

## Simultaneous Observation of Fe-F and F-Fe-F Stretching Vibrations of Fluoride Anion Ligated Tetraphenylporphyrin Iron(III) by Resonance Raman Spectroscopy

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Monofluoroiron(III) tetraphenylporphyrin, Fe(TPP)F, and difluoroiron(III) tetraphenylporphyrin, [Fe(TPP)F<sub>2</sub>]<sup>-</sup> were generated in a various non-aqueous solvents by the reaction between Fe(TPP)Cl and tetrabutylammonium fluoride TBAF·3H<sub>2</sub>O. Formation of the these complexes was detected by the appearance of the ν(F-Fe) (ν, stretching vibration) at 506 cm<sup>-1</sup> for Fe(TPP)F and the ν(F-Fe-F) at 448 cm<sup>-1</sup> for [Fe(TPP)F<sub>2</sub>]<sup>-</sup>, simultaneously, with 441.6 nm excitation by Resonance Raman (RR) spectroscopy. These assignments were confirmed by observed frequency shifts due to <sup>56</sup>Fe/<sup>54</sup>Fe and TPP/TPP-d<sub>8</sub>/TPP-N<sub>15</sub> isotopic substitutions. Difluoroiron complex is an iron(III) high-spin complex with the oxidation sensitive band at 1347 cm<sup>-1</sup> for ν<sub>4</sub> and core size/spin state sensitive band at 1541 cm<sup>-1</sup> for ν<sub>2</sub>.

### Introduction

It is important to understand the structural characteristics of the dioxygen binding sites of heme proteins and their functions.<sup>1</sup> Studies on the ligand bound form of these heme proteins and model compounds are useful to elucidate the nature of them, especially anion bound forms are in interest. Fluoride ion binding to square-planar iron porphyrins through electrochemical measurements was detected by Kadish *et al.*<sup>2</sup> for the first time. And fluoride ion coordination appears to modulate iron porphyrin redox potentials and to provide a potential route for generation of non-radical high valent iron porphyrin complexes.<sup>3-5</sup>

A number of spectroscopic studies have provided evidence for anion coordination to iron porphyrins in nonaqueous solvent.<sup>4-6</sup> Resonance Raman (RR) spectroscopy is very powerful tool for the study of fluoride binding to heme proteins and model compounds by tuning the laser frequency to their electronic transitions.<sup>7,8</sup>

Solution preparation of difluoro iron porphyrin (tetraphenylporphyrin=TPP and octaethylporphyrin=OEP) complexes have been reported in earlier articles.<sup>9-11</sup> It was known that two fluoride ions bind to iron(III) porphyrins in nonaqueous solvents to form a trans fluoride coordination and physicochemical studies have been done by NMR, ESR and electrochemical methods.<sup>4-6</sup> However, their vibrational spectra have not been reported prior to our previous work,<sup>12</sup> in which we prepared the 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin iron(III) difluoride, [Fe(TPFPP)F<sub>2</sub>]<sup>-</sup> formed by the reaction between Fe(TPFPP)Cl and tetrabutyl ammonium fluoride, TBAF·3H<sub>2</sub>O, in various nonaqueous solvents and conformed its structure by RR spectroscopy.

In this paper, we report a more complete result obtained for the analogous TPP complex by using various isotopes; *i. e.* <sup>56</sup>Fe(TPP)Cl, <sup>54</sup>Fe(TPP)Cl, Fe(TPP-d<sub>8</sub>)Cl and Fe(TPP-N<sub>15</sub>)Cl. Here, we report simultaneous observation of the RR

spectra of two fluoride adducts, the mono- and di-fluoro complexes of Fe(III)(TPP), and the solvatochromic effects of the stretching vibration of F-Fe-F band on [Fe(TPP)F<sub>2</sub>]<sup>-</sup> in various nonaqueous solvents. Especially discussed are the vibrational assignments of the high wavenumber region of their RR spectra.

### Experimental

**Compound preparation.** 5,10,15,20-tetraphenylporphyrin (H<sub>2</sub>TPP), deuterated analogue of tetraphenylporphyrin (H<sub>2</sub>TPP-d<sub>8</sub>) and <sup>15</sup>N labeled analogue of tetraphenylporphyrin (H<sub>2</sub>TPP-N<sub>15</sub>) were synthesized by literature methods.<sup>13</sup> H<sub>2</sub>TPP analogues were purified to remove tetraphenylchlorin contamination.<sup>14</sup> The metal was incorporated into H<sub>2</sub>TPP, H<sub>2</sub>TPP-d<sub>8</sub> and H<sub>2</sub>TPP-N<sub>15</sub> by refluxing the porphyrins in glacial acetic acid containing ferric chloride.<sup>15</sup> <sup>54</sup>Fe metal (98.5%) was purchased from Cambridge isotope laboratories. <sup>54</sup>Fe(TPP)Cl was synthesized by using the ferrous acetate-acetic acid method.<sup>16</sup> Tetrabutyl ammonium fluoride trihydrate (TBAF·3H<sub>2</sub>O) and the solvents, benzene, toluene, acetone and dimethylformamide (DMF), and tetrahydrofuran (THF) and methylene chloride contained in sure seal bottles were obtained from Aldrich chemical.

**Spectral Measurement.** The mono and difluoro iron porphyrin complexes were generated by adding an aliquot amount of TBAF·3H<sub>2</sub>O solution to Fe(III)(TPP)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 400 nm region (see later).

Raman scattering of dilute solution (50 μM) placed in a spinning (3,000 rpm) glass cell at room temperature was imaged onto a single monochromator (Ritsu Oyo Kogaku, DG-1000) equipped with a cooled (-20 °C) intensified photodiode array (Princeton Applied Research, 1421HQ). Excitation was made by using Kimmon Electrics model CD 1805B He-Cd (441.6 nm) laser. The laser power on the

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sample point was kept to be 5-10 mW throughout this work. Raman shifts were calibrated with  $\text{CCl}_4$  and indene. Estimated accuracy in wavenumber readings was  $\pm 1.0 \text{ cm}^{-1}$ .

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

## Results and Discussion

### Fluorination of Fe(TPP)Cl with TBAF·3H<sub>2</sub>O.

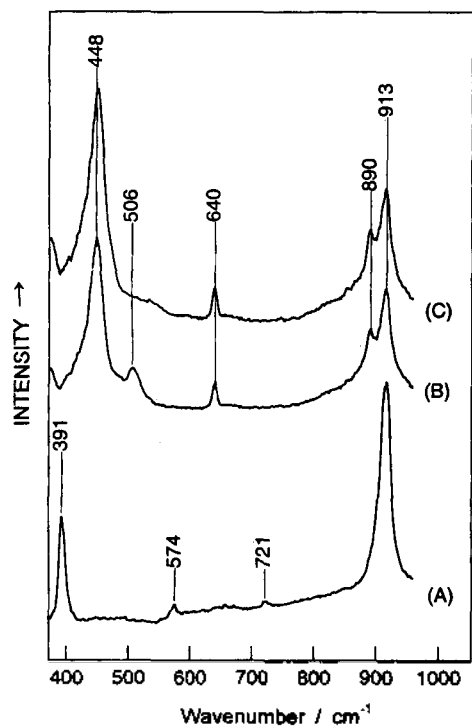
During RR experiment with reaction products of Fe(TPP)Cl and TBAF, intensity changes of RR bands were observed depending on the molar ratio,  $R$  ( $=[\text{TBAF}]/[(\text{TPP})\text{FeCl}]$ ), of two reactants. Figure 1 shows a series of RR spectra (441.6 nm excitation) which were obtained from the reaction products of Fe(TPP)Cl solution dissolved together with successive addition of TBAF in THF solvent. Figure 1(A) shows the RR spectrum obtained from Fe(TPP)Cl itself with 441.6 nm excitation. The Soret band of Fe(TPP)Cl lies at 418 nm. Hence all porphyrin modes are very weak except solvent band at  $913 \text{ cm}^{-1}$  because the excitation wavelength is far from resonance. Figure 1(B) ( $R=0.3$ ) shows two new additional bands at  $448 \text{ cm}^{-1}$  and  $506 \text{ cm}^{-1}$  compared with Figure 1(A). The band at  $448 \text{ cm}^{-1}$  increases in intensity, whereas the band at  $506 \text{ cm}^{-1}$  disappears when  $R$  goes to 2.0 [Figure 1(C)]. The nature of these two bands at  $448$  and  $506 \text{ cm}^{-1}$  will be explained later. The remaining bands at  $640$  and  $890 \text{ cm}^{-1}$  are attributed to porphyrin modes that are characteristically strong in the difluoro complex.

Electronic spectra of these reaction products were reexamined. For Fe(TPP)Cl, the  $\lambda_{\text{max}}$  of the Soret band lies at 418 nm and the Q band appears at 506 nm. when the molar

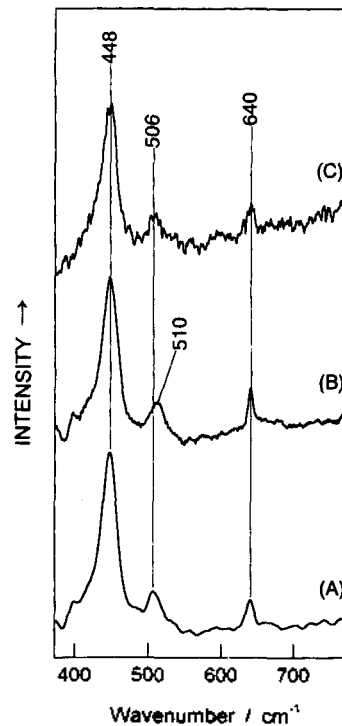
ratio,  $R$  is  $<0.3$ , the  $\lambda_{\text{max}}$  of the Soret band is blue shifted to 414 nm from that of the chloro complex and Q bands are found at 584 and 636 nm, which is attributable to Fe(TPP)F according to the previous report.<sup>11</sup> The absorbances at 444 nm (Soret band) and at 582 nm (Q band) increase with the molar ratio  $R$  to 1.5 and levels off at higher ratios. The similar pattern of absorption spectrum was previously reported by Nanthakumar and Goff<sup>5</sup> for  $[\text{Fe}(\text{TPP})\text{F}_2]^-$ . Therefore, these molar ratios were kept for the RR measurements of each species above.

**Assignments of  $\nu(\text{F-Fe})$  and  $\nu(\text{F-Fe-F})$ .** The band characteristics of the Fe-F group are readily assignable based on  $^{56}\text{Fe}/^{54}\text{Fe}$  isotope shifts. As stated previously,<sup>12</sup> the band in the  $440\text{-}460 \text{ cm}^{-1}$  region in various nonaqueous solvents has been assigned to the  $\nu_s(\text{F-Fe-F})$  on  $[\text{Fe}(\text{TPFP})\text{F}_2]^-$  [TPFP=5,10,15,20-tetrakis (pentafluorophenyl)porphyrin].

The nature of two new bands at  $448$  and  $506 \text{ cm}^{-1}$  (Figure 1) are of particular interest. Thus, in order to observe these two bands concurrently, RR spectrum was examined when  $R$  equals to 0.3 ( $\lambda_{\text{max}}=414 \text{ nm}$ ). Parts (A)-(C) of Figure 2 show the RR spectra of reaction products of TBAF and Fe(TPP)Cl containing  $^{56}\text{Fe}$ ,  $^{54}\text{Fe}$  and (TPP- $\text{N}_{15}$ ), respectively [Figures 1(B) and 2(A) are same RR spectra]. As can be seen from Figure 2, newly observed band at  $448 \text{ cm}^{-1}$  is insensitive to  $^{56}\text{Fe}/^{54}\text{Fe}$  substitution [Figure 2(A)/2(B)] and to (TPP)/(TPP- $\text{N}_{15}$ ) substitution [Figure 2(A)/2(C)]. Thus, these results provide definitive evidence for our assignment of this band to the symmetric F-Fe-F stretch,  $\nu_s(\text{F-Fe-F})$ , of  $[\text{Fe}(\text{TPP})\text{F}_2]^-$ . The upward shift in going from  $506 \text{ cm}^{-1}$  [Figure 2(A)] to  $510 \text{ cm}^{-1}$  [Figure 2(B)] and the no shift of the band at  $506 \text{ cm}^{-1}$  [Figure 2(A) vs. 2(C)] indicates that the  $506 \text{ cm}^{-1}$  vibration involves the mo-



**Figure 1.** RR spectra (low-wavenumber region) of reaction products of Fe(III)(TPP)Cl and various amounts of TBAF in THF.  $R=[\text{TBAF}]/[\text{Fe}(\text{TPP})\text{Cl}]$ . (A)  $R=0.0$ . (B)  $R=0.3$ . (C)  $R=2.0$

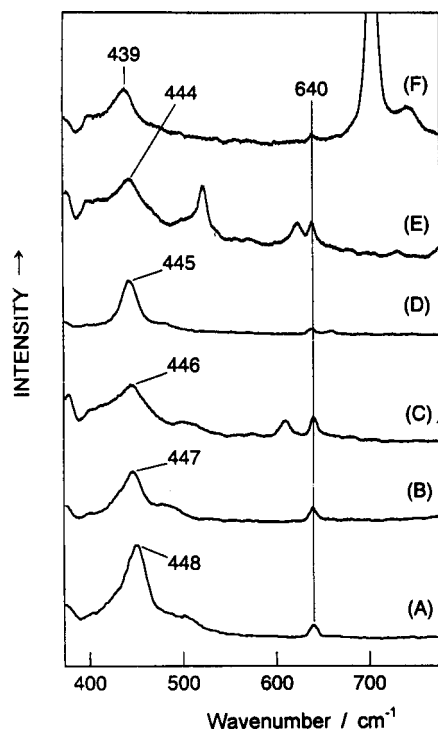


**Figure 2.** Low-wavenumber RR spectra of  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  in THF. Excitation at 441.6 nm using He-Cd laser,  $R=[\text{TBAF}]/[\text{Fe}(\text{TPP})\text{Cl}]=0.3$  ( $\lambda_{\text{max}}=414 \text{ nm}$ ). (A)  $^{56}\text{Fe}$ . (B)  $^{54}\text{Fe}$ . (C)  $^{56}\text{Fe}(\text{TPP-}\text{N}_{15})$

tion of the Fe atom. The observed shifts ( $+4\text{ cm}^{-1}$  by  $^{56}\text{Fe}/^{54}\text{Fe}$  substitution) are in perfect agreement with theoretical values expected for a Fe-F diatomic harmonic oscillator. Thus, the bands at  $506$  and  $510\text{ cm}^{-1}$  are assigned to the (F-Fe) of  $\text{Fe}(\text{TPP})\text{F}$  and its  $^{54}\text{Fe}$  analog, respectively.

It is interesting to note that the (F-Fe) ( $506\text{ cm}^{-1}$ ) and (F-Fe-F) ( $448\text{ cm}^{-1}$ ) of  $\text{Fe}(\text{TPP})\text{F}$  and  $[\text{Fe}(\text{TPP})\text{F}_2]^-$ , respectively, are lower than those of mono- [(F-Fe)= $593\text{ cm}^{-1}$ ] and difluoro- [ $\nu(\text{F-Fe-F})=456\text{ cm}^{-1}$ ]  $\text{Fe}(\text{TPFP})$  complexes reported previously;<sup>12</sup> the former is  $87\text{ cm}^{-1}$  lower and the latter is  $8\text{ cm}^{-1}$  lower. In general, the more acidic porphyrinato ligand, the less electron density on the metal iron and the more strongly  $\sigma$ -bonding from the ligand to the metal ion, resulting in a stronger metal-ligand bond. TPFP is highly acidic since the electron density on the porphyrin ring is reduced markedly due to strong electron-withdrawing property of the fluorine atoms substituted on the phenyl rings. This trend will be reversed in TMP (TMP=tetramesitylporphyrin) since the methyl groups are weakly electron-donating.

**Solvent effect of  $\nu(\text{F-Fe-F})$  on  $[\text{Fe}(\text{TPP})\text{F}_2]^-$ .** Figure 3 shows the RR spectra of  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  measured in six solvents. The band at  $640\text{ cm}^{-1}$  is due to the porphyrin skeletal mode of  $\text{Fe}(\text{TPP})$  and the other bands except the  $\nu(\text{F-Fe-F})$  band are due to each solvent. As can be seen, it clearly illustrates that a large solvent-effect influences the F-Fe-F vibration of the difluoro complex. The binding strength of the ligand  $\text{F}^-$  ion to metal ion is very strong compared with those of other anions.<sup>6</sup> Therefore, in order to inquire the effect of solvent coordination on these wavenumbers, a correlation was attempted against the sol-

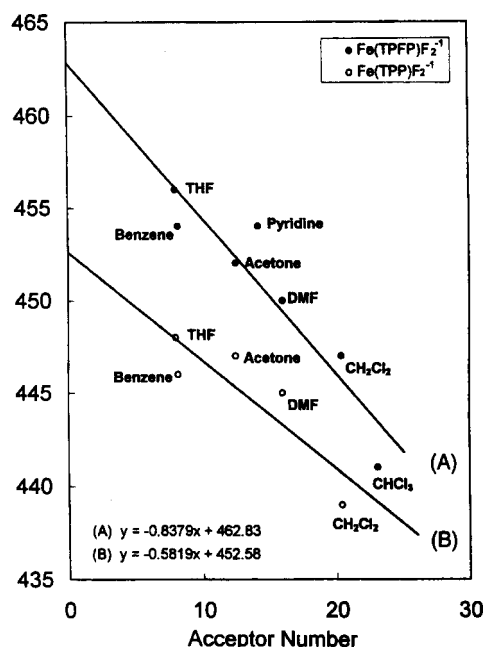


**Figure 3.** RR spectra of  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  measured in six different solvents.  $R=[\text{TBAF}]/[\text{Fe}(\text{TPP})\text{Cl}]=2.0$  ( $\lambda_{\text{max}}=414\text{ nm}$ ) Excitation at  $441.6\text{ nm}$ , in (A) tetrahydrofuran (THF), (B) Acetone, (C) benzene, (D) dimethylformamide (DMF), (E) toluene, and (F)  $\text{CH}_2\text{Cl}_2$

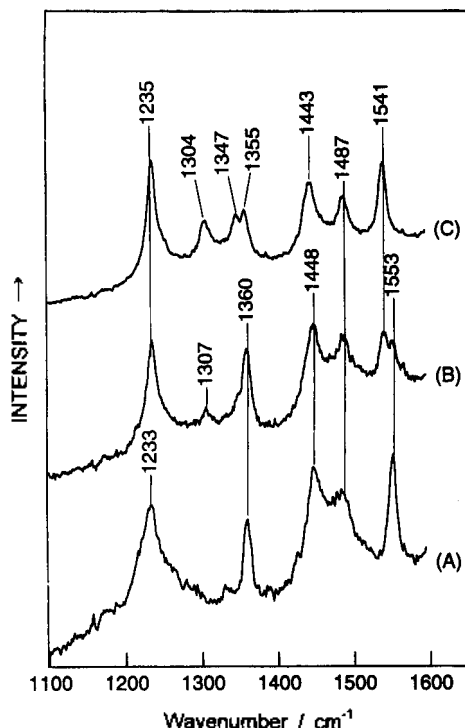
vent acceptor number<sup>17</sup> [Figure 4(B)]. A linear relationship is observed for all solvents and the F-Fe-F wavenumbers decrease linearly with increasing acceptor number of the solvents employed; [solvent(acceptor number); THF(8.0), Acetone(12.5), Benzene(8.2), DMF(16.0) and  $\text{CH}_2\text{Cl}_2$ (20.4)]. 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  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  to decrease the  $\text{F}\rightarrow\text{Fe}$  donation. Figure 4(A) was previously reported by Paeng *et al.*<sup>12</sup> Herein is reported the comparison of  $[\text{Fe}(\text{TPFP})\text{F}_2]^-$  [Figure 4(A)] with  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  [Figure 4(B)]. The intercepts (acceptor number is zero) of Figure 4(A) and 4(B) means that the F end of the polar F-Fe-F bond has no interaction with the solvent molecule. Thus, the difference ( $\Delta\nu=10\text{ cm}^{-1}$ ) between  $463\text{ cm}^{-1}$  [intercept of Figure 4(A)] and  $453\text{ cm}^{-1}$  [one of Figure 4(B)] can be counted on the difference between porphyrinato ligands as explained; *i.e.* TPFP is more acidic than TPP.

**Structure-Sensitive Vibrations.** Structural information about  $[\text{Fe}(\text{TPP})\text{F}_2]^-$  can be obtained by evaluating RR frequencies of several TPP vibrations that are sensitive to the changes in the oxidation and/or spin state.<sup>7</sup> RR spectra of TPP complexes exhibit three bands in the regions  $1370\text{--}1340$  ( $\nu_4$ ),  $1460\text{--}1440$  ( $\nu_3$ ) and  $1570\text{--}1540\text{ cm}^{-1}$  ( $\nu_2$ ) which are known to be sensitive to the changes in the oxidation and/or spin state.<sup>7,18-21</sup>

RR spectra (Figure 5) were obtained in the high wavenumber region at  $1200\text{--}1600\text{ cm}^{-1}$  with  $441.6\text{ nm}$  excitation (He-Cd laser). The RR spectrum of  $\text{Fe}(\text{III})(\text{TPP})\text{Cl}$  [Figure 5(A)] shows bands at  $1553$ ,  $1448$  and  $1360\text{ cm}^{-1}$ , which were assigned to  $\nu_2$ ,  $\nu_3$  and  $\nu_4$ , respectively. These values are typical of high-spin iron +3 valent TPPs. The  $\text{Fe}(\text{TPP})\text{F}$  was generated in Figure 5(B) ( $R=0.3$ ) and it shows a similar pattern with  $\text{Fe}(\text{TPP})\text{Cl}$ . The vibrational modes of the final product,  $[\text{Fe}(\text{TPP})\text{F}_2]^-$ , are in interest.



**Figure 4.** Plot of F-Fe-F stretching wavenumber as a function of the solvent acceptor number. Excitation at  $441.6\text{ nm}$ .



**Figure 5.** RR spectra (high-wavenumber region) of reaction products of Fe(III)(TPP)Cl and various amounts of TBAF in THF.  $R=[\text{TBAF}]/[\text{Fe}(\text{TPP})\text{Cl}]$ . (A)  $R=0.0$ . (B)  $R=0.3$ . (C)  $R=2.0$

The  $\nu_4$  band originates from  $\nu(\text{C}_\alpha\text{-N})+\delta(\text{C}_\beta\text{-H})$  (where  $\text{C}_\alpha$  and  $\text{C}_\beta$  refer to those at the  $\alpha$  and  $\beta$  positions of the pyrrole ring, respectively), and its wavenumber is known to depend upon the electron density on the  $\pi^*(e_g)$  orbital of the porphyrin core.<sup>18,19</sup> The  $\nu_4$  was down-shifted from at  $1360\text{ cm}^{-1}$  [Figure 5(A) and 5(B)] to at  $1347\text{ cm}^{-1}$  [Figure 5(C)]. Hence, this phenomena can be explained that electron density at the central iron was increased by coordination of two basic fluoride anion. When TPP-N<sub>5</sub> was employed, the band at  $1347\text{ cm}^{-1}$  shifted to  $1338\text{ cm}^{-1}$ , however, the band at  $1355\text{ cm}^{-1}$  showed no-shift. Thus, we could rule out to assign the band at  $1355\text{ cm}^{-1}$  to  $\nu_4$ .

The  $\nu_2$  was assigned to  $\nu(\text{C}_\beta\text{-C}_\beta)+\nu(\text{C}_\beta\text{-H})$  by Burke *et al.*<sup>18</sup> It has been well established<sup>18-20</sup> that this band serves as a spin state marker:  $1542\text{-}1554\text{ cm}^{-1}$  range for high-spin complexes and  $1553\text{-}1572\text{ cm}^{-1}$  for low-spin complexes regardless of the oxidation state of iron. The  $\nu_2$  band was also down-shifted from  $1553\text{ cm}^{-1}$  (monofluoro complex) to  $1541\text{ cm}^{-1}$  (difluoro complex). This assignment was confirmed by using TPP-d<sub>8</sub> ( $1520\text{ cm}^{-1}$ ). 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 hexacoordinated species with two identical ligands. This species would have a relatively larger core than a pentacoordinated high-spin species.

Thus, the final product, difluoro complex is a six-coordinate iron(III) high-spin complex with the oxidation sensitive band at  $1347\text{ cm}^{-1}$  for  $\nu_4$  and core size/spin state sensitive band at  $1541\text{ cm}^{-1}$  for  $\nu_2$ .

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