Resonance Raman Studies of Mono- and Difluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyriniron(III)

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INTRODUCTION

Largely because of the interest in the biological activities of many metalloproteins in living systems, there has been much study of model compounds especially with metalloporphyrins.1 One of these metalloporphyrins, 5,10,15,20-tetrakis(pentafluorophenyl)porphyriniron(III) chloride, Fe(III)(TPFPP)Cl, is one of the highly acidic porphyrins since the electron density on the porphyrin ring is reduced markedly owing to the strong electron-withdrawing property of the Fluorine atoms on the phenyl ring, and has been widely studied as an effective catalyst for hydrocarbon hydroxylation and epoxidation.2,3 Metalloporphyrins can bind one or two ligands at the axial coordination sites of the central metal ion. Oxidation states of metalloporphyrins are mainly determined by binding ligands. Binding of basic ‘hard’ axial ligands tends to stabilize the metal-centered oxidation.4 Anion coordinations, especially with one or two fluoride ligands, appear to modulate the iron porphyrin redox potentials and provide a potential route for the generation of non-radical high-valent iron–porphyrin complexes.4—6 A number of spectroscopic studies have provided some insights into fluoride coordination to iron porphyrins in non-aqueous solvents. It has been found that two fluoride ions bind to iron(III) porphyrins in non-aqueous solvents to form a trans fluoride coordination.5 Solution preparation and physicochemical studies of difluorinated iron–porphyrin complexes have been reported in previous papers.7—10

The utility of resonance Raman (RR) spectroscopy for the investigation of various ligand-bound heme proteins and model compounds has been demonstrated by many investigators for more than two decades. For ligand-bound heme proteins, RR spectra can provide the metal–ligand stretching and bending wavenumbers, which give information about the nature of the ligand bond. The difluorinated iron–porphyrin (tetraphenylporphyrin = TPP and octaethylporphyrin = OEP) complexes have been prepared and have been studied by NMR and ESR spectroscopy and electrochemical reactions.5,6,9 However, no vibrational data have been reported.

In this work, we prepared the 5,10,15,20-tetrakis(pentafluorophenyl)porphyriniron(III) difluoride, [Fe(TPFPP)F2]-, by reaction between Fe(TPFPP)Cl and tetrabutylammonium fluoride (TBAF·3H2O) in various non-aqueous solvents, and here we report the RR spectra of the mono and difluoro complexes of Fe(III)(TPFPP) for the first time and also the solvatochromic effects of the stretching vibration of the $\text{F}--\text{F}$ bond on $\text{Fe}--\text{F}$ band in various non-aqueous solvents. Also discussed are the vibrational assignments of the high- and low-wavenumber regions of the RR spectra.

EXPERIMENTAL

Compound preparation

5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin, $\text{H}_2\text{TPFP}$ and Fe(III)(TPFPP)Cl were purchased from
Aldrich Chemical. They were free from reduced porphyrins and used without further purification. $^{54}$Fe metal (98.5%) was purchased from Cambridge isotope laboratories. $^{54}$Fe(TPFPFP)Cl was synthesized by using the iron(II) acetate–acetic acid method. A solution of iron(II) acetate in acetic acid was prepared by refluxing iron powder with glacial acetic acid under a stream of nitrogen, this hot solution was transferred with a Pasteur pipette to a solution of the porphyrin refluxing gently in glacial acetic acid and then chloride ions were supplied by adding solid NaCl. The product was recrystallized from methylene chloride–n-hexane. Tetra-butylammonium fluoride trihydrate (TBAF · 3H$_2$O) and the solvents, benzene, pyridine, dimethylformamide (DMF) and chloroform, and tetrahydrofuran (THF) and methylene chloride contained in sealed bottles, were also obtained from Aldrich Chemical.

Spectral measurements

The mono- and difluorinated iron–porphyrin complexes were generated by adding an aliquot of TBAF · 3H$_2$O solution to Fe(III)(TPFPFP)Cl solution. Prior to each Raman measurement, the extent of the reaction between the porphyrin and fluoride was estimated by comparing the relative intensities of Soret bands around the 400 nm region (see later).

Raman scattering from a dilute solution (50 μm) placed in a spinning (3000 rpm) glass cell at room temperature was imaged on to a single monochromator (Ritsu Oyo Kogaku, DG-1000) equipped with a cooled (-20 °C) intensified photodiode-array detector (Princeton Applied Research, 1421HQ). Raman spectra were excited using a Spectra-Physics Model 2016 krypton ion laser (406.7 nm) and a Kimmon Electrics Model CD 1805B He-Cd laser (441.6 nm). The laser power at the sample was kept at 5–10 mW throughout. Raman shifts were calibrated with CCl$_4$ and indene. The estimated wavenumber accuracy was ± 1.0 cm$^{-1}$.

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

ESR 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 a TE$_{102}$. The modulation amplitude was 1 G and the microwave power was 1 mW. An Oxford ESP 900 cryostat was used. ESR samples were prepared at -78 °C and the solvent was THF.

RESULTS AND DISCUSSION

Electronic spectra of reaction products

Electronic spectra for the reaction products of Fe(III)(TPFPFP)Cl and TBAF · 3H$_2$O in various non-aqueous solvents were examined. Figure 1 shows the changes in the absorption spectra of the system depending on the molar ratio of the two compounds. (A) For [Fe(TPFPFP)Cl], the $\lambda_{max}$ of the Soret band lies at 410 nm and additional bands appear at 498 and 622 nm.

High-spin Fe(III) porphyrins normally exhibit a band above 600 nm due to the $A_{2u} \rightarrow$ Fe charge-transfer transition and the $Q$ band appears around 500 nm. (B) When the molar ratio, $R = \frac{[TBAF]}{[Fe(TPFPFP)Cl]}$, is $<0.3$, the $\lambda_{max}$ of the Soret band is blue shifted to 403 nm from that of the chloro complex. The small shoulder at 410 nm is due to unreacted Fe(TPFPFP)Cl. The band at 403 nm is attributable to Fe(TPFPFP)F, which was identified by the absorption spectrum of the authentic compound synthesized according to the previously described method.\(^{11}\) (C) When $0.3 < R < 1.5$, the Soret band is split into two distinct bands at 403 and 419 nm. (D) The absorbance at 442 nm increases with increasing molar ratio $R$ up to 1.5 and levels off at higher ratios. Hence it is the final product in this system. The band at 580 nm appeared on addition of TBAF [Fig. 1(B)] and it slightly shifted to 570 nm [Fig. 1(D)]. A similar pattern of the $Q$ band (576 nm) was previously reported by Nanthakumar and Goff\(^{10}\) for [Fe(TPP)F$_2$]$^\text{3-}$.

The Soret band of Fe(TPFPFP)Cl is located at 408 nm in CH$_2$Cl$_2$ solvent, and split into two bands at 401 and 451 nm on successive addition of TBAF to the solution (not shown). Similar patterns were obtained with other solvents (CCl$_4$, acetone, pyridine and DMF). It is presumed that the final product of this system is [Fe(TPFPFP)F]$^\text{3-}$ with the Soret band in the 440–450 nm region, whose locations vary depending on the solvents employed.\(^{12,13}\) A transient band at 419 nm is observed only in THF, which may arise from a reaction intermediate. In this paper, however, the nature of this intermediate will not be considered.
Resonance Raman spectra of \([\text{Fe(TPFPP)}F_2]^-\)

Figure 2 shows the RR spectra (441.6 nm excitation) of Fe(III)(TPFPP)Cl solution which was dissolved together with 0.0–2.0 equiv. molar ratio of TBAF in dry THF. The RR spectrum in Fig. 2(A) was obtained from Fe(TPFPP)Cl itself with 441.6 nm excitation. The Soret band of Fe(TPFPP)Cl lies at 410 nm. Hence all porphyrin modes are very weak because the excitation wavelength is far from resonance. Figure 2(B) (\(R = 0.3\)) shows two new additional bands at 456 and 593 cm\(^{-1}\) compared with Fig. 2(A). The band at 456 cm\(^{-1}\) increases in intensity when \(R\) increases to 2.0 [Fig. 2(D)]. However, the band at 593 cm\(^{-1}\) decreases in intensity in Fig. 2(C) (\(R = 1.0\)) and disappears in Fig. 2(D) (\(R = 2.0\)). The nature of the 593 cm\(^{-1}\) band will be explained later. Here we shall focus our discussion on the final product.

The most significant feature of these spectra is the marked strengthening of the 456 cm\(^{-1}\) band in the low-wavenumber region when \(R\) is raised from 0.3–2.0. The nature of the newly observed band at 456 cm\(^{-1}\) is of particular interest. Therefore, we carried out a similar experiment with \(^{54}\text{Fe(TPFPP)}Cl\) to examine this band at 456 cm\(^{-1}\) on iron isotope sensitive bands. Figure 3 shows the RR spectra of the reaction product for Fe(III)(TPFPP)Cl \([\text{Fe(TPFPP)}F\] and \(^{54}\text{Fe}\) and \(^{56}\text{Fe}\) and TBAF when \(R = 2.0\) (\(\lambda_{\text{max}} = 442\) nm) [Fig. 2(D) and 3(A)] are same RR spectra]. The band at 913 cm\(^{-1}\) is due to the solvent. Figure 3(A) and (B) are identical. This means that the newly observed band at 456 cm\(^{-1}\) is insensitive to \(^{56}\text{Fe}^{54}\text{Fe}\) substitution. Hence we carefully assigned this band to the symmetric \(F\text{-}F\) stretch, \(\nu(F\text{-}F)\), of \([\text{Fe(TPFPP)}F_2]\)\(^-\). The reasons for this assignment are as follows. (1) This band at 456 cm\(^{-1}\) cannot be attributed to the \(\nu(F\text{-}F)\) of the \(\mu\)-fluoro dimer, \([\text{Fe(TPFPP)}F]_2\), since such a vibration should show an isotopic shift upon \(^{56}\text{Fe}^{54}\text{Fe}\) substitution. (2) It cannot be assigned to the \(\nu(F\text{-}F)\) of five-coordinate Fe(TPFPP)F. It should also exhibit an isotopic shift upon \(^{56}\text{Fe}^{54}\text{Fe}\) substitution. The mono-fluoro iron complex was formed when \(R = 0.3\) and the \(\nu(F\text{-}F)\) of Fe(TPFPP)F was observed at 593 cm\(^{-1}\) (Figs 4 and 7). (3) Supplementary \(^{19}\text{F} NMR spectra for Fe(TPFPP)Cl, Fe(TPFPP)F and Fe(TPFPP)Cl–TBAF mixture helped to elucidate the structure of the product formed. As listed in Table 1, the \(^{19}\text{F} NMR peaks attributable to \(o\)- and \(m\)-phenyl fluorines in five-coordinated Fe(III)(TPFPP) analogs, which are situated in an asymmetric chemical environment with respect to the porphyrin plane, were doublets. Fe(TPFPP)F shows peaks at \(-128.2\) and \(-132.0\) ppm as a doublet for \(\text{ortho}\) and at \(-160.9\) and \(-162.5\) ppm as a doublet for the \(m\)-fluorine on the phenyl group. Also, \([\text{Fe(TPFPP)}F]_2\) \(O\) has \(^{19}\text{F} NMR peaks at \(-133.9\) and \(-136.2\) ppm for \(\text{o}\) and \(-162.1\) and \(-164.2\) ppm for \(m\)-fluorine on the phenyl group. On the other hand, \(^{19}\text{F} NMR peaks for the mixture of \(\text{Fe(III)(TPFPP)}Cl\) and an excessive amount of TBAF in THF were found at \(-138.5, -153.7\) and \(-162.0\) ppm with no splitting, indicating that the compound has a plane of symmetry. Hickman et al.\(^6\) mentioned that a high-spin difluorinated iron(III)-porphyrin complex was generated by reaction of Fe(TPFPP)Cl and \(\text{TBA}^+\text{F}^-\cdot3\text{H}_2\text{O}\). We expect that a similar reaction for Fe(TPFPP) compounds would lead to the formation of \([\text{Fe(III)(TPFPP)}F_2]\)\(^-\).

In the high-wavenumber region at 1300–1600 cm\(^{-1}\), oxidation and spin-state sensitive bands are found. RR spectra were obtained with either 441.6 nm excitation with the He–Cd laser or 406.7 nm excitation with the Kr\(^+\) laser. The former could show greater enhancement for difluoro species and the latter for monofluoro.

\[\text{Figure 2. RR spectra of reaction products of Fe(III)(TPFPP)Cl and various amounts of TBAF in THF. } R = [\text{TBAF}]/[\text{Fe(TPFPP)Cl}] \text{ Excitation at 441.6 nm using He–Cd laser. } R = (\text{A}) 0.0; (\text{B}) 0.3; (\text{C}) 1.0; (\text{D}) 2.0.\]
Figure 4. RR spectra of reaction products of Fe(III)(TPFPP)Cl and various amounts of TBAF in THF. \( R = \frac{[\text{TBAF}]}{[\text{Fe(TPFPP)Cl}]} \). Excitation at 406.7 nm using Kr\(^+\) laser. \( R = (A) 0.0; (B) 0.3; (C) 1.0; (D) 2.0. \)

The vibrational modes of the final product were strongly enhanced at 441.6 nm due to Soret excitation (Fig. 2). The oxidation-sensitive marker band (\( v_4 \)) was downshifted from 1364 \( \rightarrow \) 1351 cm\(^{-1}\). This effect can be explained by the increased electron density at the central iron caused by coordination of the two basic fluorine anions. Also, the core size/spin-state sensitive band (\( v_2 \)) was downshifted from 1561–1548 cm\(^{-1}\). The formation of the bisfluoride would also lead to a downward shift of the \( v_2 \) mode. Hexacoordinated iron porphyrins have larger cores than pentacoordinated species and hence lower skeletal-mode wavenumbers. Especially iron metal should fit the central core of the porphyrin with a six-coordinate species with two identical ligands. This species would have a relatively larger core than a five-coordinate high-spin species. As explained above, NMR data also support the final product as a six-coordinated high-spin iron(III) porphyrin. The shift is closer to an Fe(II) complex than a high-spin iron(III) species. Since the spin state/oxidation state-sensitive bands are downshifted upon formation of an \( A_{2u} \)-type porphyrin \( \pi \) cation radical, it is suspected that the two \( F^- \) ligands cause some electron withdrawal from the porphyrin’s \( A_{2u} \) orbitals and it finally forms an Fe(II) porphyrin \( \pi \) cation radical. To rule out this possibility, additionally the ESR spectra of the difluoro complex were measured. They showed a pattern of typical high-spin iron(III) species\(^{15}\) with strong \( g = 6 \) and weak \( g = 2 \) signals. These ESR data are in good agreement with other RR and NMR results.

Table 1. Fluorine-19 NMR data for Fe(TPFPP) complexes\(^a\)

<table>
<thead>
<tr>
<th>Spin and oxidation state(^b)</th>
<th>Species(^b)</th>
<th>Phenyl fluorine/ppm</th>
<th>Pymolé-H/(\delta)ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.S. Fe(III)</td>
<td>Fe(TPFPP)Cl</td>
<td>(-102.0)</td>
<td>(-152.1)</td>
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<tr>
<td></td>
<td></td>
<td>(-105.1)</td>
<td>(-154.6)</td>
</tr>
<tr>
<td>L.S. Fe(III)</td>
<td>Fe(TPFPP)(phen)</td>
<td>(-143.8)</td>
<td>(-164.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-146.5)</td>
<td>(-154.0)</td>
</tr>
<tr>
<td>H.S. Fe(III)</td>
<td>Fe(TPFPP)F</td>
<td>(-128.2)</td>
<td>(-160.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-132.0)</td>
<td>(-162.5)</td>
</tr>
<tr>
<td>L.S. Fe(II)</td>
<td>Fe(TPFPP)(pip)(_2)</td>
<td>(-137.9)</td>
<td>(-163.3)</td>
</tr>
<tr>
<td>H.S. Fe(III) dimer</td>
<td>[Fe(TPFPP)](_2)O</td>
<td>(-133.9)</td>
<td>(-162.1)</td>
</tr>
<tr>
<td>H.S. Fe(III)</td>
<td>[Fe(TPFPP)F](_2)(^-) &amp;</td>
<td>(-138.5)</td>
<td>(-153.7)</td>
</tr>
</tbody>
</table>

\(^a\)Spectra taken at 25 °C, referenced from CFCl\(_3\). All data from Ref. 15 except where indicated.

\(^b\)Abbreviations: H.S., high spin; L.S., low spin; phen, phenyl group; pip, piperidine.

\(^c\)In CD\(_2\)Cl\(_2\) solution.

\(^d\)In toluene-\(d_8\) solution.

\(^e\)In DMSO-\(d_6\) solution.

\(^f\)This work, in THF-\(d_8\) solution.

Thus, the final product, the difluoro complex, is an iron(III) high-spin complex with the oxidation sensitive band at 1351 cm$^{-1}$ for $v_4$ and a core size/spin-state sensitive band at 1548 cm$^{-1}$ for $v_2$.

Solvent effect of $v_4$(F–Fe–F) on [Fe(TPFPP)F$_2$]$_2^-$

Figure 5 shows the RR spectra of Fe(TPFPP)F$_2^-$ measured in eight solvents. The bands at 728 and 491 cm$^{-1}$ are due to the porphyrin skeletal mode of Fe(TPFPP) and the other bands except the $v$(F–Fe–F) band are due to each solvent. As can be seen, the wavenumbers for F–Fe–F shift significantly as a function of the solvent. The values obtained for these F–Fe–F stretching wavenumbers are presented in Table 2. The binding strength of the ligand F$^-$ ion is very strong compared with those of other anions (ClO$_4^-$ < Br$^-$ < Cl$^-$ < N$_3^-$ < F$^-$), and this was reflected in the half-wave potential.

To determine the effect of solvent coordination on these wavenumbers, a correlation was attempted against the solvent acceptor number (Fig. 6). The concept of acceptor number, which is a measure of the electrophilic character of various organic solvents, was developed initially by Gutman. A linear relationship is observed for all solvents and the Fe–F wavenumbers decrease linearly with increasing acceptor number of the solvents employed. The larger the acceptor number of a solvent is, the more strongly the solvent molecules interact with the electron pairs at the F end of the polar Fe–F bond in Fe(TPFPP)F$_2^-$ to decrease the F → Fe donation.

**Resonance Raman spectra of Fe(TPFPP)F**

Kitagawa and co-workers$^{17}$ reported that the Fe–F wavenumbers in Fe(III)(OEP)F and Fe(OEC)F are located at 606 and at 608 cm$^{-1}$, respectively, as shown by RR spectroscopy. The IR spectrum exhibited an Fe–F band at 600 cm$^{-1}$ according to Alben.$^{18}$ Figure 4 shows the RR spectra of Fe(III)(TPFPP)Cl solution dissolved together with a 0.0–2.0 equiv. molar ratio of TBAF in dry THF, obtained with 406.7 nm excitation. Figures 2 and 4 were obtained under the same experimental condition except for the excitation radiation, 441.6 and 406.7 nm, respectively. Figure 4(B) is very similar to those for Fe(TPFPP)Cl [Fig. 4(A)] except for one additional band at 593 cm$^{-1}$, which also appears in
Figure 7. Low-wavenumber RR spectra of [Fe(TPFPP)F] in THF. Excitation at 406.7 nm using Kr laser. R = [TBAF]/[Fe(TPFPP)Cl] = 0.3 (λ = 403 nm). (A) 56Fe; (B) 54Fe.

Fig. 2(B), with relatively strong intensity. The band at 593 cm⁻¹ decreases in intensity in Fig. 4(C) (R = 1.0) and disappears in Fig. 4(D) (R = 2.0).

In order to examine the nature of the 593 cm⁻¹ band, we carried out the same experiment with 54Fe(TPFPP)Cl. Figure 7 shows the RR spectra of Fe(III)(TPFPP)Cl [(A) 56Fe and (B) 54Fe] mixed with TBAF when R = 0.3 (λ = 403 nm). In addition to typical TPFPP macrocycle vibrations, Fig. 7 shows a number of bands that are sensitive to 56Fe-54Fe substitution. When 56Fe(TPFPP)Cl was used, new bands appeared at 593 and 838 cm⁻¹ [Fig. 7(A)] and these bands shifted to 597 and 840 cm⁻¹ [Fig. 7(B)], respectively, on 56Fe-54Fe substitution. The observed shift of the former bands (Δv = 4 cm⁻¹ = 597–593 cm⁻¹) is in excellent agreement with the theoretical value (Δv = 4 cm⁻¹) expected for a diatomic Fe–F vibrator. Thus, the bands at 593 and 597 cm⁻¹ are assigned to the 1cm⁻¹ (Fe–F) of Fe(TPFPP)F and its 54Fe analog, respectively.

Another 54Fe–56Fe isotope-sensitive RR band at 838 (840) cm⁻¹ shows a different intensity under the same conditions, which appears only with 406 nm excitation and is upshifted by about 2 cm⁻¹ upon isotope substitution; this region is assigned to the symmetric in-plane pyrrole ring deformation vibration mode.

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