

# Articles

## Resonance Raman Characterization of (Oxoferryl)tetraphenylporphyrin Formed during Photodisproportionation of $(\text{Fe}(\text{TPP}))_2\text{O}$ in a Detergent Micelle at Room Temperature

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We report the formation and characterization of (oxoferryl)tetraphenylporphyrin ( $(\text{TPP})\text{Fe}^{\text{IV}}=\text{O}$ ) as a result of photodisproportionation of the  $\mu$ -oxo dimer,  $(\text{Fe}(\text{TPP}))_2\text{O}$ , obtained on solubilization of  $\text{Fe}(\text{TPP})\text{Cl}$  in an aqueous alkaline TX-100 detergent micelle, under 441.6 nm laser excitation at room temperature and at  $-50^\circ\text{C}$ . The other photoproduct is identified as a five-coordinated, high-spin (5cHS) ferrous complex.

### Introduction

The oxoferryl group  $\text{Fe}^{\text{IV}}=\text{O}$  is believed to be a reaction intermediate in the mechanism of action of peroxidases,<sup>1</sup> oxygen transfer<sup>2</sup> species in cytochrome P-450, and autoxidation of Fe(II) porphyrins.<sup>3</sup> Several groups have reported the formation of iron(IV) oxo-porphyrin complexes by chemical, photochemical, and electrochemical methods at low temperatures and characterized them by various techniques.<sup>4–6</sup> On the other hand, room-temperature stabilization and characterization of the oxoferryl species in only a few synthetic porphyrins and natural enzyme systems like myoglobin and peroxidases have been reported in the recent past.<sup>6b,7–9</sup> Table 1 gives the  $\text{Fe}^{\text{IV}}=\text{O}$  stretching and other relevant Raman frequencies for some selected systems. However, we have not come across any report

of oxoferryl species of simple iron tetraphenylporphyrins having been observed in aqueous systems at room temperature. In this report, we present optical absorption and RR data to show that  $\text{Fe}(\text{TPP})\text{Cl}$  in an alkaline micellar medium exists as a  $\mu$ -oxo dimer,  $(\text{Fe}(\text{TPP}))_2\text{O}$ , which on photoexcitation with a 441.6 nm laser line at room temperature and under anaerobic conditions at  $-50^\circ\text{C}$  undergoes photodisproportionation yielding the oxoferryl  $(\text{TPP})\text{Fe}^{\text{IV}}=\text{O}$  species and a five-coordinated, high-spin (5cHS) ferrous  $\text{Fe}^{\text{II}}(\text{TPP})(\text{L})$  complex. To the best of our knowledge this is the first evidence of the formation of an (oxoferryl)porphyrin at room temperature as a result of direct photoinduced fission of the  $(\text{Fe}(\text{TPP}))_2\text{O}$  complex in an aqueous system.

### Experimental Section

2-Methylimidazole (2-MeIm), 1-methylimidazole (1-MeIm), and the detergent Triton X-100 (TX-100) were purchased from Sigma Chemical Co. and were used as received.  $\text{Fe}(\text{TPP})\text{Cl}$  was obtained from Aldrich Chemical Co. 1,2-Dimethylimidazole (1,2-MeIm) was purchased from Merck. Triply distilled water was used for preparing the aqueous micellar, NaOH, HCl, and pH buffer solutions.

Resonance Raman (RR) spectra were recorded in the  $90^\circ$  scattering geometry with a SPEX Ramalog 1403 spectrometer equipped with a cooled RCA 31034 photomultiplier and photon-counting electronics. Excitation lines at 441.6 and 406.7 nm were provided by Liconix Model 4240 He–Cd and Spectra-Physics Model 165 Ar<sup>+</sup> ion lasers, respectively. Anaerobic conditions were achieved by degassing the sample solutions using at least three freeze–pump–thaw cycles and/or by bubbling argon gas for about 30 min. Raman shifts were routinely calibrated with known lines of indene.

### Results and Discussion

The inset in Figure 1 shows the absorption spectrum of  $\text{Fe}(\text{TPP})\text{Cl}$  solubilized in alkaline aqueous TX-100 detergent

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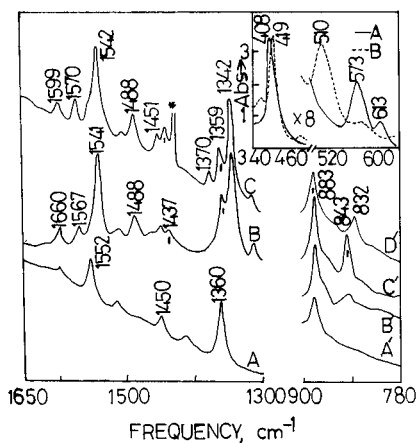
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**Table 1.** Fe<sup>IV</sup>=O Stretching and a Few Other Raman Frequencies (cm<sup>-1</sup>) for Selected Iron Porphyrin Systems

species	$\nu(\text{Fe}^{\text{IV}}=\text{O})$	$\nu_2$	$\nu_4$	solvent: temp (°C) <sup>a</sup>	ref
Fe <sup>IV</sup> =O(TPP)	852	1575	1374	Ar: -250	5a
Fe <sup>IV</sup> =O(OEP)	852	1551	1379	Ar: -258	5b
Fe <sup>IV</sup> =O(TMP)	843	1570	1368	toluene: -80	3b
Fe <sup>IV</sup> =O(TMP)	845			toluene: -46	3c
Fe <sup>IV</sup> =O(TPP)	843	1570	1370	micelle: RT, -50	b
(THF)Fe <sup>IV</sup> =O(2,6-Cl <sub>2</sub> TPP)	841			THF: -50	4e
(DMF)Fe <sup>IV</sup> =O(2,6-Cl <sub>2</sub> TPP)	829		1370	THF: -50	4e
(DMF)Fe <sup>IV</sup> =O(TPP)	832		1371	micelle: RT, -50	b
(1-MeIm)Fe <sup>IV</sup> =O(2,6-Cl <sub>2</sub> TPP)	818		1370	THF: -50	4e
(THF)Fe <sup>IV</sup> =O(TPivPP)	829	1566	1370	THF: -50	4b
(1-MeIm)Fe <sup>IV</sup> =O(TPivPP)	807	1566	1370	THF: -50	4b
(1-MeIm)Fe <sup>IV</sup> =O(TPP)	820	1566	1369	toluene: -120	4c
(1-MeIm)Fe <sup>IV</sup> =O(OEP)	820		1385	toluene: -120	4b
(CH <sub>3</sub> OH)Fe <sup>IV</sup> =O(TMP)	828	1562	1363	CH <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH: -80	4b
(OH)Fe <sup>IV</sup> =O(TMPyP)	763	1577	1370	H <sub>2</sub> O, pH 13: RT	6b
(TMP <sup>+</sup> )Fe <sup>IV</sup> =O(MeOH)	831	1517	1335	CH <sub>2</sub> Cl <sub>2</sub> : -80	4a
(TMP <sup>+</sup> )Fe <sup>IV</sup> =O(CClO <sub>4</sub> )		1509	1325	CH <sub>2</sub> Cl <sub>2</sub> : -80	4a

<sup>a</sup> RT = room temperature; micelle = alkaline aqueous TX-100. <sup>b</sup> This work.



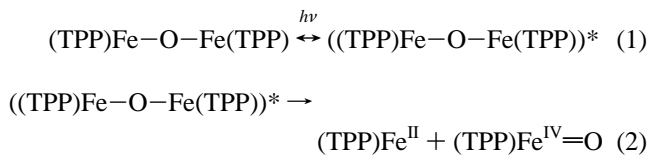
**Figure 1.** Resonance Raman spectra of Fe(TPP)Cl solubilized in TX-100 micelle at pH 11: (A, A') aerobic; (B, B') anaerobic conditions at room temperature; (C, C') anaerobic conditions at -50 °C; (D') anaerobic conditions with DMF at -50 °C. Concentration of Fe(TPP)-Cl: 0.1 mM. Concentration of TX-100: 3%. Excitation: 441.6 nm. Power at the sample:  $\approx 3$  mW. Asterisk denotes plasma line. **Inset:** Optical absorption spectra of Fe(TPP)Cl (30  $\mu$ M) in 3% TX-100 (aq) at (A) pH = 11 and (B) pH  $\approx 1.8$ . Path length: 10 mm.

micelle under aerobic conditions. The absorption bands at 408, 573, and 613 nm correspond to the Soret and the Q bands, respectively, of the  $\mu$ -oxo dimer at pH 11, and those at 419, 510, and 573 nm, to that of the chloro complex Fe(TPP)Cl (pH  $\leq 1.8$ ), in agreement with reported values.<sup>10</sup> The interconversion of these two complexes on reaction with strong alkaline and HX acids is well-known.<sup>10,11</sup> The similarity of the absorption spectra of these two complexes to that in noncoordinating organic solvents indicates that both the complexes, normally insoluble in water, become solubilized in the hydrophobic region of the micelle. The RR bands at 1360 cm<sup>-1</sup> ( $\nu_4$ ), 1450 cm<sup>-1</sup> ( $\nu_3$ ), and 1552 cm<sup>-1</sup> ( $\nu_2$ ) (Figure 1A) along with a medium-intensity band at 363 cm<sup>-1</sup> ( $\nu_8$ ) in the low-frequency region (spectrum not shown) attributable to the symmetric Fe-

O-Fe stretching mode establish the  $\mu$ -oxo-dimeric nature of the species<sup>12</sup> present under these experimental conditions at pH 11.

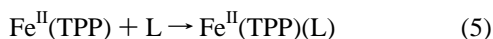
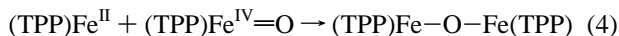
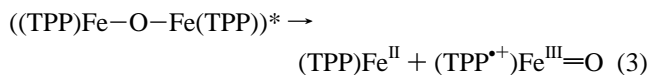
On degassing of the solution, a complex RR spectral pattern develops at room temperature, shown in Figure 1B. The new RR bands at 1541, 1437, 1342, 1229, and 371 cm<sup>-1</sup> (the last two bands not shown) can be identified with the  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ ,  $\nu_1$ , and  $\nu_8$  modes, respectively, for the 5cHS ferrous complex Fe<sup>II</sup>-(TPP)L, on the basis of the reported values in literature.<sup>12</sup> The weak band at 1359 cm<sup>-1</sup> indicates the presence of a minor quantity of the  $\mu$ -oxo dimer. In addition to these, extra features at 1567 and 843 cm<sup>-1</sup> (polarized; depolarization ratio  $\rho = 0.4$ ) are also present in the room-temperature spectra (Figure 1B,B') whose intensities increase considerably in the spectra recorded at -50 °C along with a clearly identifiable band at 1370 cm<sup>-1</sup> (Figure 1C,C'). The observed features in Figures 1B,B' and 1C,C' cannot be attributed to a 6cLS complex, as the bands at 1557 cm<sup>-1</sup> ( $\nu_2$ ), 1354 cm<sup>-1</sup> ( $\nu_4$ ), and 382 cm<sup>-1</sup> ( $\nu_8$ ) for the Fe<sup>II</sup>-(TPP)(1-MeIm)<sub>2</sub> complex observed by us (spectra not shown) are distinctly different from those in Figure 1B,C.

In order to identify the species responsible for the extra Raman features, it is pertinent to consider the results of recent time-resolved transient absorption studies<sup>13</sup> which have shown that (Fe(TPP))<sub>2</sub>O undergoes photodisproportionation in aprotic solvents on excitation with light of wavelength less than 500 nm to yield the photoproducts according to the following scheme:



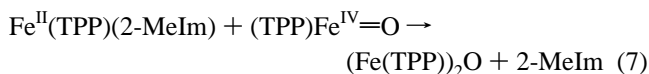
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where L is an external ligand.

Our RR data do not indicate the presence of  $(\text{TPP}^{*\text{+}})\text{Fe}^{\text{III}}=\text{O}$  species in the photoproducts of  $(\text{Fe}(\text{TPP}))_2\text{O}$ , as the RR marker bands for this species are quite distinct.<sup>4a,6c</sup> When dimethylformamide (DMF) is added to the anaerobic solution of  $(\text{Fe}(\text{TPP}))_2\text{O}$ , the RR spectra at low temperature (Figure 1D') showed a shift of the 843  $\text{cm}^{-1}$  band to 832  $\text{cm}^{-1}$ . This is close to the earlier observed<sup>4c</sup> frequency (829  $\text{cm}^{-1}$ ) for a six-coordinated, oxoferryl complex with DMF as the sixth ligand trans to the ferryl oxygen. However, addition of 2-MeIm reduced the yield of ferryl complex formation according to the following mode of decay,<sup>13b</sup> in addition to the route given in eq 4:



Further confirmation for the presence of  $(\text{TPP})\text{Fe}^{\text{IV}}=\text{O}$  species is provided by Raman experiments as a function of laser power. The yield of photodisproportionation is expected to increase (eq 2) with an increase in laser power, but the negligible pathway for recombination of the  $\text{Fe}^{\text{II}}(\text{TPP})$  and  $(\text{TPP})\text{Fe}^{\text{IV}}=\text{O}$  species (eq 4) at the low laser powers becomes dominant<sup>13a</sup> at higher laser powers. This effect along with the instability of the oxoferryl species at higher temperatures as a result of local heating at higher laser powers<sup>3b</sup> would decrease the yield of the oxoferryl species. We have observed that the 843, 1370, and 1570  $\text{cm}^{-1}$  bands perceptibly weaken with an increase in laser power from 3 to 10 mW at 441.6 nm even at  $-50^\circ\text{C}$ . All

these experiments provide clear and unambiguous evidence for the formation of oxoferryl species in the photoproduct of  $(\text{Fe}(\text{TPP}))_2\text{O}$ . From a comparison of previous work on oxoferryl complexes (Table 1), the RR bands observed by us for the photoproduct of  $(\text{Fe}(\text{TPP}))_2\text{O}$  in the detergent micelle at 843, 1370, and 1570  $\text{cm}^{-1}$  can be unambiguously associated with the  $\nu(\text{Fe}^{\text{IV}}=\text{O})$  stretching,  $\nu_4$ , and  $\nu_2$  modes, respectively, of the 5cLS oxoferryl complex. The intensity of these bands increases at  $-50^\circ\text{C}$ , consistent with the expected stabilization of the oxoferryl complex at low temperatures.

The expected RR spectrum for the other four-coordinated, intermediate-spin  $\text{Fe}^{\text{II}}(\text{TPP})$  photoproduct is not observed by us. Instead, we observe RR bands characteristic of a 5cHS, ferrous  $\text{Fe}^{\text{II}}(\text{TPP})(\text{L})$  complex with associated axial ligand L which could be either a hydroxyl ion or a water molecule. Because of the nonobservation of the  $\nu_{\text{Fe}-\text{OH}}$  stretching mode<sup>6b</sup> around the reported value of 463  $\text{cm}^{-1}$  at pH 11 by us and from the position of other observed bands at 1542 ( $\nu_2$ ), 1342 ( $\nu_4$ ), 1229 ( $\nu_1$ ), and 371 ( $\nu_8$ )  $\text{cm}^{-1}$ , we suggest that the ferrous photoproduct is coordinated axially by a water molecule<sup>12d</sup> which is stabilized inside the hydrophobic core due to hydrogen bonding with the ether oxygen<sup>14</sup> of the TX-100 micelle.

In conclusion, we have presented the first evidence, supported by other control experiments, of formation of the 5cLS oxoferryl complex  $(\text{TPP})\text{Fe}^{\text{IV}}=\text{O}$  characterized by the  $\text{Fe}^{\text{IV}}=\text{O}$  stretching,  $\nu_4$ , and  $\nu_2$  modes at 843, 1370, and 1567  $\text{cm}^{-1}$ , respectively, at room temperature in an alkaline aqueous TX-100 detergent micelle as a result of photodisproportionation of  $(\text{Fe}(\text{TPP}))_2\text{O}$  with 441.6 nm laser excitation.

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