Generation of a Stable σ-Bonded Iron(IV) Porphyrin. Formation and Reactivity of $[(OETPP)Fe^{IV}(C_6H_5)]^{n+}$ (*n* = 1–3; OETPP = Dianion of 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-Tetraphenylporphyrin)

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Summary: This work reports the first generation and spectral characterization of a σ-bonded iron(IV) porphyrin which is stable in nonaqueous media at room temperature, as well as the first monomeric iron(III) porphyrin to undergo three reversible one-electron oxidations. It also gives the first example where the migration of a σ-bonded axial ligand occurs from a doubly and not singly oxidized iron porphyrin.

High-valent iron porphyrins have attracted a great deal of interest due to their importance in oxidative catalytic processes[2–14] which occur in many biological systems.[15–18] The chemical or electrochemical oxidation of synthetic iron porphyrins containing hydroxide[5,19–22] or methoxide[4,19] axial ligands can result in highly reactive Fe(IV) derivatives, most of which are seen only at low temperature. Iron(IV) complexes have also been suggested as the initial product of $(OEP)Fe(C_6H_5)$ and $(TPP)Fe(C_6H_5)$[23] electrooxidation in nonaqueous media.[24–26] However, this reaction is followed by migration of the axial ligand to give an iron *N*-phenylporphyrin[24] and a spectroscopic characterization of the high-valent complex has, to date, only been possible at low temperature.[27]

All known monomeric iron(III) porphyrins had been shown to undergo a maximum of two reversible oxidations. The expected formation of *both* iron(IV) π cation radicals and dications after an initial Fe^{III}/Fe^{IV} reaction has never been observed, and there still remained the question as to whether these two higher oxidized forms of the porphyrin might be chemically or electrochemically generated from a given synthetic monomeric iron(III) complex. This question is answered in the present communication, which reports the first monomeric iron(III) porphyrin to undergo three reversible one-electron oxidations.

All $(P)Fe(C_6H_5)$ complexes synthesized to date have contained low-spin iron(III) or exist in a spin equilibrium, depending upon the specific porphyrin macrocycle.[26,28,29] The σ-bonded compound investigated in this present study is $(OETPP)Fe(C_6H_5)$, where OETPP is the dianion of 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin. It was prepared by the classical reaction of phenylmagnesium bromide with (OETPP)FeCl using literature procedures[26] and contains low-spin iron(III).[30,33]

A cyclic voltammogram[33] of $(OETPP)Fe(C_6H_5)$ in benzonitrile (PhCN) containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) shows three reversible one-electron oxidations at $E_{1/2}$ = 0.28, 1.09, and 1.31 V vs SCE. These are labeled as processes I–III in Figure 1a. The first may be compared to an $E_{1/2}$ value of 0.48 V for oxidation of $(OEP)Fe(C_6H_5)$ under the same solution conditions and is the most facile oxidation ever observed for an iron(III) porphyrin in nonaqueous media. The difference in $E_{1/2}$ values between processes I and II is 810 mV, while that between processes II and III is 220 mV. The latter value can be compared with a 250-mV separation generally observed between the formation of OEP or TPP

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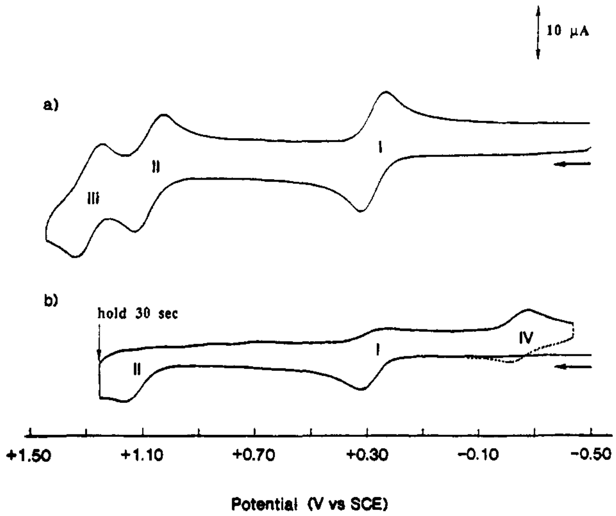

Figure 1. Cyclic voltammograms of 8.0×10^{-4} M (OETPP)-$Fe(C_6H_5)$ in PhCN (0.1 M TBAP) at (a) 0 °C for a scan rate of 0.3 V/s and (b) 23 °C for a scan rate of 0.1 V/s.

π cation radicals and dications[34] and suggests that process I is metal-centered, i.e., involves an Fe(III) → Fe(IV) transition.

Spectroelectrochemical[33] data (Figure 2a) also provide evidence for generation of an iron(IV) complex at room temperature. The singly oxidized species has absorptions at 357, 426, and 538 nm and lacks bands between 600 and 800 nm which would be diagnostic of a porphyrin π cation radical. The oxidation is spectrally reversible, and the 538-nm band of $[(OETPP)Fe(C_6H_5)]^+$ can be compared to bands at 540 to 550 nm for Fe(IV)–oxo complexes of the type (P)FeO.[35,36]

The σ-bonded iron(IV) complex was also generated by chemical oxidation of (OETPP)$Fe(C_6H_5)$ using 1 equiv of phenoxathiinylium hexachloroantimonate[37] in CH_2Cl_2 or $CDCl_3$ (for NMR studies) and quantitatively gave (OET-PP)$Fe^{IV}(C_6H_5)(SbCl_6)$, which has a UV–visible spectrum identical with the one observed in PhCN by thin-layer spectroelectrochemistry (Figure 2a). The ^1H NMR spectrum of this compound is shown in Figure 3 and is characterized by high-field chemical shifts for the axial phenyl proton resonances. Such changes have previously been reported for singly oxidized phenyliron tetraarylporphyrin complexes at 213 K,[27] but in the present case they

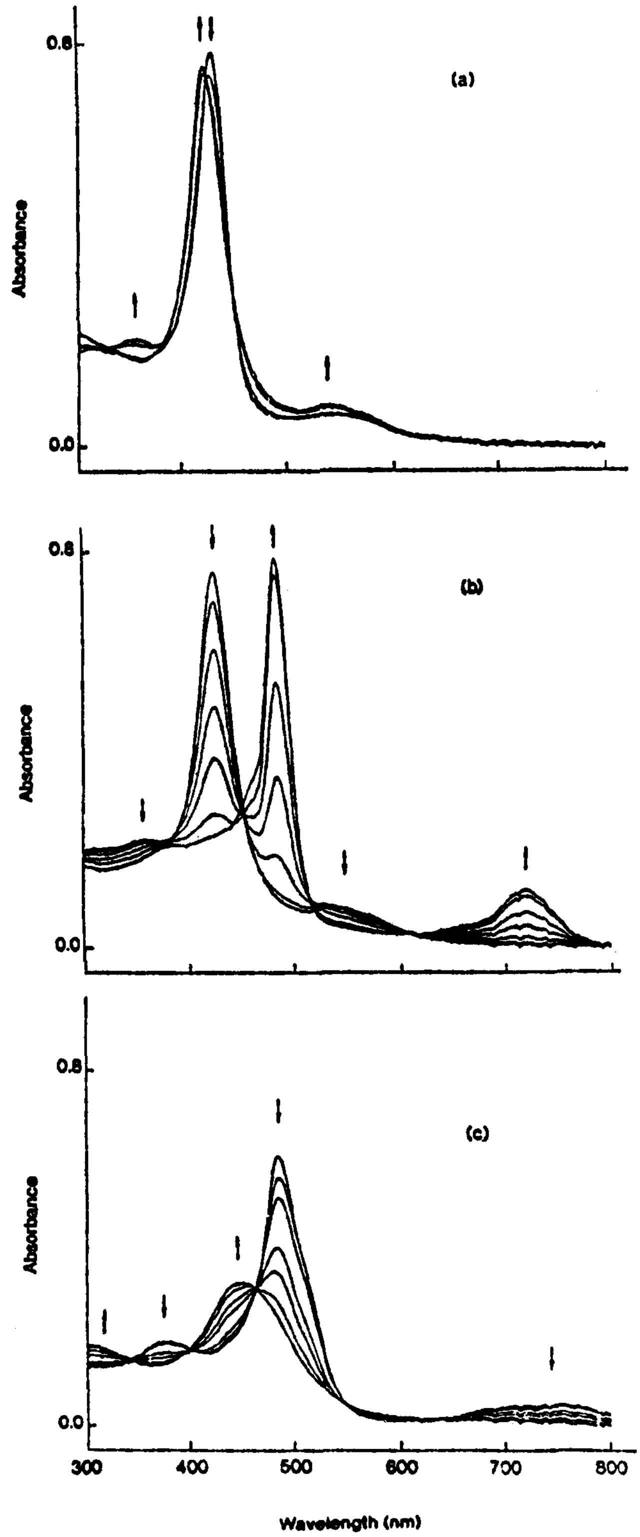

Figure 2. Time-resolved thin-layer electronic absorption spectra of 4.0×10^{-4} M (OETPP)$Fe(C_6H_5)$ in PhCN (0.2 M TBAP) at room temperature for the conversion of (a) (OETPP)$Fe^{III}(C_6H_5)$ to $[(OETPP)Fe^{IV}(C_6H_5)]^+$ at 0.5 V, (b) $[(OETPP)Fe^{IV}(C_6H_5)]^+$ to $[((N\text{-}C_6H_5)OETPP)Fe^{III}]^{2+}$ at 1.2 V, and (c) $[((N\text{-}C_6H_5)OETPP)Fe^{III}]^{2+}$ to $[((N\text{-}C_6H_5)OETPP)\text{-}Fe^{II}]^+$ at −0.50 V.

(30) The free base (OETPP)H_2 was prepared from benzaldehyde and 3,4-diethylpyrrole by following the literature procedure.[31] Iron was inserted using the ferrous chloride hydrate method.[32] (OETPP)$Fe(C_6H_5)$ was prepared by the classical reaction[24] of phenylmagnesium bromide with (OETPP)FeCl: a benzene solution of phenylmagnesium bromide was added dropwise via a syringe to 50 mg of (OETPP)FeCl (0.054 mmol) in 50 mL of freshly distilled benzene under argon. The reaction mixture was quenched with 5 mL of deaerated distilled water, after which the organic layer was washed twice with water, the two layers were separated, and the organic phase was dried over $MgSO_4$. After filtration, the dry benzene solution was passed through a column of basic alumina using benzene as eluent. The solvent was removed by evaporation under reduced pressure. Recrystallization of the resulting solid from a benzene/heptane mixture gave 34 mg (65% yield) of (OETPP)$Fe(C_6H_5)$. Anal. Calcd for $C_{66}H_{65}FeN_4$: C, 81.71; H, 6.75; N, 5.78. Found: C, 81.46; H, 6.85; N, 5.53. Spectroscopic data for (OETPP)$Fe(C_6H_5)$: UV–vis (C_6H_5; λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})): 432 (105.7), 537 (11.6, broad absorption). ^1H NMR (C_6D_6; from $SiMe_4$ at 294 K; δ, ppm): 14.39, 12.66, −0.74, −2.40 (16 H, α-CH_2), 7.51, 6.66, 5.42, 5.20, 4.29 (20 H, phenyl H_{por}), 1.22 (12 H, β-CH_3), 0.39 (12 H, β′-CH_3), −89.14 (2 H, o-$H_{axial\ ligand}$), 2.09 (2 H, m-$H_{axial\ ligand}$), −30.87 (1 H, p-$H_{axial\ ligand}$). ESR (toluene at 100 K): $g_x = 1.87$, $g_y = 2.24$, $g_z = 2.64$.

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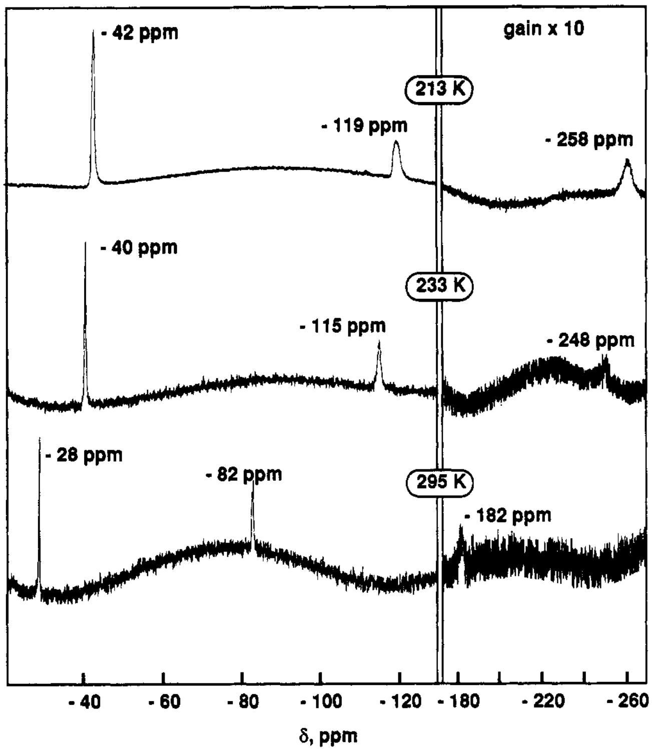
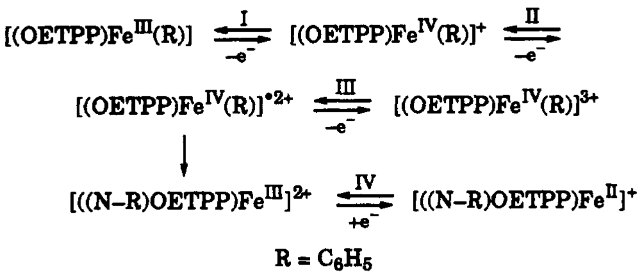


Figure 3. ^{1}H NMR spectrum showing axial phenyl proton resonances of oxidized $(OETPP)Fe^{IV}(C_6H_5)(SbCl_6)$ in $CDCl_3$ at 213, 233, and 295 K.

Scheme I



are observed at room temperature, consistent with a stable Fe(IV) species. The resonance assignments are as follows: *o*-H, −182/−258 ppm; *m*-H, −82/−119 ppm; *p*-H, −28/−42 ppm. Moreover, the rhombic EPR signals characteristic of the starting low-spin σ-bonded iron(III) complex totally disappear after oxidation and no new signal is observed. All of these data are in good agreement with formation of a stable $S = 1$ phenyliron(IV) complex at room temperature.

The second room-temperature oxidation of (OETPP)-$Fe(C_6H_5)$ is reversible at scan rates higher than 0.3 V/s, but the doubly oxidized species undergoes a chemical reaction on longer time scales, which results in a new one-electron-transfer at $E_{1/2} = -0.25$ V vs SCE (process IV in Figure 1b). UV–visible spectral changes obtained during the second oxidation are illustrated in Figure 2b. These changes are not reversible, and stepping the potential from +1.2 to −0.5 V (Figure 2c) generates a spectrum unlike that of the neutral or singly oxidized σ-bonded porphyrin. The final product formed after the second reversible one-electron oxidation (process II) and following coupled chemical reaction has bands at 382, 486, and 721 nm and is attributed to $[((N\text{-}C_6H_5)OETPP)Fe^{III}]^{2+}$. The product obtained after controlled-potential reduction at −0.5 V (process IV in Figure 2c) has only a single broad band at 448 nm and is assigned to $[((N\text{-}C_6H_5)OETPP)Fe^{II}]^{+}$.

The electrogeneration of $[((N\text{-}C_6H_5)OETPP)Fe^{III}]^{2+}$ would involve an iron to nitrogen migration of the C_6H_5 ligand in $[(OETPP)Fe^{IV}(C_6H_5)]^{2+}$ and is similar to migrations involving the conversion of $[(P)Fe^{IV}(C_6H_5)]^{+}$ to $[((N\text{-}C_6H_5)P)Fe^{II}]^{+}$ prior to a further one-electron oxidation to give the final iron(III) product, $[((N\text{-}C_6H_5)P)\text{-}Fe^{III}]^{2+}$ (P = OEP, TPP).[24] The results in this present study differ from those in the literature in that migration of the axial ligand is from the doubly oxidized species, i.e., an iron(IV) π cation radical, and leads directly to the iron(III) *N*-phenylporphyrin *via* the overall electrochemical EEC mechanism shown in Scheme I.

The reversible electrode reaction at $E_{1/2} = -0.25$ V is assigned as the Fe^{III}/Fe^{II} reaction of $[((N\text{-}C_6H_5)OETPP)\text{-}Fe^{III}]^{2+}$. This value differs from $E_{1/2}$ for the first electroreduction of $(OETPP)FeClO_4$[38] but should be compared to potentials for the reduction of $[((N\text{-}C_6H_5)TPP)Fe^{III}]^{2+}$ ($E_{1/2} = -0.06$ V) or $[((N\text{-}C_6H_5)OEP)Fe^{III}]^{2+}$ ($E_{1/2} = -0.18$ V) under similar experimental conditions. The more negative potential for the Fe^{III}/Fe^{II} reaction of $[((N\text{-}C_6H_5)\text{-}OETPP)Fe^{III}]^{2+}$ is expected in light of the higher basicity of the OETPP macrocycle with respect to that of OEP or TPP.[31]

In summary, this work reports the first generation and spectral characterization of a σ-bonded iron(IV) porphyrin which is stable in nonaqueous media at room temperature as well as the first monomeric iron(III) porphyrin to undergo three one-electron reversible oxidations. It also gives the first example where the migration of a σ-bonded axial ligand occurs from a doubly and not singly oxidized iron porphyrin.

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(38) The first reduction of $(OETPP)Fe^{III}ClO_4$ occurs at $E_{1/2} = -0.17$ V vs SCE in PhCN (0.1 M TBAP).