

Synthesis and Characterization of the Cationic Porphyrin *meso*-Tetrakis(2,3,5,6-tetrafluoro-*N,N,N*-trimethyl-4-aniliniumyl)porphyrin

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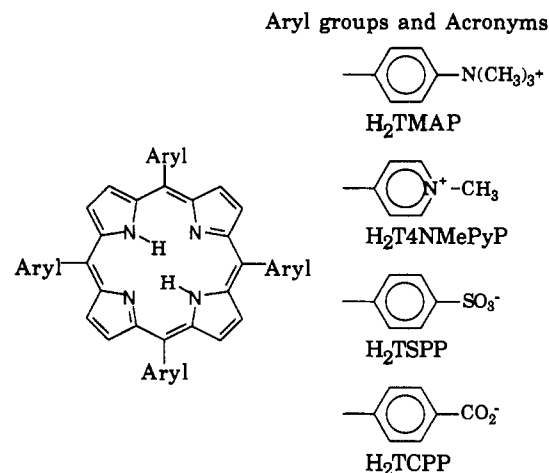
The cationic porphyrin *meso*-tetrakis(2,3,5,6-tetrafluoro-*N,N,N*-trimethyl-4-aniliniumyl)porphyrin and its metal complexes, $M(\text{TF}_4\text{TMAP})^{n+}$ ($M = \text{H}_2, \text{Ni}^{\text{II}}, \text{Co}^{\text{II}}, n = 4; M = \text{Co}^{\text{III}}, \text{Fe}^{\text{III}}, n = 5$), have been synthesized via methylation of the corresponding *meso*-tetrakis(2,3,5,6-tetrafluoro-*N,N*-dimethyl-4-anilanyl)porphyrin, $M(\text{TF}_4\text{DMAP})$, and have been characterized by NMR and UV-vis spectroscopies and electrochemistry. These porphyrins have redox potentials which are very similar to those of the cationic porphyrins $M(\text{TNMePyP})^{n+}$ but have less tendency to dimerize or adsorb onto surfaces. $\text{Fe}^{\text{III}}(\text{TF}_4\text{TMAP})^{5+}$ is monomeric in aqueous solution, with a $\text{p}K_a$ for coordinated water of 6.0 (μ 0.1). None of the water-soluble cobalt and nickel porphyrins studied could electrocatalyze the reduction of protons to H_2 at $\text{pH} > 4$, but they did react with electrophiles such as iodomethane.

Introduction

The development of water-soluble porphyrins is very important because it facilitates the detailed study of proton-coupled redox reactions such as the reductions of O_2 , N_2 , H^+ , and CO_2 . However, the synthetic chemistry of water-soluble porphyrins has lagged behind the development of nonaqueous porphyrins. An examination of most synthetic water-soluble porphyrins shows that in many respects they are similar to tetraphenylporphyrin because the center of the porphyrin is relatively unperturbed by the introduction of a water-solubilizing group (Figure 1a).¹ A major reason for this lack of variability is that water solubilization requires the deliberate modification of porphyrins, and additional functionalization and purification become more difficult.

Several exceptions to the above generalizations are shown in Figure 1b. The sulfonated tetraphenylporphyrins TDSPP^{n-} and $\text{TCl}_2\text{SPP}^{n-}$, which contain ortho methyl or chloro substituents, have been used by Bruce to study the chemistry of oxidized porphyrins and their behavior as oxygenation catalysts²⁻⁴ in protic media. However, the alkyl substituents and sulfonato groups on these porphyrins are electron-donating and disfavor reductive processes. The coordination chemistry of the iron(III) derivative of the rotational atropisomers of methylated (nicotinamidophenyl)porphyrin (MenicPh)₄ P^{n+} has been studied in detail,⁵ and a brief report of the chemistry of the iron complex of the chlorinated porphyrin $\text{TCl}_2\text{4NMePyP}^{n+}$ has been reported.⁶ These porphyrins control access to the metal center through steric effects and also offer binding environments which are significantly different from the hydrogen pocket of the porphyrins in Figure 1a. None of

a. Common Water-soluble Synthetic Porphyrins



b. Modified Water-Soluble Porphyrins

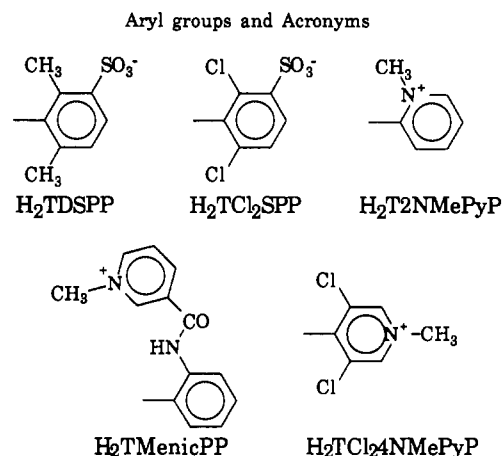


Figure 1. Water-soluble tetraarylporphyrins discussed in this paper.

these sterically hindered porphyrins have been used for a detailed study of reduced metalloporphyrin species.

The porphyrins in Figure 1a, and their metal complexes, have additional disadvantages besides lack of variability at the metal center. Many of the porphyrins can aggregate in solution, either

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- (1) Abbreviations for porphyrin dianions used in this paper: TMAP = tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrinato; T4NMePyP = tetrakis(*N*-methyl-4-pyridiniumyl)porphyrinato; T2NMePyP = tetrakis(*N*-methyl-2-pyridiniumyl)porphyrinato; TSPP = tetrakis(4-sulfonato-phenyl)porphyrinato; TCPP = tetrakis(4-carboxylatophenyl)porphyrinato; TDSPP = tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrinato; TCl₂SPP = tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrinato; TMenicPP = tetrakis(2-(*N*-methylnicotinamido)phenyl)porphyrinato (α and β refer to orientation of the substituents above and below the porphyrin plane); TCl₂4NMePyP = tetrakis(3,5-dichloro-*N*-methyl-4-pyridiniumyl)porphyrinato.
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through π - π interactions⁷⁻¹⁰ or through more specific bonding interactions such as formation of μ -oxo dimers.^{5,11-13} These possibilities complicate kinetic analysis because the aggregates may have reactivity different from that of the monomers and the monomer-aggregate interconversion may be slow. In addition, many of these simple porphyrins adsorb onto glassware or electrode surfaces,^{5,14,15} complicating kinetic and equilibrium studies. This has been of particular concern in studies of electrocatalysis, where adsorbed porphyrins have been shown to be catalytically active and have significantly altered redox and acid-base behavior compared to that of the solution species.¹⁶⁻¹⁹ This has frequently prevented researchers from obtaining data concerning the electrocatalytic properties of these porphyrins in solution. Even porphyrins which are known to be nonadsorbing under "normal" conditions can become strongly adsorbing when they are reduced.^{15,20}

The electrocatalysis of proton reduction by water-soluble cobalt porphyrins was first reported by Spiro, using Co(T4NMePyP) and Co(TMAP).¹⁵ This study was complicated by the adsorption of the porphyrins on all electrode surfaces tested, but it seemed to indicate that Co^I porphyrins could interact with protons to evolve H₂, and coulometric experiments showed that at -0.95 V vs SCE the current efficiency for dihydrogen evolution on Hg was 95% in 0.1 M trifluoroacetic acid. This current study attempted to explore this reactivity in homogeneous solution and extend it to other cationic water-soluble porphyrins.

The report by Kadish²¹ that treatment of tetrakis(pentafluorophenyl)porphyrin with metal ions in refluxing dimethylformamide gives the porphyrin tetrakis(2,3,5,6-tetrafluoro-*N,N*-dimethyl-4-aniliny)porphyrin, H₂TF₄DMAP, has led to a new series of cationic water-soluble metalloporphyrins based on the methylation of this porphyrin. Thus, methylation of H₂TF₄DMAP leads to tetrakis(2,3,5,6-tetrafluoro-*N,N,N*-trimethyl-4-anilinium)porphyrin, H₂TF₄TMAP⁴⁺ (Figure 2). The synthesis, characterization, and reactivity of the iron, cobalt, and nickel complexes of this porphyrin are reported in this paper.

Experimental Section

Initial studies used tetrakis(pentafluorophenyl)porphyrin from Mid-century Chemicals. Pentafluorobenzaldehyde, pyrrole, boron trifluoride etherate, and methyl trifluoromethanesulfonate were obtained from Aldrich Chemicals and were distilled immediately before use. (*Caution!* Methyl trifluoromethanesulfonate is potentially extremely hazardous; inhalation of vapor and contact with skin should be avoided.²²) Solvents were of analytical grade and were used as supplied. All other chemicals were of analytical or pure grade and were used as supplied. Air-sensitive compounds were manipulated in Schlenkware (N₂ atmosphere) or in a drybox (Vacuum Atmospheres, Ar atmosphere).

Solvents for electrochemical studies were purified as follows. Acetonitrile was distilled from CaH₂ under nitrogen, DMSO and DMF

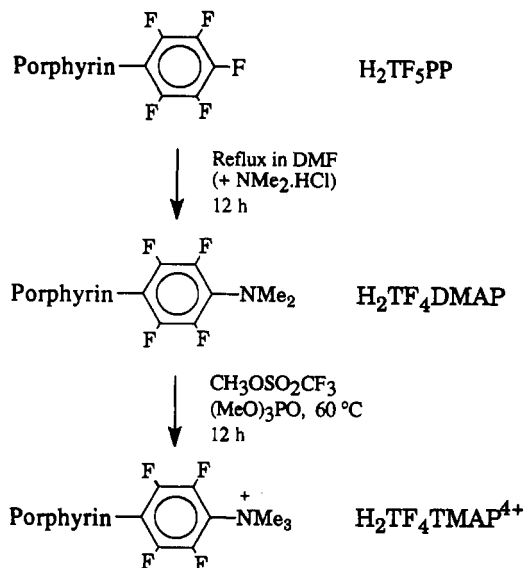


Figure 2. Synthesis and structure of the cationic fluorinated porphyrins.

were vacuum-distilled, and water was purified using a Barnstead Nanopure system (18 MΩ cm). Tetrabutylammonium perchlorate was prepared from tetrabutylammonium bromide and perchloric acid, recrystallized from ethyl acetate, and dried under vacuum before use. (*Caution!* Perchlorate salts are potentially explosive and should be handled with extreme care.) Cyclic voltammetry was performed in a three-electrode cell under nitrogen or argon. The working electrode was either glassy carbon (EG&G or BAS) or platinum wire, and the counter electrode was platinum gauze. The aqueous electrochemistry used homemade or commercial (Corning) SCE reference electrodes, while nonaqueous electrochemical experiments used a silver wire/1 mM AgPF₆, 0.10 M TBAP in acetonitrile reference and were referenced to ferrocene as a standard. Electrochemical experiments used PAR 173 and 175 controllers and either Houston Instruments or Elotek X-Y plotters. All electrochemical experiments were thermostated at 25.0 ± 0.2 °C unless otherwise noted.

Spectrophotometric measurements were performed using a Milton Roy Spectronic 3000 diode array spectrophotometer. pH measurements used an Orion 501 pH meter calibrated with commercial buffers (Baker or Fisher). pH_{obs} measurements quoted in this paper are the values shown on the meter in 50% (w/w) acetonitrile-water solution after calibration of the electrode with aqueous buffers. ¹H and ¹⁹F NMR spectra were obtained on a Bruker 250, 270, or 360 spectrometer. ¹H NMR data are quoted as δ (ppm) vs TMS, and ¹⁹F NMR data are quoted as δ (ppm) vs CFCl₃. Elemental analyses were performed by Oneida Research Services Inc, Whitesboro, NY.

Synthesis. 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin (H₂TF₅-PP) was prepared using the method reported by Lindsey,²³ using DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) as the oxidant. The most successful results (yields ca. 30%) were obtained with 1 mM BF₃-Et₂O as catalyst.

The cobalt complex of TF₄DMAP was prepared in one step using the DMF reflux method reported by Kadish.²¹ The purple solid obtained upon vacuum evaporation of the DMF was recrystallized from chloroform-ethanol-heptane (1:1:1), giving lustrous purple crystals (82-90%).

The free base and other metalloporphyrins required the addition of dimethylammonium chloride to obtain the desired product. The nickel derivative was synthesized as follows: H₂TF₅PP (0.13 mmol), Ni(C₂H₃O₂)₂·4H₂O (1.3 mmol), and (CH₃)₂NH·HCl (3.9 mmol) were refluxed in DMF (40 mL) under N₂ for 12 h. The solvent was removed under reduced pressure, yielding a purple solid which was recrystallized from ethanol-chloroform-heptane, 1:2:2 (yield 88%). The other M(TF₄-DMAP) complexes were prepared in a similar manner and had NMR spectra which agreed with those published previously.²¹ Fe^{III}(TF₄-DMAP)Cl had not been reported previously. ¹H NMR (CDCl₃): 4.36 (s, 24H, NMe₂), 80.2 (br, 8H, pyrrole β -H). ¹⁹F NMR (CDCl₃): -105.73 and -109.11 (4F and 4F', F' fluorines), -123.99 and -126.42 (4F and 4F', F fluorines).

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Table 1. Selected Physical Data for the Porphyrins Reported in This Paper

complex	UV-vis: solvent; λ , nm (log ϵ)	δ		E_{av} , V vs FeCp ₂ ⁺⁰
		<i>o</i> -F (F') ^b	<i>m</i> -F (F'') ^b	
H ₂ TF ₄ DMAP ^a	CH ₂ Cl ₂ ; 419 (5.45), 510 (4.32), 544 (3.70), 586 (3.85)	-140.3	-152.5	
Fe ^{III} (TF ₄ DMAPCl)	CH ₂ Cl ₂ ; 352, 417, 506, 644	-105.7	-124.0	
		-109.1	-126.4	
Co ^{II} (TF ₄ DMAP) ^a	CH ₂ Cl ₂ ; 410 (5.41), 526 (4.23), 553 (3.95)	-136.6	-150.8	-1.130 ^c
Ni ^{II} (TF ₄ DMAP) ^a	CH ₂ Cl ₂ ; 412 (5.26), 526 (4.20), 557 (3.90)	-140.4	-152.3	-1.410 ^d
H ₂ TF ₄ TMAP ⁴⁺	DMSO/acetone; 412 (5.59), 507 (4.62), 540 (4.10), 582 (4.23)	-134.9	-137.0	
Fe ^{III} (TF ₄ TMAP) ⁵⁺	CH ₃ CN; 353, 409, 506, 625	-132.3	-135.8	-1.150 ^e
Co ^{II} (TF ₄ TMAP) ⁴⁺	CH ₃ CN; 406 (5.22), 526 (4.08), 544 (4.00)	-130.7	-136.4	-1.040 ^e
Co ^{III} (TF ₄ TMAP) ⁵⁺	CH ₃ CN; 429 (5.20), 546 (4.16)	-134.9	-136.9	
Ni ^{II} (TF ₄ TMAP) ⁴⁺	CH ₃ CN; 399 (5.34), 521 (4.18), 557 (4.11)	-135.5	-137.5	-1.210 ^d

^a From ref 21. ^b M(TF₄DMAP) measured in CDCl₃; M(TF₄TMAP)⁴⁺ measured in CD₃CN. ^c Measured in DMSO-0.1 M TBAP. ^d Measured in DMF-0.1 M TBAP. ^e Measured in acetonitrile-0.1 M TBAP.

Methylation was performed with methyl trifluoromethanesulfonate in trimethyl phosphate at 50–60 °C. A typical preparation was as follows:

[Co(TF₄TMAP)](CF₃SO₃)₄. Co(TF₄DMAP) (0.17 mmol) and freshly distilled methyl trifluoromethanesulfonate (400 μ L) were stirred in trimethyl phosphate (15 mL) at 60 °C for 12 h under N₂; then methanol (2 mL) was added to destroy unreacted methyl trifluoromethanesulfonate. A red precipitate was obtained by slowly adding the reaction mixture to rapidly stirred ether (50 mL). The solid was washed with ether and dried in vacuo. The porphyrin was recrystallized by vapor diffusion of diethyl ether into an acetonitrile solution of the porphyrin in the glovebox (yield 97%). The Co(II) porphyrin had moderate stability toward air oxidation in the solid state but was stored in the glovebox. Anal. Calcd for C₆₀H₄₄N₈O₁₂F₂₈S₄Co.H₂O: C, 39.90; H, 2.57; N, 6.20. Found: C, 39.54; H, 2.53; N, 6.12. ¹H NMR (CD₃CN): 4.45 (s, 36H, N(CH₃)₃⁺), 13.4 (br, 8H, pyrrole β -H). ¹⁹F NMR (CD₃CN): -78.24 (s, 12F, CF₃SO₃⁻), -130.70 (br, 8F, F'), -136.38 (br, 8F, F'').

The following porphyrins were made in a similar manner:

[H₂TF₄TMAP](CF₃SO₃)₄. ¹H NMR (CD₃CN): -3.11 (s, 2H, core H), 4.11 (s, 36H, N(CH₃)₃⁺), 9.27 (s, 8H, pyrrole β -H). ¹⁹F NMR (CD₃CN): -135 (d, 8F, F'), -137 (q, 8F, F'').

[Ni(TF₄TMAP)](CF₃SO₃)₄.CH₃CN. Anal. Calcd for C₆₂H₄₇N₉O₁₂F₂₈S₄Ni: C, 40.72; H, 2.59; N, 6.89. Found: C, 39.27; H, 2.62; N, 7.00. ¹H NMR (CD₃CN): 4.07 (s, 36H, N(CH₃)₃⁺), 9.25 (s, 8H, pyrrole β -H). ¹⁹F NMR (CD₃CN): -136.1 (d, 8F, F'), -137.6 (d, 8F, F'').

[Co^{III}(H₂O)₂(TF₄TMAP)](PF₆)₃ was prepared by reaction of the Co(II) complex with ferric nitrate in acetonitrile-water and was precipitated with NH₄PF₆. ¹H NMR (CD₃CN): 4.10 (s, 36H, N(CH₃)₃⁺), 9.26 (s, 8H, pyrrole β -H). ¹⁹F NMR (CD₃CN): -135 (d, 8F, F'), -137 (d, 8F, F'').

[Fe^{III}(TF₄TMAP)](CF₃SO₃)₃ was characterized by NMR and UV-vis spectra only. ¹H NMR (CD₃CN): 5.21 (s, 36H, N(CH₃)₃⁺), 71.8 (br, 8H, pyrrole β -H). ¹⁹F NMR: -132.3 (br, 8F, F'), -135.8 (s, 8F, F'').

Results and Discussion

Synthesis and Characterization. Tetrakis(pentafluorophenyl)porphyrin was prepared using the method described by Lindsey,²³ which gives a higher yield and more pure product than the alternative Rothmund condensation in refluxing acetic acid. The incorporation of cobalt(II) and regiospecific substitution of fluorine by dimethylamine occur in one step as described by Kadish.²¹ However, in our hands the yields and purities of the Fe^{III}, Ni^{II}, and free base porphyrins were improved greatly if dimethylammonium chloride was added to the refluxing solution. The cationic porphyrins were then prepared via methylation of the dimethylaniline substituent, using methyl trifluoromethanesulfonate in trimethyl phosphate at 50–60 °C. The desired porphyrins were isolated as PF₆⁻, CF₃SO₃⁻, and Cl⁻ salts. The PF₆⁻ salts showed good solubility in acetonitrile and acetone and slight solubility in water but were insoluble in alcohols. The CF₃SO₃⁻ salts showed good solubility in acetonitrile and methanol and moderate solubility in water. Chloride salts were soluble in water but insoluble in polar organic solvents. All the PF₆⁻ and CF₃SO₃⁻ complexes were recrystallized by slow diffusion of ether into an acetonitrile solution of the porphyrin. However, the crystals formed were either too small or else too disordered for complete X-ray crystal characterization.

The methylation causes downfield shifts of about 5 ppm in the F' fluorine atoms and a shift of about 15 ppm in the fluorines (F'') adjacent to the anilinium group (Table 1). These shifts mean that in the cationic porphyrins the resonances are within 2 ppm. Assignment of the resonances was made on the basis of the greater shifting and broadening of F' in the paramagnetic porphyrins and of the larger splitting of the F' signal in unsymmetrically substituted Co(III) complexes. The electronic effect was also observed in the UV-visible spectrum, where methylation caused a blue shift in the Soret band (Table 1). The methylation also caused marked positive shifts in the reduction potentials of the porphyrins, and this is discussed in more detail below.

The nickel porphyrin is four-coordinate and diamagnetic in the solid state and in noncoordinating solvents, but in the presence of bases such as *N*-methylimidazole and pyridine it becomes paramagnetic and either five- or six-coordinate. These changes were monitored by UV-vis spectrophotometry, electrochemistry, NMR, EPR, and susceptometry measurements and will be described in a subsequent paper.

The iron(III) derivatives of the TF₄DMAP and TF₄TMAP⁴⁺ ligands have been synthesized. The uncharged Fe^{III}(TF₄DMAP)Cl is five-coordinate and high-spin in chloroform solution, and this is manifested both by the low-field signal for the pyrrole β -H ¹H NMR resonance (-80 ppm) and by the chemical shifts and inequivalence of the fluorines on the two faces of the porphyrin ring in the ¹⁹F NMR (Table 1). There are 5 equiv of CF₃SO₃⁻ to balance charge in acetonitrile solutions of Fe^{III}(TF₄TMAP)⁵⁺, and these anions are in rapid exchange between coordinated and uncoordinated species at room temperature, giving one broadened average peak in the ¹⁹F NMR at -76.3 ppm and only single peaks for the ortho (F') and meta (F'') fluorines. When the temperature is lowered to -28 °C, the CF₃SO₃⁻ signal narrows and the faces of the porphyrin become inequivalent in a manner similar to that reported previously for high-spin iron(III) porphyrins undergoing slow axial-ligand exchange.²⁴ However, no resonance for the coordinated CF₃SO₃⁻ was observed. There was no signal near 14 ppm in the ¹H NMR spectra (the region corresponding to a μ -oxo dimer) under neutral conditions in aqueous solution, demonstrating that the Fe(III) porphyrin remains monomeric in solution,^{5,12} in contrast to water-soluble porphyrins with hydrogens in the phenyl ortho positions. This was confirmed at higher concentrations in the electrochemical studies (vide infra). Non-ionic fluorinated porphyrins have been shown to form μ -oxo dimers in nonaqueous solution,²⁵ so it is possible that a combination of Coulombic repulsion and steric interaction of the fluorines is decreasing dimerization in these porphyrins. Preliminary experiments with hypochlorite in base suggest that this porphyrin has a stable iron(IV) oxidation state as was reported for iron tetrakis(*N*-methyl-2-pyridiniumyl)porphyrin.²⁶

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Table 2. First Reduction Potentials for Selected Metalloporphyrins Obtained from Cyclic Voltammetry

	E_{av}^a , V vs $FeCp_2^{+/0}$	pH ^b	E_{av}^b , V vs SCE
Co(TF ₄ TMAP) ⁴⁺	-0.960	5.83 ^c	-0.622 ^c
		7.22	-0.623
Co(T2NMePyP) ⁴⁺	-0.827	3.04	-0.640
		7.35	-0.644
Co(T4NMePyP) ⁴⁺	-0.961	5.65	-0.711
		7.35	-0.714
Co(TMAP) ⁴⁺	-0.96 ^d		
Ni(TF ₄ TMAP) ⁴⁺	-1.21 ^e	5.99 ^c	-0.860 ^c
		10.00	-0.875
Fe(TF ₄ TMAP) ⁵⁺	-1.15	3.03 ^c	0.107 ^c
		4.96	0.095
		8.33	-0.051
		11.01	-0.188

^a $E_{av} = (E_{pc} + E_{pa})/2$. Measured in acetonitrile-0.1 M TBAP unless otherwise stated. ^b $E_{av} = (E_{pc} + E_{pa})/2$. Measured in H₂O with 0.1 M NaNO₃ unless otherwise stated. ^c Measured in 50% (w/w) acetonitrile-H₂O with 0.1 M NaNO₃. ^d From ref 15. ^e Measured in DMF-0.1 M TBAP.

The cobalt(II) complexes are slowly oxidized by O₂ in solution, and the rate of oxidation is increased greatly in the presence of phosphines. The Co(III) bis(phosphine) complex so formed shows a hyper spectrum (Soret peaks of similar intensity at 376 and 474 nm), which has previously only been reported for thiolate-containing derivatives of Co(III).²⁷ The Co(III) mono(phosphine) complex could be formed by reaction of equal concentrations of Co^{II}(TF₄TMAP)⁵⁺ and PBU₃ in acetonitrile and shows a "normal" Soret region.

Electrochemistry. The electrochemistry of cobalt tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (Co(T4NMePyP)), which was reported by Spiro to reduce protons to dihydrogen electrocatalytically,¹⁵ was studied first. The porphyrin does not adsorb to a deactivated glassy carbon electrode to any measurable extent, so that the aqueous chemistry of this porphyrin could be studied without the complications due to adsorption reported earlier. In contrast to the previous studies, no reaction of the Co^I porphyrin on the cyclic voltammetric time scale (2–20 s) at pH > 4 was observed. In the pH range 4 < pH < 10 there was no dependence of the Co^{II/I} redox potential on pH, which means that protonation of the Co^I species is not significant on the seconds time scale in this pH range. This suggests that the catalytic behavior observed by Spiro is connected with adsorption of the porphyrin onto electrodes. Attempts to study the nickel analog, or use a mercury electrode to access more acidic conditions, were confounded by adsorption upon reduction. Attempts to counteract this problem by adding additional ionic groups via alkylation of the pyridine nitrogen of *meso*-tetrakis(4-pyridiniumyl)porphyrin with chloroacetic acid or sodium 2-bromoethanesulfonate¹⁴ did not prevent this adsorption. Our approach was then altered to one involving developing steric hindrance above and below the porphyrin plane to prevent adsorption, and this led to investigations of the halogenated derivatives described in this paper. A further effect of this steric hindrance is to inhibit dimer formation or bimolecular reactions.

A comparison of the redox behavior of some of these fluorinated porphyrins with that of unfluorinated analogs is given in Table 2. The cationic fluorinated porphyrins cannot be studied under strongly reducing conditions because an irreversible reduction occurs at -1.674 V vs $FeCp_2^{+/0}$ (Figure 3). This probably involves the perfluorinated trimethylanilinium groups,²⁸ since the reduction is not seen with the unfluorinated analog, M(TMAP), or with the fluorinated (dimethylaniliniumyl)porphyrin, M(TF₄DMAP).

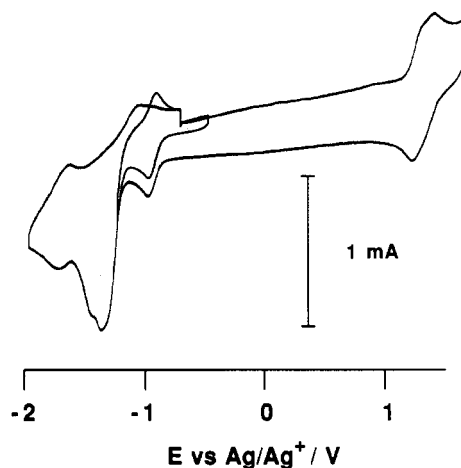


Figure 3. Cyclic voltammogram of Ni(TF₄TMAP)⁴⁺ at a GCE in acetonitrile (0.1 M (TBA)PF₆). Potentials are with respect to Ag/Ag⁺ (1 mM). Scan rate is 200 mV s⁻¹.

However, the cationic porphyrins appear quite stable at more moderate potentials in the absence of significant concentrations of nucleophiles.²⁹

The electrochemical results for the cobalt porphyrins are reported in Tables 1 and 2. In nonaqueous solution the Co(III/II) couple is poorly behaved (slow kinetics) and was not analyzed in detail. The Co(II/I) couple is well defined in all solvents used and shifts from -1.130 to -1.040 V vs $FeCp_2^{+/0}$ in DMSO (0.1 M TBAP) upon methylation. Addition of methyl iodide causes the reduction to become irreversible, presumably due to the irreversible formation of a cobalt-alkyl complex. In 50% MeCN-H₂O the Co(II/I) couple is independent of observed pH from 8.95 to 2.74, and the ratios of cathodic and anodic currents indicate that no reaction of the Co(I) species occurs on the cyclic voltammetric time scale. At low observed pH (<2.74) the cathodic current increased and the anodic current decreased, but analysis in this region was confounded by the proximity of the solvent limit. The measured reduction potentials are significantly more positive than those of most metalloporphyrins and are comparable to the isomeric TNMePyP reduction potentials (Table 2).

The electrochemical behavior of Ni(TF₄DMAP) and Ni(TF₄TMAP)⁴⁺ in 0.1 M TBAP in DMF is shown in Table 1. The first reduction has been moved almost 200 mV more positively upon methylation. This reduction is assigned to the reduction of the porphyrin ring, rather than reduction to Ni^I, on the basis of studies of other nickel porphyrins.^{30,31} Comparison with the results for the cobalt porphyrins (+100 mV shift in Co^{II/I} reduction potential) shows that methylation has a far larger effect on reduction of the porphyrin ring than on reduction of the metal. This shift in reduction potential alters the reactivity of the nickel porphyrins so that Ni(TF₄DMAP)⁻ reduces added methyl iodide in DMF catalytically, while Ni(TF₄TMAP)³⁺ reacts irreversibly with no increase in peak current (E_c, process³²). Kadish et al. noted that Ni(TF₄DMAP)⁻ does not react catalytically with methyl iodide in tetrahydrofuran solution,³¹ so the reactivity is clearly strongly solvent dependent. This may be an example of the significant role of axial ligands in such reactivity. Electrochemistry of the cationic nickel porphyrin in 50%MeCN-H₂O

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Table 3. Iron(III/II) Reduction Potentials and Acid Dissociation Constants for Fe(III) Porphyrins in Aqueous Solution

	E' , V vs SCE	$pK_{a1}(\text{Fe}^{\text{III}})$
$\text{Fe}^{\text{III}}(\text{TF}_4\text{TMAP})^{5+}$	0.110 ^a	6.0 ^{a,j}
$\text{Fe}^{\text{III}}(\text{T2NMePyP})^{5+}$	0.066 ^b	5.1, ^b 5.4 ^c
$\text{Fe}^{\text{III}}(\text{T4NMePyP})^{5+}$	-0.055 ^d	5.79 ^e
$\text{Fe}^{\text{III}}(\alpha\beta\alpha\beta\text{-MenicPh}_4\text{P})^{5+}$	-0.186 ^f	6.09 ^e
$\text{Fe}^{\text{III}}(\text{TDSPP})^{3-}$	-0.28 ^g	6.55 ^g
$\text{Fe}^{\text{III}}(\text{TSPP})^{3-}$	-0.23 ^h	7.0 ⁱ

^a Measured in 50% acetonitrile-H₂O-0.1 M NaNO₃. ^b 0.1 M Na₂SO₄, ref 33. ^c 0.05 M Na₂SO₄, ref 34. ^d 0.1 M NaNO₃, ref 39a. ^e 0.1 M NaNO₃, ref 5. ^f 0.1 M NaNO₃, ref 39b. ^g 0.2 M NaNO₃, ref 4. ^h 0.1 M H₂SO₄, ref 35. ⁱ 0.1 M NaNO₃, ref 11. ^j 0.1 M CF₃CO₂Na.

showed no sign of adsorption, in contrast to studies with Ni-(T4NMePyP)⁴⁺. The first reduction was observed at -850 mV vs SCE at pH_{obs} 10.99 and moved slightly to -880 mV at pH_{obs} 5.03. The ratio of cationic to anodic peak current was close to 1 above pH_{obs} 5, showing that the reduced porphyrin is unreactive in aqueous solution on the cyclic voltammetric time scale. The pH range was limited by the proximity of the bulk solvent reduction at low pH_{obs} (<4).

A study of the electrochemistry of Fe^{III}(TF₄TMAP)⁵⁺ in water showed that the iron(III/II) couple is quasi-reversible and is pH dependent with a pK_a for the iron(III) of 6.0 ± 0.1 (μ = 0.1 M). There was no evidence for a dimer in the electrochemical measurements (0.4 mM porphyrin). Table 3 compares this result to those of other reports of iron porphyrin reduction potentials and pK_a's.^{4,5,11,33-35} For all the previous porphyrins, there is a linear relationship between the Fe(III/II) reduction potential and the pK_a for water coordinated to Fe(III), with a slope ΔpK_a/ΔE' of about 4. This may be compared to the case of metal hydrides, in which the dissociating proton is attached directly to the metal center, where the slope is near 10, reflecting the greater dependence on the electron density at the metal.³⁶ However, the

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pK_a for Fe^{III}(TF₄TMAP)⁵⁺ is 1 pH unit higher than this trend probably as a result of the nonpolar Fe^{III} environment. Electrochemistry of the iron porphyrin in poorly buffered solution gave split peaks for the Fe(III/II) couple similar to those reported recently by Bruice.^{4,37} As has been reported previously, electrochemistry under these conditions cannot provide data on the thermodynamics of the solution species.³⁸ There is a subsequent reduction of the porphyrin at -0.980 V vs SCE in acetonitrile-water which is almost independent of pH in the range 12.13-6.16.

Conclusions

We have synthesized and characterized a new family of cationic porphyrins in which the two faces of the porphyrin are protected by fluorine atoms. The fluorines lower the water solubility but also decrease the extent of aggregation or adsorption of the porphyrins. Studies of the Fe, Co, and Ni derivatives of these porphyrins show behavior similar to that of other water-soluble porphyrins, apart from the reduced tendency to form dimers or aggregates. We have been unable to reproduce the previously reported H⁺ reduction electrocatalysis by homogeneous solutions of water-soluble cationic porphyrins. Further studies on the effects of axial-ligand binding and reactions with electrophiles will be presented in a subsequent paper.

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