LUMO gap is affected by not only the distortion but also the strength of an electron-withdrawing group and the positions of substituents.

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Supporting Information Available: UV−visible spectrum of **6**; UV−visible spectrum change of **5** on concentration change; ^{1}H NMR spectra of **5**, **6**, **9**, and **10**; ^{19}F NMR spectra of **5** and **6**; and table of redox potentials of **1**, **2a**, **3**, **4**, **5**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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