Transformation of Fe^{III}TMP *N*-Oxide to a Two-electron Oxidized Equivalent of Fe^{III}TMP Complex (TMP = 5,10,15,20-tetramesitylporphyrin)

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The reaction of Fe^{III}TMP *N*-oxide (**1a**) with an excess amount of trifluoroacetic acid (TFA) gave a two-electron oxidized equivalent of Fe^{III}TMP *via* a protonated form of (**1a**), and the product is assigned to be a Fe^{III}TMP dication complex.

The active species responsible for oxygenations by cytochrome P-450 is considered to be an oxo–ferryl porphyrin cation radical.[1] While an iron(III) porphyrin *N*-oxide complex has been highlighted as an alternative species based on M.O. calculations,[2] our recent preparation of Fe^{III}TMP *N*-oxide (**1a**) shows that (**1a**) itself cannot oxidize hydrocarbons and alkenes.[3] Accordingly, if the *N*-oxide intermediate is formed in the oxygen activation reaction by cytochrome P-450, further transformation of the *N*-oxide to a more reactive species should be considered.

We report the first example of transformation of Fe^{III} porphyrin *N*-oxides (**1**) to a two-electron oxidized equivalent

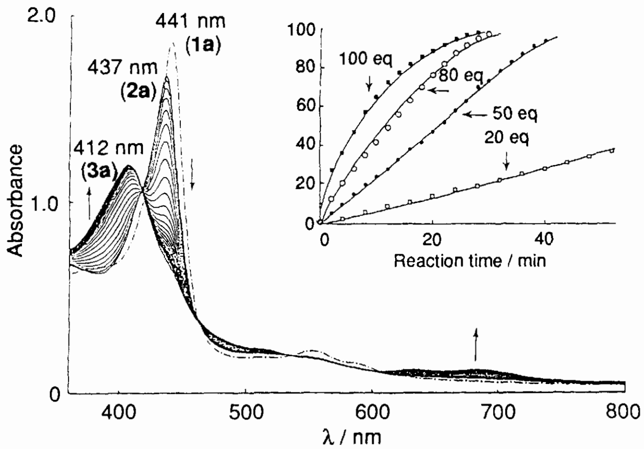


Figure 1. Time-dependent spectral changes of (**1a**) (2.0×10^{-5} M) upon the addition of TFA in toluene at −28 °C. *inset*: Effect of acid (TFA) in the conversion of (**2a**) to (**3a**).

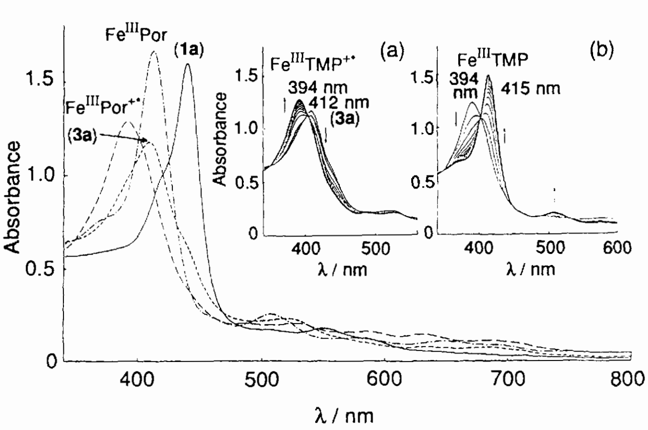
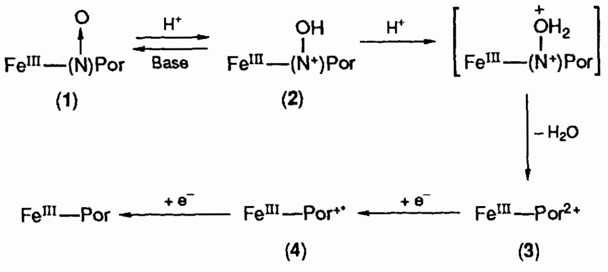


Figure 2. Comparison of UV–VIS spectra of (**1a**), (**3a**), $\mathrm{Fe^{III}TMP^{+\bullet}}$, and $\mathrm{Fe^{III}TMP}$ (1.7×10^{-5} M) in toluene at −20 °C observed in the reaction of (**1a**) with TFA. *inset*: (a) Spectra changes of (**3a**) to $\mathrm{Fe^{III}TMP^{+\bullet}}$ at −20 °C (cycle time: 10 min), (b) Decomposition of $\mathrm{Fe^{III}TMP^{+\bullet}}$ to $\mathrm{Fe^{III}TMP}$ at room temperature (cycle time: 40 min).

of $\mathrm{Fe^{III}}$ porphyrin, possibly the corresponding $\mathrm{Fe^{III}}$ porphyrin dication species, which are isoelectronic with oxo–ferryl porphyrin cation radicals.

The reaction of (**1**) *with an acid*: The reaction of $\mathrm{Fe^{III}TMP}$ *N*-oxide [(**1a**), TMP: 5,10,15,20-tetramesitylporphyrin] with an excess amount of trifluoroacetic acid (TFA) in toluene at *ca.* −30 °C gave a new species (**3a**), the soret band of which appears at 412 nm, *via* the transient formation of an intermediate (**2a**) (Figure 1). Titration of (**1a**) with TFA indicates that 1 mol of acid is required to complete the reaction of (**1a**) to yield (**2a**). Addition of an acid scavenger such as pyridine to a toluene solution of (**2a**) immediately reproduced (**1a**). Further, the red-shifted soret band of (**2a**) in a UV–VIS spectrum indicated the structure to be an *N*-substituted iron porphyrin.[4] Similar reactions were observed when $\mathrm{Fe^{III}TDCPP}$ *N*-oxide (**1b**, TDCPP: 5,10,15,20-tetrakis-2,6-dichlorophenylporphyrin) was treated with TFA under the same condition. Reactions of heterocyclic *N*-oxides with electrophiles such as proton and acyl halides at the *N*-oxide oxygen are commonly observed to afford the *N*-hydroxy and *N*-acyloxy derivatives.[5] Thus, (**2a**) is assigned to be a protonated form of (**1a**).



Scheme 1

Conversion of (**2**) *to* (**3**): While the treatment of (**1a**) with one equiv. of TFA afforded (**2a**) as a stable species at −30 °C under the diluted condition (*ca.* 10^{-5} M), further reaction of (**2a**) took place to form (**3a**) when additional TFA was introduced. The rate of formation of (**3a**) was dependent on the amount of TFA added. More acid accelerates the (**3a**) formation (Figure 1, inset). The reaction of (**2b**) with TFA proceeded like (**2a**), however, the rate of (**3b**) formation became much slower and suggests positive-charge deposition on the porphyrin ring during the reaction.

Octaethylporphyrin *N*-oxide was reported to react with acetic anhydride to afford 5-acetoxyoctaethylporphyrin *via* isoporphyrin formation.[6] If a similar reaction proceeds for (**2a**) the corresponding isoporphyrin would be formed. Isoporphyrin iron complexes have characteristic optical spectra in the visible and near-IR regions.[7] An optical spectrum of (**3a**) is different from that expected for $\mathrm{Fe^{III}TMP}$ isoporphyrin. In addition, (**3a**) slowly changes to $\mathrm{Fe^{III}TMP^{+\bullet}}$ (**4a**)[8] at −30 °C or above [Figure 2(a)]. Finally, (**4a**) is reduced to $\mathrm{Fe^{III}TMP}$ when the solution is warmed to room temperature [Figure 2(b)].† The spectra for all the species formed in the reaction of (**1a**) with TFA are shown in Figure 2. Replacement of toluene with chlorobenzene as solvent decreases the rates of these two reactions. These results imply that (**3a**) is in either the one- or two-electron oxidized state from the parent $\mathrm{Fe^{III}TMP}$ complex. There are several candidates for the structure of (**3a**), *i.e.* one-electron oxidized: $\mathrm{Fe^{IV}TMP}$, two-electron oxidized: $\mathrm{Fe^{IV}TMP^{+\bullet}}$, $\mathrm{Fe^{V}TMP}$, and $\mathrm{Fe^{III}TMP^{++}}$, however, the former two species can be eliminated because of their characteristic optical spectra.[3b,8] Further, possible formation of $\mathrm{Fe^{V}TMP}$ seems very unlikely since addition of thioanisole or triphenylphosphine to a toluene solution of (**3**) at −30 °C did not cause spectroscopic changes.[9]

Finally, we have attempted to titrate (**3a**) with iodide ion to confirm its oxidation state. In the presence of TFA, addition of tetra-*n*-butylammonium iodide did not cause any spectral changes for (**3a**) at −35 °C, however, neutralization of the toluene solution by pyridine was allowed to reduce (**3a**) for several hours to $\mathrm{Fe^{III}TMP}$ with 2 equiv. of iodide, consistent with the structure of (**3a**) being $\mathrm{Fe^{III}TMP}$ dication. The EPR spectrum of (**3a**) at −150 °C shows two broad absorptions at $g = 4.2$ and 2.05, similar to that of $\mathrm{Fe^{III}TPP(ClO_4)}$.[10]

Though the second oxidation potential obtained by cyclic voltammetry of some $\mathrm{Fe^{III}}$ porphyrin complexes has been attributed to the $\mathrm{Fe^{III}}$ porphyrin dication formation, their physical properties such as UV–VIS and EPR spectra are not available yet.[11] However, metalloporphyrin dication species of Zn, Mg, and Ni have been prepared and well-characterized by electrochemical oxidation and the optical spectra of these dication porphyrins[12] are very similar to those obtained for

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† While the reduction mechanism of (**3**) to (**4**) is not clear, (**3**) may be going to Fe(IV)-porphyrin cation radical or reacting as a charge-transfer complex with the solvent, and this aspect of the chemistry of (**3**) is under investigation.

(3). These dications are known to react with nucleophiles such as methanol and H_2O to afford the isoporphyrin,[7a,12a] while **(3a)** did not react with methanol since the mesityl and *o*-dichlorophenyl groups could prevent the reactions. For example, ZnTPP and ZnTMP gave half-wave potentials for the first and second one-electron oxidations in CH_2Cl_2 at 0.77, 1.11,[10] and 0.73, 1.11 (V *vs.* SCE), respectively.‡ Upon addition of methanol, almost all of the second reduction wave of ZnTPP corresponding to the reduction of the dication species disappeared, while the cyclic voltammogram of ZnTMP remains unchanged.

These observations indicate the structure of **(3)** to be Fe^{III} porphyrin dication. Scheme 1 shows the summary of the reactions of **(1)** with an acid. While **(3)** does not react even with Ph_3P, Fe^{III} porphyrin dication has been recently suggested as Compound 0, a precursor of Compound I, in the reaction of H_2O_2 with horseradish peroxidase.[13] Thus, further characterization and reactivity of **(3a)** is currently under investigation.

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‡ So far, we have failed in the electrochemical preparation of Fe^{II} TMP dication for physical measurements. Perhaps, the dication species is unstable under the conditions used.