# Preparation, Characterization, and Reactions of Novel Iron(III) Porphyrin Dication Complexes

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**Abstract:** A dication complex of (*meso*-tetramesitylporphynato)iron(III) ($Fe^{III}TMP$) has been prepared by the reaction of $Fe^{III}TMP$ *N*-oxide with trifluoroacetic acid in toluene at low temperature. The electronic structure of the complex is characterized to be ferric high spin with rhombic symmetry on the basis of iodometric titration and UV–vis, $^2H$ NMR, and EPR spectroscopies. A value of $E/D$, which shows rhombicity of the heme environment, was estimated to be 0.29 by EPR measurement. An unusually high $E/D$ value indicates that the symmetry of the ligand field around the iron is rather similar to those of nonheme ferric complexes, and the porphyrin ring could exhibit large nonplanarity. While tetraphenylporphyrin dication complexes of Zn, Mg, and Ni are known to react with methanol to afford the corresponding isoporphyrins, the dication complex of $Fe^{III}TMP$ was found to react with methanol to yield $Fe^{III}TMP$ *N*-methoxide, possibly due to the sterric barrier of the *o*-methyl groups of mesitylene. The $Fe^{III}TMP$ dication is not thermally stable and is readily reduced to the $Fe^{III}TMP$ $\pi$-cation radical even at −25 °C in toluene. The dication complex of (*meso*-tetrakis(2,6-dichlorophenyl)porphynato)iron(III) ($Fe^{III}TDCPP$) was also prepared by the same reaction. The preparation of the dication complex of Fe(III) porphyrin demonstrates possible manipulation of the two-electron-oxidized equivalent in various forms by Fe porphyrin, i.e., the O=Fe(IV) porphyrin $\pi$-cation radical, O=Fe(V) porphyrin, Fe(III) porphyrin *N*-oxide, and the Fe(III) porphyrin dication.

## Introduction

Recent model studies of cytochrome P-450 by using iron complexes of tetraphenylporphyrin derivatives have served to elucidate the detail of the active species responsible for the oxygenation of foreign compounds, i.e., a two-electron-oxidized oxo–iron complex, equivalent to compound I of peroxidases.[1] On the other hand, Fe(III) porphyrin *N*-oxide had been proposed for a possible description of the active species on the basis of the chemical and spectroscopic behavior of Fe(III) porphyrin–carbene adducts.[2] However, the candidacy of the *N*-oxide has been ruled out by recent preparation of its model complex, $Fe^{III}TMP$ *N*-oxide (**1a**).[3a,b] In our effort to transform **1a** to the reactive species, we have found the reaction of **1a** and acid gives a new FeTMP complex (**3a**), which is formally two electron oxidized from $Fe^{III}TMP$. Preliminary work indicates **3a** being the $Fe^{III}$ TMP dication.[4] Interestingly, an Fe(III) porphyrin dication intermediate has been recently suggested as a candidate of compound 0, a precursor of compound I, in the reaction of $H_2O_2$ with horseradish peroxidase;[5] however, UV–vis spectra of compound 0 are different from that of **3a**.

Metalloporphyrin dication complexes of Mg, Zn, and Ni have been prepared by electrochemical oxidation and characterized by UV–vis spectroscopy.[6] Though the second oxidation potential obtained by cyclic voltammetry of some Fe(III) porphyrin complexes was attributed to Fe(III) porphyrin dication formation,[7] their physical properties such as UV–vis, EPR, and NMR spectra have never been observed, possibly due to their instability under the conditions. Thus, preparation, characterization, and elucidation of the structure and reactivities of Fe(III) porphyrin dication complexes are quite important. Especially, it allows us to fulfill a series of two-electron-oxidized forms of Fe(III) porphyrin complexes.

In this paper, we report the preparation, characterization, and reactions of the novel $Fe^{III}TMP$ dication and $Fe^{III}TDCPP$ dication complexes.

## Results and Discussion

**Preparation and Characterization of $Fe^{III}TMP$ *N*-Oxide (1a).** $Fe^{III}TMP$ *N*-oxide (**1a**) was prepared in the reaction of $Fe^{III}TMP(OH)$ and *m*CPBA in toluene at 0 °C according to the procedure reported before.[3] While **1a** has been characterized to be ferric high spin bearing the bridged Fe–O–N structure based on the magnetic susceptibility (5.4 $\mu_B$)[3a,b] and resonance Raman spectroscopy,[3c] its EPR signal was not well-defined. In addition, no $\beta$-pyrrole proton resonances of **1a** have been identified by $^1H$ NMR, because of broadening of signals. In this study, we have successfully prepared an EPR sample of **1a** to observe well-defined signals at $g$ = 9.0, 5.0, 3.8, and 3.5 (Figure 1a). Though the UV–vis spectrum of the EPR sample solution shows almost complete formation of **1a** (Figure 1a, inset), the EPR spectrum gives some signals due to impurities. The signals observed at 7.1, 6.1, and 1.98 are readily attributed to unreacted $Fe^{III}TMP(OH)$ and $Fe^{III}TMP$(*m*-chlorobenzoate) in comparison with the authentic samples, respectively. These assignments are further

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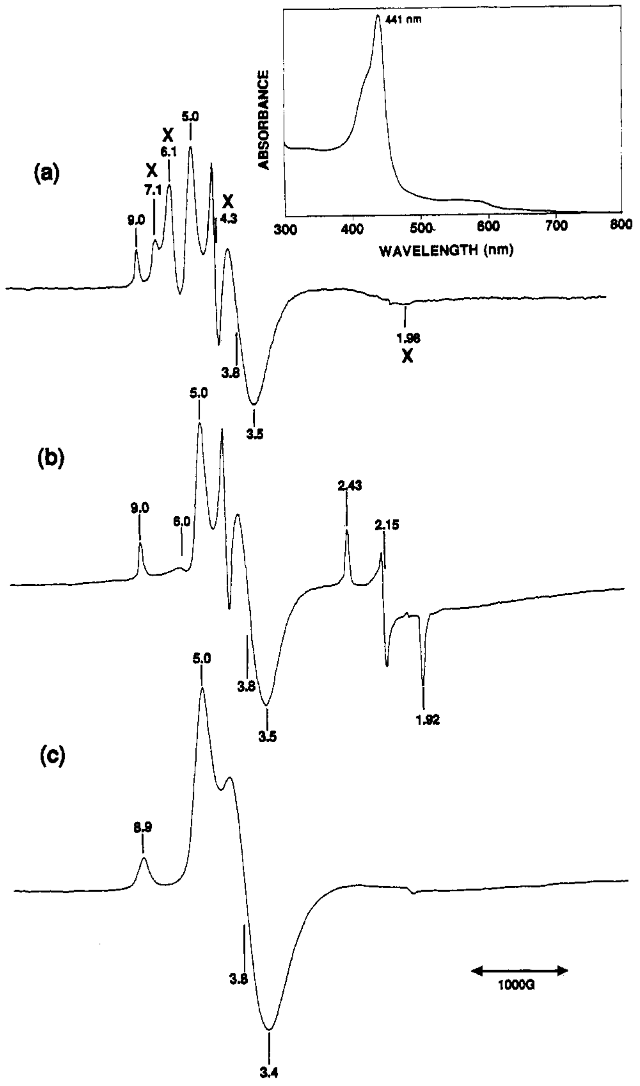

**Figure 1.** (a) EPR spectrum of Fe$^{III}$TMP *N*-oxide (**1a**) in toluene at 77 K; inset, UV–vis spectrum of the EPR sample solution; (b) an excess amount of pyridine added to a; (c) EPR spectrum of Fe$^{III}$EDTA $\mu$-peroxide in $H_2O$ at 77 K.

confirmed by adding an excess amount of pyridine to the EPR solution, causing the replacement of the absorption at 7.1 and 6.1 by those at 2.43, 2.15, and 1.92, according to the formation of the ferric low-spin complex, Fe$^{III}$TMP(Py)$_2$ (Figure 1b), while the signals observed at 9.0, 5.0, 3.8, and 3.5 remain unchanged. In addition, a sharp signal at 4.3 comes from a nonheme ferric complex due to the decomposition of **1a**. That the $E/D$ value for **1a** is estimated to be 0.20 by the $g$-value–$E/D$ diagram[8] indicates unusually large rhombicity of the ligand field. Very similar rhombicity in the EPR spectrum has been also observed for an Fe$^{III}$EDTA $\mu$-peroxide complex[9] (Figure 1c). The amounts of Fe$^{III}$TMP and nonheme iron(III) species remaining as impurities in the EPR sample solution were estimated in comparison of the UV–vis and EPR[10] spectra shown in Figure 1 with authentic samples to be <5% and <2%, respectively.

In order to identify the chemical shifts of $\beta$-pyrrole in **1a**, the $^2$H NMR spectrum of **1a**-$\beta$-pyrrole-$d_8$ at −50 °C in toluene was examined, since no appreciable resonances were observed by $^1$H NMR. As shown in Figure 2, **1a**-$\beta$-pyrrole-$d_8$ gives four pyrrole deuterium signals at 41.2, 71.7, 106, and 126 ppm. Appearance of the intense peak at 106 ppm is caused by overlapping of a small amount of $\beta$-pyrrole-$d_8$ of Fe$^{III}$TMP(*m*-chlorobenzoate) remaining in the sample solution. Curie plots of the temperature dependency of the chemical shifts of **1a** are shown in Figure 2 (inset). The linear behavior of the resonances is indicative of the spin state of **1a** being unchanged over the accessible temperature range. Observation of $\beta$-pyrrole deuterium resonances in the downfield and EPR spectroscopic feature is in good agreement with the previous assignment of **1a** to be ferric high spin with large rhombic symmetry.[3]

**Reaction of Fe(II) Porphyrin *N*-Oxides (1) with Acid.** Reaction of **1a** with acid was examined by UV–vis spectroscopy at low temperature. Upon addition of trifluoroacetic acid (TFA) to a toluene solution of **1a** at ca. −30 °C, an immediate spectral change of **1a** to **2a** followed by relatively slow spectral changes to **3a** was observed (Figure 3). While the reaction of TFA and Fe$^{III}$TDCPP *N*-oxide (**1b**) shows similar spectroscopic changes (Figure 3, inset), **3b** is less stable than **3a** under the reaction conditions.

Titration of **1** with TFA indicates that the stoichiometric amount of acid is consumed to complete the conversion of **1** to **2**. Upon the addition of an acid scavenger such as pyridine to a toluene solution of **2**, instantaneous reproduction of **1** was observed. The red-shifted soret band of **2** in the UV–vis spectrum is indicative of *N*-substituted iron porphyrin complex formation.[11] In addition, heterocyclic *N*-oxides are known to react with electrophiles such as proton and acyl halides at the *N*-oxide oxygen to yield the corresponding *N*-hydroxy and *N*-acyloxy derivatives.[12] Thus, **2** is assigned as a protonated form of **1**.

**Conversion of 2 to 3.** While the stoichiometric reaction of **1a** with TFA affords **2a** as a stable species at −30 °C under the diluted condition (ca. $10^{-5}$ M), introduction of additional TFA to the solution accelerates further reaction of **2a** to **3a**. The rate of formation of **3a** was dependent on the amount of TFA added, as described before.[4] The reaction of **2b** with TFA took place like **2a**; however, the rate of **3b** formation became much slower. In addition, slow decomposition of **3a** to the Fe$^{III}$TMP cation radical (**4a**)[13a] at −30 °C was observed. Finally, **4a** is reduced to Fe$^{III}$TMP when the solution is warmed to room temperature.[4] Replacement of toluene with chlorobenzene as the solvent decreases the rates of **4a** formation ($k_{\mathrm{tol}} = 4.8 \times 10^{-4}$ s$^{-1}$, $k_{\mathrm{Cl}} = 2.0 \times 10^{-4}$ s$^{-1}$). These results are summarized in Scheme I.

The transformation of **3a** to the corresponding Fe(III) porphyrin cation radical implies that **3a** is at least one (and possibly two) electron oxidized from the parent Fe$^{III}$TMP species. Though there are several candidates for the structure of **3a**, i.e., Fe$^{IV}$TMP, Fe$^{IV}$TMP$^{\bullet+}$, Fe$^{V}$TMP, and Fe$^{III}$TMP$^{2+}$, the former two species are readily eliminated from our consideration on the basis of their characteristic optical spectra.[13] Very recently, Goff and we have independently prepared O=Fe(V) porphyrin[14] and found that the UV–vis spectra of O=Fe(V) porphyrin complexes are very different from that of **3a**. More surprisingly, optical spectra of metalloporphyrin dication species of Zn, Mg, and Ni prepared by electrochemical oxidation are very similar to that obtained for **3a**.[6] Especially, no appreciable Q band for **3a** in the visible region is quite indicative of the loss of two electrons in the $A_{2u}$ (HOMO) orbital of the porphyrin ring.[6a] In addition,

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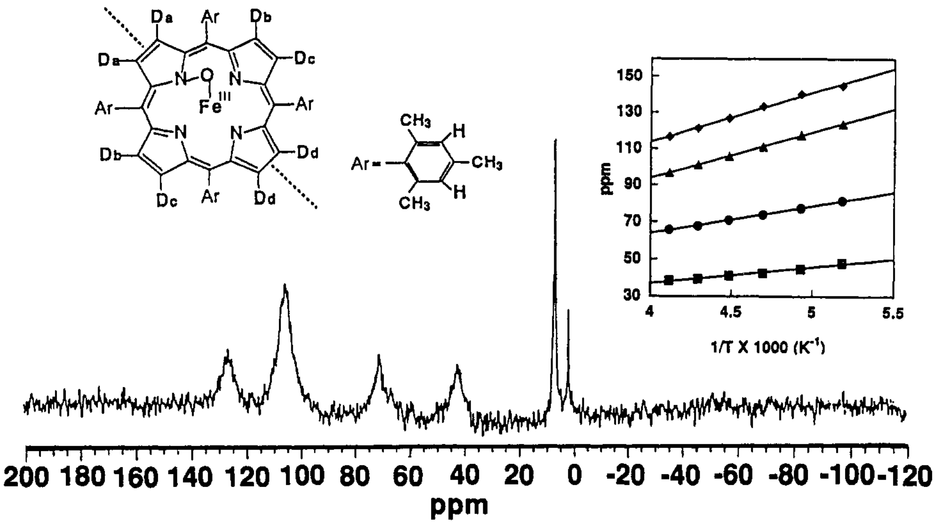


**Figure 2.** $^2$H NMR spectrum (pyrrole-*d*) of **1a** in toluene at –50 °C; inset, Curie plots.

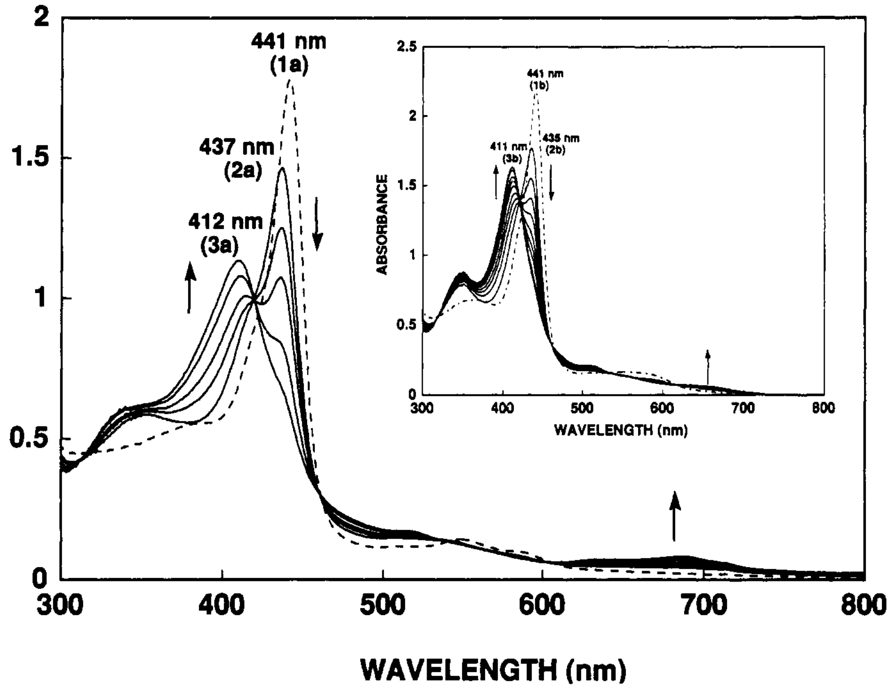
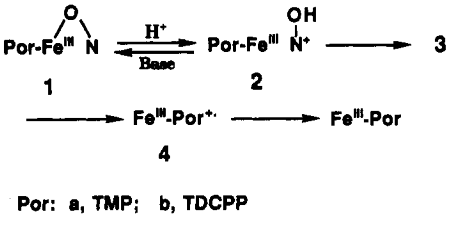


**Figure 3.** Time-dependent UV–vis spectral changes of **1a** (2.0 × $10^{-5}$ M) upon the addition of 16 molar equiv of TFA in toluene at –30 °C, cycle time 2 min; inset, time-dependent UV–vis spectral changes of **1b** (1.9 × $10^{-5}$ M) upon the addition of 50 molar equiv of TFA in toluene at –30 °C, cycle time 2 min.

**Scheme I**



iodometric titration of **3a** showed the completion of the reduction of **3a** to Fe$^{III}$TMP by 2 molar equiv of I$^-$. All the results support the Fe$^{III}$TMP dication formulation for **3a**. To get into the detail of the structure of **3a**, we have examined **3a** by EPR and $^2$H NMR spectroscopies.

**Further Characterization of the Fe$^{III}$TMP Dication Complex. EPR Spectral Measurement for 3a.** Like the reactions in a UV-cell, EPR spectral changes for the formation of **3a** were examined. When 40 equiv of TFA was added to a toluene solution of **1a** at –80 °C, an EPR spectral change giving new signals at 9.5 and 4.25 for **3a** was observed (Figure 4a,b). As indicated before, the starting solution of **1a** contains a small amount of unreacted Fe$^{III}$TMP species, which reacts with TFA to afford Fe$^{III}$TMP-(TFA) with an EPR signal at $g = 6.1$. Upon warming the solution to –30 °C, the intensity of the signals observed at 9.5 and 4.25 gradually decreases according to the reduction of **3a** by toluene to afford the EPR silent Fe$^{III}$TMP cation radical (**4a**) (Figure 4c,d). The reactions in the EPR sample solution were simultaneously monitored by means of UV–vis spectroscopy to confirm the formation of **3a** and **4a** in Figure, parts 4b and 4d, respectively. Appearance of the free radical signal at $g = 2.005$ in Figure 4 and discouragement of the reduction rate of **3a** in chlorobenzene indicate that the solvent itself is a reductant of **3a**.

The EPR spectroscopic measurements described above are a clear demonstration of **3a** being a ferric high-spin complex having rhombic symmetry, with *E*/*D* value of 0.29. The large *E*/*D* value indicates that the porphyrin ring of the dication complex exhibits large nonplanarity.[15]

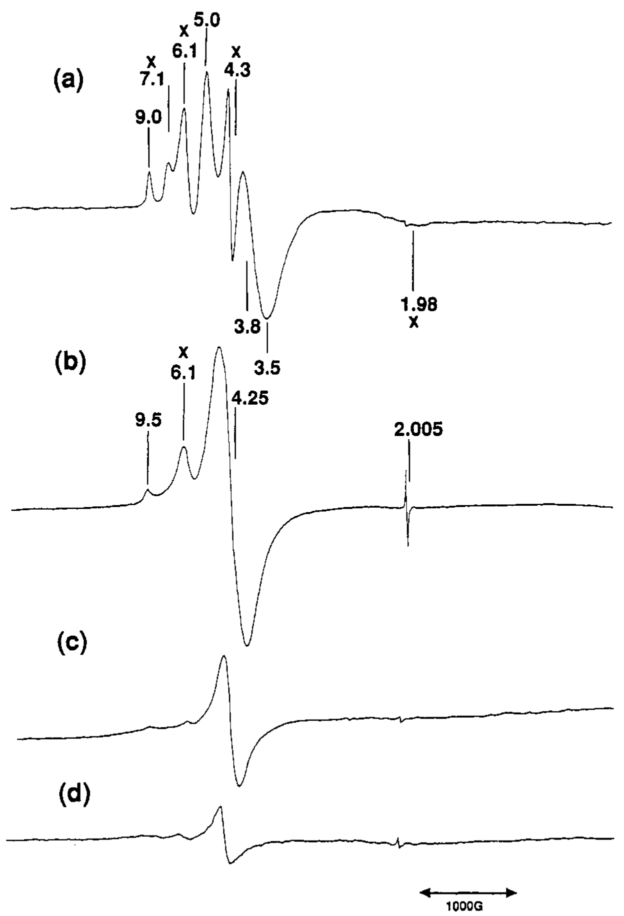


**Figure 4.** EPR spectral changes for the formation of **3a** in toluene at 77 K: (a) **1a**; (b) 40 molar equiv of TFA added to a; (c) 1 h after at −30 °C; (d) 2 h after at −30 °C.

**Table I.** Chemical Shifts of the β-Pyrrole Deuterium in Toluene at −80 °C

| complex | shifts (ppm) |
|---|---|
| $\mathrm{Fe^{III}TMP}$ *N*-oxide (**1a**) | 48, 82, 124, 145 |
| $\mathrm{Fe^{III}TMP^{2+}}$ (**3a**) | 118 (−75)[a] |
| $\mathrm{Fe^{III}TMP^{\bullet +}}$ (**4a**) | 108 |

[a] A small signal at −75 ppm was also observed, although we were not able to assign it.

**Deuterium NMR Spectral Changes for the Formation of 3a.** The reaction of **1a**-β-pyrrole-$d_8$ with TFA was also examined by $^2$H NMR spectroscopy. According to the formation of **3a**, four β-pyrrole deuterium signals of **1a** were replaced with a single resonance at 118 ppm.[16] In addition, the chemical shift of the signal obeys Curie's law in the temperature range −80 to −40 °C. Replacement of the resonance at 118–108 ppm was observed when the temperature was raised to −30 °C, according to the formation of the $\mathrm{Fe^{III}TMP}$ cation radical (**4a**). The chemical shifts of the β-pyrrole deuterium resonances for **1a**, **3a**, and **4a** are summarized in Table I. The conversion of **1a** to **3a**, and then to **4a**, in the NMR sample solution was also confirmed by UV–vis spectroscopic measurements. A large downfield hyperfine shift of the β-pyrrole deuterium resonance for **3a** indicates the location of an unpaired electron in the $d_{x^2-y^2}$ orbital, as in the case of the ferric high-spin ($S = 5/2$) complex.

There are two types of orbitals ($A_{1u}$ and $A_{2u}$) in the HOMO of metalloporphyrins, and the HOMO of $\mathrm{Fe^{III}TMP}$ is known to be $A_{2u}$.[17] The $A_{2u}$ orbital of the porphyrin ring exhibits large electron density at the *meso* carbons and pyrrole nitrogens. In the case of the $\mathrm{Fe^{III}TMP}$ dication, the loss of two electrons from the $A_{2u}$ orbital induces substantial amounts of positive charge at the *meso* carbons and pyrrole nitrogens. Therefore, the ligand field around the central iron turns much weaker and the energy level of the $d_{x^2-y^2}$ orbital becomes lower. These effects apparently favor the electronic configuration of ferric porphyrin dication complexes to be in the high-spin state. These considerations are consistent with the observation of the β-pyrrole deuterium resonance at 118 ppm at −80 °C and the EPR spectrum of **3a** at 77 K.

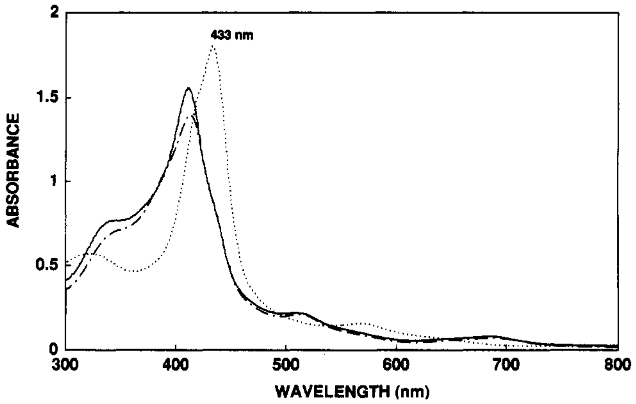


**Figure 5.** UV–vis spectral change for the reaction of **3a** ($2.6 \times 10^{-5}$ M) with methanol: (a) (—) **3a**; (b) (···) an excess amount of methanol added to a; (c) (–·–) an excess amount of TFA added to b.

Iodometric titration and UV–vis, EPR, and NMR spectroscopic measurements are in good agreement with the formulation of **3** being the Fe(III) porphyrin dication. It has been known that the reactions of methanol with metalloporphyrin dication complexes such as $\mathrm{Zn^{II}}$–, $\mathrm{Mg^{II}}$–, and $\mathrm{Ni^{II}TPP}$ dication complexes are commonly observed to produce the corresponding isoporphyrins.[18] Thus, we have examined the reaction of **3a** and methanol.

**Reaction of the $\mathrm{Fe^{III}TMP}$ Dication with Methanol.** When an excess amount of methanol was added to a $\mathrm{CH_2Cl_2}$–toluene solution of **3a** at −30 °C, the soret band was blue shifted by 20 nm, as presented in Figure 5. The UV–vis spectrum of the product (**5a**) is clearly different from those of isoporphyrins, which show intense absorbance at a near-IR region.[18] More importantly, the UV–vis spectrum of **5a** is quite similar to that of **2a**, and an EPR spectrum of **5a** gave signals at 9.2 and 4.22, indicating **5a** to be a ferric high-spin complex having a substituent at a pyrrole nitrogen. When an excess amount of TFA was added to the resulting solution, **3a** was re-produced with a small loss of intensity. These results suggest **5a** being $\mathrm{Fe^{III}TMP}$ *N*-methoxide by nucleophilic attack of methanol at a pyrrole nitrogen of **3a** instead of a *meso* position, since the *meso* position of **3a** is protected by the *o*-methyl groups of mesitylene. In order to characterize **5a**, demetalation of **5a** was carried out by adding HCl–AcOH.[3] Surprisingly, the $^1$H NMR spectrum of the demetalated product of **5a** is identical to that of $\mathrm{H_2TMP}$ *N*-oxide, as described in the experimental section. FAB mass spectroscopy ($\mathrm{M^+}$, 798; $\mathrm{M^+} - \mathrm{O}$, 782) also provides evidence that the demetalated product is $\mathrm{H_2TMP}$ *N*-oxide. Though the formation of $\mathrm{H_2TMP}$ *N*-oxide upon treatment of **5a** with acid was observed, the UV–vis spectrum of **5a** is different from that of **1a**. This implies the hydrolysis of $\mathrm{Fe^{III}TMP}$ *N*-methoxide during the demetalation.

The production of $\mathrm{Fe^{III}TMP}$ *N*-methoxide from **3a** demonstrates that the formal oxidation state of **3a** is the same as that

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of **1a**, i.e., two electron oxidized from the Fe$^{III}$TMP complex, consistent with iodometric titration of **3a**. EPR and NMR spectra provide solid evidence for the electronic structure of the central iron being in the ferric high-spin state. In addition, the loss of a Q band in the UV–vis spectrum of **3** is typical of the dication formation, but were different from those of the Fe(IV) porphyrin cation radical and Fe(V) porphyrin. These results are a clear demonstration of the formulation of the Fe(III) porphyrin dication complex for **3**.

The preparation of the dication complex of Fe(III) porphyrin shows possible manipulation of the two-electron-oxidized equivalent in various forms by Fe porphyrin, i.e., the O=Fe(IV) porphyrin $\pi$-cation ratical,[13b] O=Fe(V) porphyrin,[14] Fe(III) porphyrin *N*-oxide,[3] and the Fe(III) porphyrin dication.

In conclusion, we have prepared novel Fe(III) porphyrin dication complexes by the reaction of Fe(III) porphyrin *N*-oxides and TFA. The electronic structure of the dication is determined to be ferric high spin with unusually large rhombic symmetry on the basis of EPR and $^2$H NMR measurements. The reaction of methanol with the Fe$^{III}$TMP dication affords Fe$^{III}$TMP *N*-methoxide instead of isoporphyrin.

## Experimental Section

**Materials.** $CH_2Cl_2$ and toluene were distilled from $CaH_2$. *m*CPBA was purified by washing with an aqueous sodium bicarbonate solution. $H_2TMP$ and $H_2TDCPP$ was prepared by the reported method with modification.[18] Iron was inserted into $H_2TMP$ and $H_2TDCPP$ by a standard procedure. Fe$^{III}$TMP(OH) and Fe$^{III}$TDCPP(OH) were prepared as described earlier.[20] Fe$^{III}$EDTA $\mu$-peroxide was prepared by the method previously reported.[9]

**Physical Measurement.** $^2$H NMR spectra were recorded at 46.1 MHz on a Nicolet NT-300 spectrometer, and the $^1$H NMR spectrum was recorded at 500 MHz on a GE Omega 500 spectrometer. Chemical shifts are reported either relative to residual solvent resonances (toluene $\delta$ 7.2, $CH_2Cl_2$ $\delta$ 5.3) or relative to that of tetramethylsilane. UV–vis spectra were obtained with a Shimadzu 2200 spectrophotometer equipped with thermoelectric cold cells. EPR spectra were obtained with a JEOL PE-2X spectrometer.

**Preparation of Deuterated Porphyrin.** Mesitylene was treated with 10 M sulfuric acid-$d_2$ at 50 °C for 1 h twice to afford 60%-enriched mesitylene-$d_3$, as estimated from the $^1$H NMR spectrum.[21] Conversion of mesitylene-$d_3$ to mesitaldehyde-$d_2$ was accomplished by a literature method.[22] Pyrrole-$d_5$ was prepared by acetic acid-$d_1$ exchange, as described by Fajer et al.[23] Pyrrole-$d_8$ and *m*-$d_8$ $H_2TMP$ were prepared from pyrrole-$d_5$ and mesitaldehyde-$d_2$ in the usual manner.[19]

**Preparation of 1.** To a stirred solution of Fe$^{III}$TMP(OH) (5 mg, 6.3 mmol) in toluene (10 mL) was slowly added a solution of *m*CPBA (3 mg, 18.9 mmol) in toluene (5 mL) at 0 °C. Completion of the reaction was monitored by UV–vis spectral changes of the solution. Fe$^{III}$TDCPP *N*-oxide (**1b**) was also prepared in the same manner at –5 °C.

**Preparation of the NMR and EPR Samples of 1a and 3a.** A round-bottom flask was charged with Fe$^{III}$TMP(OH) (5.0 mg, 6.8 $\mu$mol), sodium acetate (100 mg, 1.2 mmol), and toluene (10 mL). The resulting solution was stirred at –10 °C, and *m*CPBA was added stepwise until complete formation of **1a**. Evaporation of the solvent at –30 °C reduced the volume to ca. 1 mL. The toluene solution was transferred to an NMR or EPR tube at –60 °C. The NMR and EPR samples of **3a** were prepared by the addition of a toluene solution of TFA to the NMR and EPR samples of **1a**.

**Preparation of the EPR Sample of 5a.** A 200-$\mu$L toluene solution of TFA (40 molar equiv) was added to a 10-mL toluene solution ($10^{-4}$ M) of **1a** at –80 °C to afford **3a**. The resulting solution was added to 60 mL of $CH_2Cl_2$ which had been precooled at –80 °C to obtain a $CH_2Cl_2$–toluene solution (6:1) of **3a**. The complete formation of **5a** can proceed either by adding a large excess amount of methanol or by introducing a small excess amount of methanol containing *n*-$Bu_4NOH$ to neutralize the solution. Evaporation of the solution at –30 °C reduced the volume to ca. 3 mL. The solution was transferred to an EPR tube at –60 °C for the measurement.

**Demetalation of 5a.** A 25-mL HCl–AcOH (1:4) solution was added to a 200-mL solution of **5a** at –30 °C. After complete color change from yellow to green, the solution was washed with saturated $NaHCO_3$ solution. The $CH_2Cl_2$ solution was evaporated at –5 °C to a volume of 50 mL, and the resulting solution was then submitted to column chromatography ($SiO_2$). The product was eluted with benzene–ethyl acetate (10:1) to give a dark brown band which contained $H_2TMP$ *N*-oxide. The yield of the *N*-oxide was 39%. $^1$H NMR (ppm in $CD_2Cl_2$), pyrrole, $\delta$ 8.53 (4 H, ABq, $J = 20.8, 5.0$), 8.42 (2 H, s), 7.50 (2 H, s); *m*-H, 7.26 (8 H, s); *p*-Me, 2.60 (12 H, s); *o*-Me, 1.88 (12 H, s), 1.89 (12 H, s); *N-H*, 1.72 (2 H, s).

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