# Resonance Raman Spectra of Fluoride Anion Ligated Ferryloxo Tetramesitylporphyrin π Cation Radical Compounds

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## Introduction

It has been known that two oxo iron porphyrin intermediates, commonly referred to as compound **I** and compound **II**,[1] are involved in the catalytic cycles of heme-dependent enzymes such as peroxidases and catalases.[2] A generation of such high-valent isolated synthetic metalloporphyrin derivatives is of interest in terms of biomimetic studies.[3] Two-electron oxidation found in the initial step of the catalytic cycle is also obtained by reaction with oxo transfer reagents and seemingly yields an oxo iron(IV) porphyrin π cation radical species (compound **I**).[4] Since Groves *et al.*[4a] first reported the production of a ferryloxo tetramesitylporphyrin π cation radical [(TMP•+)Fe$^{IV}$=O, **1**], which took place through the reaction of iron(III) tetramesitylporphyrin chloride [(TMP)Fe$^{III}$-Cl, **2**-Cl] and *m*-chloroperoxybenzoic acid (mCPBA) at −78 °C, extensive studies have been made in many laboratories.[5] The utility of resonance Raman (RR) spectroscopy to study the high-valent oxo iron porphyrin π cation radical has been demonstrated by many investigators.[3a]

Hashimoto *et al.*[6] obtained RR spectra of a green compound which has a typical property of ferryloxo porphyrin π cation radical. The record of the RR spectra was made using a spinning cell for the species generated from the reaction of mCPBA with **2**-Cl in CH$_2$Cl$_2$ and methanol mixture solution at −78 °C. The RR band of ν(Fe=O) appeared at 828 cm$^{-1}$ ([$^{16}$O]mCPBA), and shifted to 792 cm$^{-1}$ ([$^{18}$O]mCPBA), and he later reassigned it to **1**-methanol (**1**-MeOH) species, after studying the RR spectra of **1**-(alcohol) with four different alcohols.[7]

Kincaid *et al.*,[8] however, suspected that the RR spectra obtained by Hashimoto *et al.* might result from a photoproduct owing to its photolability of the 828 cm$^{-1}$ species and insisted that the ν(Fe$^{IV}$=O) band at 802 cm$^{-1}$ (767 cm$^{-1}$) from the reaction of **2**-Cl with [$^{16}$O]mCPBA ([$^{18}$O]mCPBA) in CH$_2$Cl$_2$ solution could be assigned to a 5-coordinated π cation radical species, shown as **1**. Consequently, the ν(Fe=O) RR bands were seen at 828 cm$^{-1}$ with the presence of MeOH, and at 802 cm$^{-1}$ without. The explanation of the frequency difference has been provided through the difference between alcohol-coordinated (6-coordinated) and noncoordinated (5-coordinated) compounds; nonetheless, it runs counter to the rule of trans ligand effects.[9] Finally, an attempt was made by Hashimoto *et al.* to explain through the difference between alcohol-coordinated and *m*-chlorobenzoate (mCB)-coordinated compounds, as following; Groves and Watanabe[4e,f] previously inferred that mCB, the product of mCPBA by its reaction with **2**-Cl, was coordinated to the iron(IV) ion at the position trans to the oxo ligand.

However, it seems difficult to accept the reasoning, because the RR spectrum obtained from the species produced by oxidation with ozone (no mCPBA)[10] is identical with the one obtained by Kincaid *et al.*[8a] Recently, Gross and Nimri[11] reported the data of the various NMR and EPR spectra for **1**-X (X = Cl, F, etc.). They suggested that the **1**-Cl species was generated by the oxidation of **2**-Cl with ozone in CH$_2$Cl$_2$ solution. It should be noted that the UV−Vis spectrum obtained from the oxidation reaction of **2**-Cl with mCPBA, and the one from the oxidation reaction with ozone, are superimposable. This means that both products belong to the same species. Therefore, the green product obtained by Kincaid *et al.* could be assigned to the **1**-Cl (6-coordinated) species instead of the 5-coordinated one. From all of those controversies, we intend to prepare a fluoride-ligated π cation radical porphyrin in order to have a clear-cut evaluation of the green compounds of Hashimoto *et al.* and Kincaid *et al.* and to observe the trans ligand effects on a π cation radical porphyrin.

## Experimental Section

**Compound Preparation.** 5,10,15,20-Tetramesitylporphine (H$_2$-TMP) was purchased from Midcentry (Posen, IL). H$_2$TMP was free from reduced porphyrin and was used without further purification. The metal was incorporated into H$_2$TMP by refluxing the porphyrin in dimethylformamide (DMF) containing ferrous chloride under a nitrogen atmosphere.[12] Fe(TMP)F was synthesized according to the previously described method.[13]

Oxygen-labeled mCPBA [$^{16}$O$^{16}$O, $^{18}$O$^{18}$O, and scrambled ($^{16}$O$^{16}$O: $^{16}$O$^{18}$O:$^{18}$O$^{18}$O = 1:2:1)] was prepared by the methods of Johnson[14] and Brown.[15] The reaction product was checked by the O−O stretching vibration band in the Raman spectra. Tetrabutylammonium fluoride trihydrate (TBAF·3H$_2$O) and solvents, DMF and methylene chloride (CH$_2$Cl$_2$), were also purchased from Aldrich Chemical Co. and dried by reflux over sodium metal and calcium hydride, respectively, prior to use.

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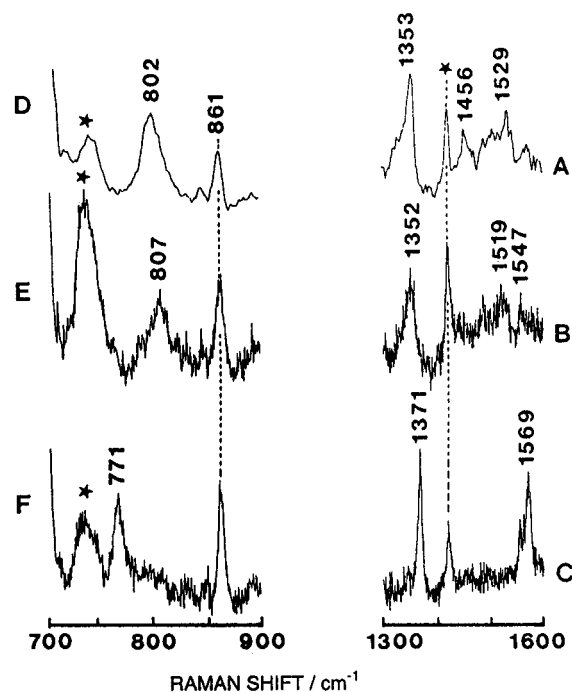
**Figure 1.** Resonance Raman spectra obtained from the reaction product of (A) $Fe^{III}(TMP)Cl + [^{16}O]$mCPBA, (B) $Fe^{III}(TMP)F + [^{16}O]$mCPBA, (C) $Fe^{III}(TMP)Cl + TBAF \cdot 3H_2O + [^{16}O]$mCPBA, (D) same as (A), (E) same as (B), and (F) $Fe^{III}(TMP)F + [^{18}O]$mCPBA, in $CH_2Cl_2$ at $-78$ °C. Asterisks indicate $CH_2Cl_2$ solvent. Experimental conditions: excitation, 406.7 nm and $\sim$5 mW (line focus on the sample surface); sample concentration, $\sim$1 mM (iron porphyrin). Resonance Raman spectra were collected at 1 cm$^{-1}$ intervals at a rate of 1 s/point, and accumulated three scans.

**Spectral Measurement.** Low-temperature Raman experiments were performed using a low-temperature stirred dewar cell (LSC) which was stirred with magnetic stirring bar rotated by externally mounted stirring rod. The sample solution was degassed by nitrogen gas for at least 30 min before use. All reactants were introduced by syringe. The samples were kept at $-78$ °C by a dry ice–acetone solution.

RR spectra were recorded on a Spex Model 1403 double monochromator coupled with a Hamamatsu R-928 photomultiplier and a Spex DM1B data station. Excitation at 406.7 nm was made with a Coherent Model Innova 100-K3 Kr$^+$ ion laser. The laser power on the sample was kept at $\sim$5 mW. In order to avoid fast sample decomposition, backscattering geometry was set up with two small mirrors and a cylindrical lens to produce a line focus on the sample surface.[16] The line image on the scattering surface was about 4 mm high. Thus, the power density on the sample was at least 20-fold lower than in the case of a point focus produced by a conventional spherical lens. Estimated accuracy in frequency readings was ±1.0 cm$^{-1}$.

Electronic spectra were measured in the region of 700–300 nm using a Shimadzu UV-200 spectrophotometer.

EPR spectra were obtained at 4 K with a Bruker ESP 300S spectrometer operating at 9.4 GHz. The microwave frequency was 100 kHz, and the cavity was TE$_{102}$. Modulation amplitude was 1 G, and the microwave power was 1 mW. An Oxford ESP 900 cryostat was used. EPR samples were prepared at $-78$ °C, and the solvent was $CH_2Cl_2$.

## Results and Discussion

Figure 1 shows RR spectra recorded with the 406.7 nm excitation line of Kr$^+$ ion laser. Figures 1A and 1D were reproduced from the reaction product of **2**-Cl and $^{16}$O-mCPBA in $CH_2Cl_2$, which was identical with the RR spectra of the authentic compound previously observed by Kincaid *et al.*[8a]

Figures 1B and 1E were obtained from the reaction product of **2**-F and $^{16}$O-mCPBA in $CH_2Cl_2$ (Let's refer to this reaction product as **3**). As seen in Figures 1A and 1B, the high frequencies in both figures show a big similarity in the patterns of band shift in oxidation and spin state sensitive bands; $\nu_4$ downshifts by 19 cm$^{-1}$ to 1352 cm$^{-1}$, and $\nu_2$ by 20 cm$^{-1}$ to 1547 cm$^{-1}$. These amounts of downshift are derived from the corresponding values of $\nu_4$ and $\nu_2$ observed for ferryloxo tetramesitylporphyrin non-radical complex, $O=Fe^{IV}(TMP)$, refered to as **4** hereafter. In particular, it is illustrated in Figure 1B that there was a typical decrease in the intensity of all macrocycle modes upon generation of **3**. Thus, it is consistent with the expected A$_{2u}$ type $\pi$ cation radical formation.[17]

In the low-frequency region, Figure 1E was obtained with [$^{16}$O]mCPBA and exhibits the typical band of tetramesitylporphyrin at 861 cm$^{-1}$ and a new band at 807 cm$^{-1}$. The new band shifts to 771 cm$^{-1}$ when [$^{18}$O]mCPBA is applied (Figure 1F). A similar experiment with an isotopically scrambled mCPBA gives two distinct Raman bands at 807 and 771 cm$^{-1}$ with equal intensity (not shown). The fact that no new band is seen between these two bands rules out the possibility of assigning these bands to the $\nu$(O–O) of the peroxo species, (TMP)FeOOFe(TMP). The observed shift ($\Delta\nu = 36$ cm$^{-1}$) is in good agreement with the calculated value ($\Delta\nu = 35$ cm$^{-1}$) expected for a diatomic Fe–O vibrator. Thus, the bands at 807 and 771 cm$^{-1}$ can be assigned to the $\nu$(Fe=O) of the **1**-X species. The structure of that will be discussed.

The band at 802 cm$^{-1}$ was assigned to the $\nu$(Fe=O) of **1**, which is 5-coordinated according to Kincaid *et al.*,[8a] while Hashimoto *et al.*[7] assigned the same band to the $\nu$(Fe=O) on **1**-mCB, which is 6-coordinated. Their explanation suggests that in Figure 1D and E the same $\nu$(Fe=O) frequencies be shown from the oxidation product of mCPBA and the porphyrins, although the porphyrins differ in the ligands they have as being **2**-Cl or **2**-F. However, the oxidation products possess different values (802 cm$^{-1}$ with **2**-Cl, 807 cm$^{-1}$ with **2**-F, as initial porphyrin) for $\nu$(Fe=O). Thus, it is assumed that they both have different environments due to axial ligands, which means they have different ligands trans to the oxo ligand. It is possible to explain the band at 802 cm$^{-1}$ (Figure 1D) to **1**-Cl and 807 cm$^{-1}$ (Figure 1E) to **1**-F. The ligand with higher $\sigma$ donor property overcomes in the competition for coordination if the concentration of ligands were same. Actually, the concentration of F$^-$ (or Cl$^-$) is same as that of mCB in that reaction.

Also, these assignments are supported by the pyrrole chemical shifts by NMR.[18,19] It is well-known that the pyrrole chemical shifts in iron(III) porphyrins are very sensitive to the field strengths of the axial ligands. The NMR values of pyrrole hydrogen decreased as Cl > F ≫ MeOH and it is reversibly proportional to the frequencies of $\nu$(Fe=O) as 802, 807, and 828 cm$^{-1}$ for **2**-X (Cl, F, and MeOH, respectively). These values are also consistent with our assignment. The ligands, mCB and OClO$_3$ show very close $\sigma$ donor properties according to RR data,[20] and OClO$_3$ and MeOH also show similarity.[11a] Thus, it is inferred that ligands mCB and MeOH will have a

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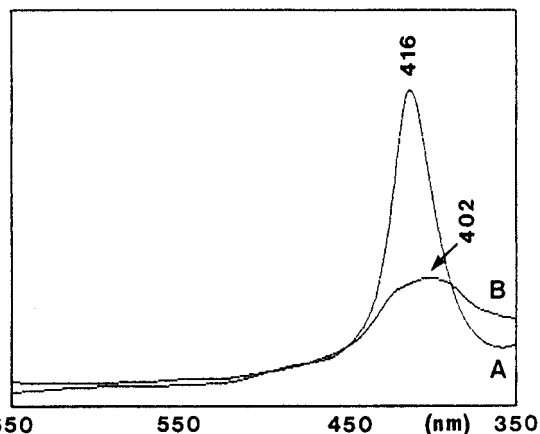(20) Paeng, I. R.; Paeng, K.-J. *Bull. Kor. Chem. Soc.* **1995**, *16*, 997–1000.
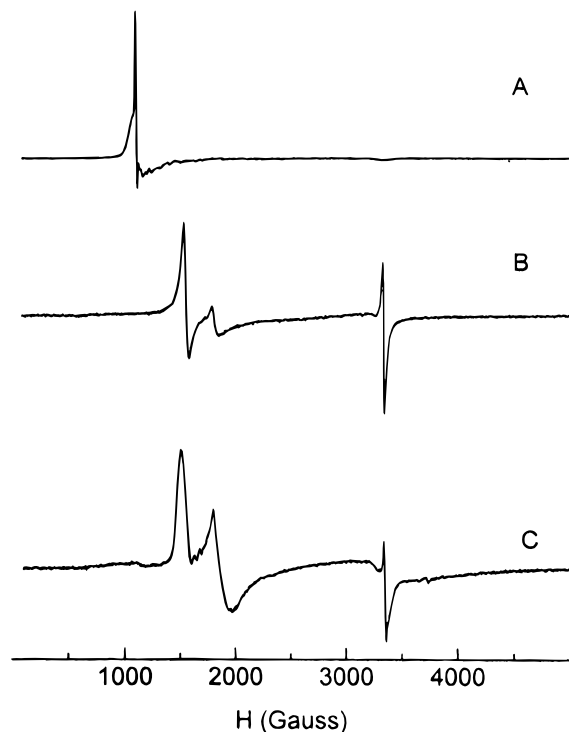
**Figure 2.** X-band EPR spectra observed at 4 K in $CH_2Cl_2$ from the reaction product of (A) $Fe^{III}(TMP)Cl$ + TBAF·$3H_2O$, (B) $Fe^{III}(TMP)$-Cl + mCPBA, and (C) $Fe^{III}(TMP)Cl$ + TBAF·$3H_2O$ + mCPBA.



**Figure 3.** UV−Vis spectra observed in $CH_2Cl_2$ at −78 °C from (A) $Fe^{III}(TMP)Cl$ + TBAF·$3H_2O$ and (B) $Fe^{III}(TMP)Cl$ + TBAF·$3H_2O$ + mCPBA.

similar $\sigma$ donor strength, and it is considered that the band will appear at 828 $cm^{-1}$ if mCB were coordinated to the sixth position.

The photolability of the $\pi$ cation radical porphyrins is still in controversy. Horseradish peroxidase (HRP) compound **1** in aqueous solution has been known to be subject to efficient photodegradation.[21] Figure 1C was obtained from the oxidation product of **2**-Cl reacted with mCPBA in the presence of TBAF·$3H_2O$; let us refer to this reaction product as **5**. It shows distinctly different RR spectra compared with Figure 1A and B, $\nu_2$ (1569 $cm^{-1}$) and $\nu_4$ (1371 $cm^{-1}$). These frequencies are very close to the values (1565 and 1369 $cm^{-1}$) of those in the nonradical ferryloxo porphyrin, **4**.[3a] Thus, it can be assumed that nonradical ferryloxo-like species are produced in the presence of TBAF·$3H_2O$, according to high-frequency RR spectrum.

Additionally, we examined the EPR spectrum of **5** to characterize the electronic configuration in the iron and porphyrin ring environment. Figure 2A is an EPR spectrum for a mixture of **2**-Cl and TBAF·$3H_2O$ in $CH_2Cl_2$ frozen solution and shows an axially coordinated fluoride complex, **2**-F. Figure 2B was obtained from a reaction product of **2**-Cl and mCPBA in

$CH_2Cl_2$, and exhibits the typical $\pi$ cation radical porphyrin ring with signal at 3350 G ($g$ = 2.008), which is identical to the one that is in the published reference.[11] Figure 2C obtained from **5** shows EPR signals at 3350 G ($g$ = 2.008) due to a free-radical porphyrin ring, and at 1500 G indicating the nonsymmetrical system of iron(III) due to a free-radical porphyrin ring, and at 1500 G indicating the nonsymmetrical system of iron(III) ion with large zero-field splitting respect to $g\beta H$. This result provides strong metal ligand interaction between iron, ligands, and orthorhombic field. It should mention that an EPR spectrum with **3** (not shown) is same as Figure 2C. The species **4** is EPR silent.

In order to consider whether **5** examined by EPR is a mixture of the EPR silent ferryloxo nonradical porphyrin and ferryloxo $\pi$ cation radical porphyrin, a UV−Vis spectrum of **5** was investigated at low temperature (−78 °C). As seen in Figure 3, the Soret band of **5** is shifted to 402 nm with decreasing intensity from 416 nm by reaction product of **2**-Cl and TBAF·$3H_2O$. Despite the fact that the RR spectrum for **5** (Figure 1C) supports the nonradical complex, **4**-F, it is possibly interpreted as a photoproduct of **1**-F by laser according to EPR and UV−Vis spectra, *i.e.*, the reaction product of **5** also produces a $\pi$ cation radical porphyrin, **1**-F, the same as **3**. The photolability of $\pi$ cation radical porphyrins in aqueous solution is under examination in our group.

In summary, we detected a fluoride-coordinated ferryloxo $\pi$ cation radical porphyrin by RR spectroscopy, assigned the reaction product **3** to **1**-F, and reassigned the green compounds of Hashimoto *et al.* and Kincaid *et al.* to **1**-MeOH and **1**-Cl, respectively.

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