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# Picosecond Absorption Studies on the Excited State of ($\mu$-Oxo)bis[(tetraphenylporphinato)iron(III)]

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**Abstract:** We have measured the kinetics and spectra of the intermediates of ($\mu$-oxo)bis[(tetraphenylporphinato)iron(III)] in various solvents. The spectra of the intermediate species were measured at various intervals of time from -100 to 4.3 ns after excitation with a 532- or 355-nm 25-ps pulse. The intermediate state, possibly a cation radical, was assigned to a monomer that forms the photodissociated pair $TPPFe^{II+}$ + $TPPFe^{III}–O^-$ and yields a small amount of disproportionation reaction products, $Fe^{II}TPP$ and $TPPFe^{IV}{=}O$.

Iron porphyrins have been the subject of intensive investigations over the past years. The partially filled d orbital system of iron porphyrins lie in an energy range that spans from below the highest filled $\pi$ orbital of the tetrapyrrole system to above the lowest unfilled $\pi^*$ orbital.[1] The addition of spin-spin and spin-orbit interactions of the d electrons give numerous sets of available energy levels, which are easily perturbed by axial ligation, porphyrin ring substituents, and local field gradients in the environment.[2] This wide range of electronic energy configurations can easily be seen in the rich absorption spectra of iron porphyrins and hemoproteins.[3,4]

The decay of excited states in iron porphyrins[5] are to a very large extent radiationless with lifetimes in the picosecond and subpicosecond range.[6-9] In spite of these short excited-state lifetimes, some iron porphyrins are known to undergo photochemistry. In the presence of short-chain alcohols, (protoporphyrin)iron(III) chloride and (deuteroporphyrin)iron(III) chloride can give photocatalytic oxidation of aliphatic alcohols when irradiated at 355 nm.[10,11] In addition, the (tetraphenylporphyrin)iron(III) complex can also photocatalyze hydrocarbon hydroxylation through a peroxyl radical chain mechanism.[12]

Ligand ejection from hemes is a well-studied process. CO and $O_2$ photodissociation from ferrous hemoproteins has been extensively studied on the nanosecond and picosecond time scale.[13-15] More recently the picosecond events of NO photodissociation from ferric hemoproteins[16] have been examined. Other nitrogenous ligands such as piperidine and pyridine are also known to undergo photodissociation from iron porphyrins.[9,17] The required transformations in the excited state are not known in detail, but many of the studies on photodissociation from the ferrous state indicate the existence of an intermediate with a lifetime of ~15-40 ps.[8,9,13,14] Similar transients have been observed in ferrous porphyrins that have no ligands or in which there is no evidence of ligand dissociation.[8,9] Much less is known of the initial events in the photochemistry of the ferric porphyrins. The recent description[18] of the photochemical oxidation of triphenylphosphine by ($\mu$-oxo)$Fe^{III}TPP$, $[Fe^{III}TPP]_2O$, has indicated the possibility of an intramolecular redox reaction from the excited state in these compounds. There appears to be a disproportionation of $[TPPFe^{III}]_2O$ as follows:

$$TPPFe^{III}\text{–}O\text{–}Fe^{III}TPP \rightarrow TPPFe^{II} + TPPFe^{IV}{=}O \quad (1)$$

in an internal redox reaction, which can as an alternative give

$$TPPFe^{III}\text{–}O\text{–}Fe^{III}TPP \rightarrow TPPFe^{II} + TPP^{\bullet}Fe^{III}{=}O \quad (2)$$

in which the porphyrin is oxidized to a $\pi$ cation radical and is strongly antiferromagnetically coupled to the Fe(III).

It is interesting to note that while the photochemical transformations take place within 100 ns,[19] the excited-state lifetime of most ferric porphyrins is less than 1 ps.[5,6] We have examined the picosecond evolution of the photoexcited $\mu$-oxo dimer $[Fe^{III}TPP]_2O$ by means of picosecond absorption spectroscopy in order to better understand the mechanism of the energy dissipation of the excited state in iron porphyrins.

## Experimental Section

**Chemicals.** Iron(III) tetraphenylporphyrin chloride was obtained from Strem Chemicals. All solid chemicals were reagent grade, and solvents were either reagent or spectroscopic grade. The $\mu$-oxo-bridged $Fe^{III}TTP$ dimer was prepared by a modification of the Dolphin et al. method.[20] Approximately 10 mg of $TTPFe^{III}Cl$ in 30 mL of methylene chloride was shaken with 30 mL of 2 M NaOH for 10 min. The aqueous phase was discarded, and the procedure was repeated two more times. The methylene chloride phase was then washed three times with approximately 50 mL of $H_2O$. The methylene chloride was then evaporated under nitrogen at 40 °C, and the $\mu$-oxo compound was taken up in a small amount of benzene. The compound was chromatographed on a 2.5 × 25 cm silicic acid column. The silicic acid had been dried at 120 °C for 6 h and was poured into the column as a benzene slurry. The pure $[Fe^{III}TPP]_2O$ was eluted with benzene.

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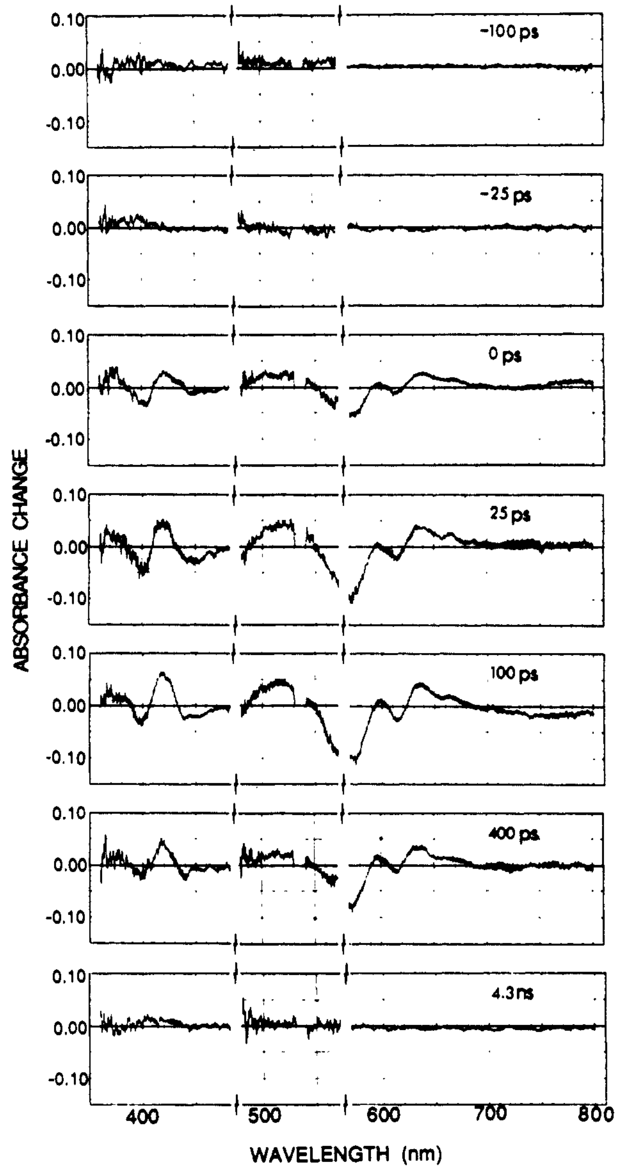

Figure 1. Difference absorption spectra at three wavelength regions: 360–480, 480–570, and 570–800 nm at times after 532 nm, 25 ps FWHM, excitation of a deoxygenated solution of [Fe$^{III}$TPP]$_2$O in benzene. Due to pump energy variation from one wavelength range to the next, there is no direct correlation of band intensities between the difference sets of spectra for each time spectrum. The absence of absorbance change in the 532-nm spectral region is the result of a notch filter used to reject any scattered 532-nm excitation light.

**Picosecond Studies.** The picosecond spectroscopy studies were performed with the apparatus similar to the one described earlier by us.[15] The optical density of the sample at 532 nm in a 2-mm cell was 0.3–0.5 for longer wavelength experiments and was diluted to ~0.1 for experiments done in the Soret region. All samples were deoxygenated by 6–10 freeze–pump–thaw cycles. The photon density of the 25 ps excitation pulses was adjusted so that the energy of the excitation pulse vs $\Delta A$ followed Beer's law. No change in the lifetime values were observed by decreasing further the intensity of the excitation pulse.

## Results

With 532 nm as the pumping pulse, the difference spectra, $\Delta A$ vs $\lambda$, were followed over the spectral range from 360 to 800 nm in three discrete experiments: (1) 360–480, (2) 480–570, and (3) 570–800. Figure 1 shows the observed $\Delta A$ vs $\lambda$ in these three spectral regions.

**Time-Resolved Difference Spectra. (a) (μ-Oxo)bis[TPPFe(III)] in Benzene.** Excitation of (μ-oxo)TPPFe$^{III}$ with a single 532-nm 25-ps FWHM pulse resulted in the difference spectra shown in Figure 1. The times at which the spectra were recorded are in reference to the excitation pulse. For example, $t = -100$ ps represents the spectrum taken $t = 100$ ps before the excitation pulse arrived at the sample, and 100 ps designates that the spectra were taken 100 ps after excitation. Note that at $t = 0$ ps, there is both bleaching and absorption detected in the difference spectra (Figure 1). This is due to the finite 25-ps width of the excitation and probe pulses, and our designation of $t = 0$ ps corresponds to the time when the center of the excitation pulse passes through the sample. For example, at $t = -100$ ps, the excitation pulse has not arrived at the sample yet; therefore, no change is observed in the $\Delta A$ vs. $\lambda$ spectra, Figure 1, compared to the normal steady-state (time-independent) spectrum, shown in Figure 2.

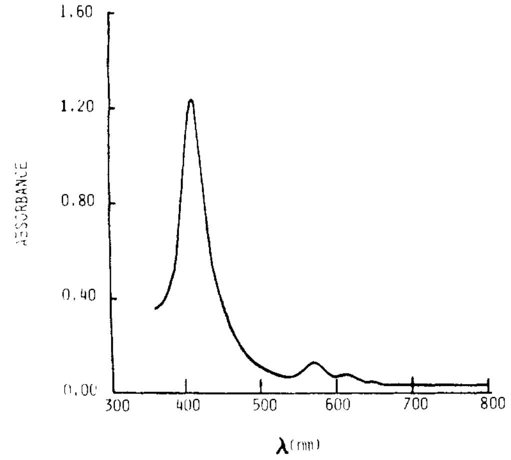

Figure 2. Electronic absorption spectra of deoxygenated [Fe$^{III}$TPP]$_2$O in benzene. The sample used in the 480–800-nm region was ~5 times more concentrated than the sample used in the 360–480-nm studies, shown above.

Table I. Absorbance Changes, Corresponding to Figure 1, of Parent and Intermediate Species at Times Indicated

| band, nm | time, ps -100.0 | -25.0 | 0.0 | 25.0 | 100.0 | 400.0 |
|---|---|---|---|---|---|---|
| 370 | 0.0 | 0.0 | 0.020 | 0.022 | 0.030 | 0.031 |
| 400 | 0.0 | 0.0 | -0.035 | -0.045 | -0.040 | -0.020 |
| 422 | 0.0 | 0.0 | 0.043 | 0.062 | 0.045 | 0.028 |
| 450 | 0.0 | 0.0 | -0.012 | -0.030 | -0.034 | -0.020 |
| 515 | 0.0 | 0.0 | 0.023 | 0.045 | 0.048 | 0.027 |
| 572 | 0.0 | 0.0 | -0.050 | -0.100 | -0.102 | -0.082 |
| 600 | 0.0 | 0.0 | 0.015 | 0.010 | 0.006 | 0.010 |
| 615 | 0.0 | 0.0 | -0.010 | -0.021 | -0.027 | -0.012 |
| 635 | 0.0 | 0.0 | 0.035 | 0.042 | 0.039 | 0.028 |
| 650 | 0.0 | 0.0 | 0.020 | 0.022 | 0.019 | 0.013 |
| 665 | 0.0 | 0.0 | 0.010 | 0.022 | 0.025 | 0.015 |
| 770 | 0.0 | 0.0 | 0.0 | -0.020 | 0.008 | 0.010 |

At $t = 0$ ps, the Soret band with a maximum at 409 nm has started to bleach, and simultaneously a new absorption band at 420 nm appears. In addition, the Q band at 571 nm is bleaching while a broad absorption centered at ~510 nm appears at the same time.

The general behavior of the absorption bands are shown in Table I. It is evident that an immediate bleaching of the Soret, charge-trasfer band ($\lambda_{max} = 612$ nm), and $Q$ ($\lambda_{max} = 571$ nm) band is observed while in the low-intensity charge-transfer band ($\lambda_{max} = 650$ nm) the absorption intensity increases. This does not necessarily mean that 650-nm band does not bleach because the intensity of a broad transient absorption may overwhelm the low-intensity bleached band at 650 nm.

New transient absorption bands appear immediatey at 370, 420, 500–550, and 600 nm and a broad absorption between 630 and 700 nm with possible intensity maxima at 640, 660, and 690 nm. May we point out again that these transient absorption are due to difference spectra.

After reaching a maximum, the bands do not seem to shift in wavelength as a function of time, and the general features, other than intensity, are time independent even though some of the side bands appear to become sharper and more defined because of higher intensity. The kinetics of the major ground-state absorption bands depicted in the form of $-\Delta A$ at 612, 571, and 410 nm show (Table I) an immediate bleach and a long recovery to the ground state. Figure 1 shows the kinetics of the difference spectra in benzene. The evolution and decay of the transient absorption bands at 665, 640, and 510 nm seem to follow a similar sharp risetime and slower decay. The 420-nm band does not decay as fast as the three others.

At ~100 ps after excitation, the intensity of the ground-state Soret band bleaching has started to decrease, but the new 420-nm absorption band clearly continues to grow while the remaining peak intensities slightly increase or remain unchanged. This is characteristic of an excited-state system where more than one transient species is represented in the decay sequence. If the ground state were replaced by a single excited state species so that the excitation sequence was the group state followed by a single excited-state species, then as the ground state bleaching disappears the excited-state absorptions would also decrease in intensity with the same kinetics. Our data shows this not to be the case and leads to the proposal that there is more than one transient species present in the excited-state relaxation of the $\mu$-oxo compound. In addition, this transient must have a $\lambda_{max}$ in the 400-nm range in order for the ground-state band to be almost entirely regenerated only in the Soret region, 410 nm, within 400 ps. This excited-state absorbance causes an anomolously short decay time constant of ~100 ps for the bleach at 410 nm. The 420-nm absorption band remains strong and was calculated to have a decay time constant of more than 500 ps.

The progression of the excited-state difference spectra, $\Delta A$ vs $\lambda$, at 0, 25, 100, and 400 ps and 4.3 ns shown in Figure 1, indicate that the Q band at 571 nm bleaches instantaneously, as does the charge-transfer band at 615 nm. In contrast, a new transient absorption grows at 640 and 665 nm. After 25 ps, these bands have achieved their maximum intensity, and there is virtually no change from 25 to 100 ps. From 100 to 400 ps, these bands decrease in intensity; however, the decay rates are not the same. The long-wavelength 665-nm absorption and 612-nm bleaching were found to have similar rates of decay, which differ from the other bands' decay kinetics.

Comparison of the excited-state difference spectra after excitation at 355 nm with the 532-nm excitation shows that in both cases the new 420-nm transient absorption band continues to increase up to 100 ps, while the ground-state bleach at ~400 nm has already begun to collapse at 100 ps. In addition, the spectra taken after 355-nm excitation were found to decay with a slightly slower rate than the spectra following 532-nm excitation.

The difference spectra of $[Fe^{III}TPP]_2O$ for the 360–480 nm spectral range in pyridine solvent with $O_2$ shows the bleaching of the ground-state Soret band and the rise of the new 420-nm band follow the same kinetics as in benzene. The time constant for the disappearance of the bleaching of the ground-state Soret is approximately 100 ps, while the 420 band has a lifetime of greater than 500 ps.

No photochemistry was observed in any of the experiments presented here. In agreement with the observation that the ground state was completely repopulated within 4.3 ns. No accumulation of photoproducts was seen after approximately 1000 flashes in an unstirred cuvette. The admission of oxygen also gave no change in kinetics the range of 360–480 nm after excitation at 355 nm.

## Discussion

**The Nature of the Excited State(s).** The strongly antiferromagnetically coupled Fe(III) porphyrins in the ($\mu$-oxo)bis-$[TTPFe^{III}]$[21] are separated by a ring to ring distance of 5.2 Å hindered from closer approach by the bulk of the phenyl rings.[22,23] Resonance Raman studies have shown that the excitation of one ring does not migrate to the other since no exciton splitting has been observed.[24-27] Both the resonance Raman studies[27] and the X-ray crystallography studies[22,23] indicate that the dimer maintains the iron in a structure similar to the high-spin iron ion in TTP-$Fe^{III}Cl$.

While our present experiments are not designed to provide exact spectroscopic details of the excited state, several features of the excited-state kinetic sequence can be seen. The time-resolved spectra of $[TPPFe^{III}]_2O$ in benzene show that the absorption band at 420 nm continues to grow after the excitation pulse has passed. This observation indicates this band is not an initially excited state but rather a new species formed subsequently to excitation but before the final products appear. The data shows that the ground-state Soret band at ~410 nm is recovering at 100 ps while the 420 band is still growing; this seems to be anamolous, because normally the ground state should only be repopulated as the final excited state decays into the ground state. We interpret this experimental observation as the result of the appearance of an absorption band in the same spectral region as the bleached band. Since the absorption grows in the opposite direction to the bleaching, the intensity of the ground state band bleaching would appear to be decreasing when in reality the growth of the absorption band in the same spectral region causes the decrease of the bleaching intensity.

It is possible that the excited state decays immediately to intermediate species during the pulse width and thereafter all observed spectral changes are due to the conversion of the intermediates to photoproducts. It is also possible, though not very probable, that an electronically excited state(s) may persist longer than the excitation pulse.

**The Nature of the Photoproducts.** Peterson et al.[19] have presented strong evidence that the photooxidation of triphenylphosphine by $[Fe^{III}TPP]_2O$ proceeds by the photodisproportionation sequence:

$$TPPFe^{III}\text{–}O\text{–}Fe^{III}TPP \xrightarrow[<440\ nm]{h\nu} TPPFe^{II} + TPPFe^{IV}{=}O$$

which results in the strongly oxidizing ferryl compound, TPP-$Fe^{IV}{=}O$.

This photoreaction could only be observed when the ferryl compound was trapped by the basic $Ph_3P$ and showed increasing quantum yield with photolysis wavelengths of <440 nm.

In their experiments, no disproportionation photoproducts could be seen at 100 ns if there was not $Ph_3P$ unless $O_2$ was present, in which case the bleaching of the porphyrin was thought to be due to attack of a radical species on the porphyrin ring itself. The $[TPPFe^{III}]_2O$ also catalyzed a slower photooxidation of alkenes in the presence of pyridine. In the absence of oxygen, we could detect no photoproducts. In our experiments, we find that at 4.3 ns after excitation the original spectrum was regenerated regardless of whether the excitation was 355 or 532 nm, whether $O_2$ was present or not, and whether the solvent was benzene or pyridine.

It is difficult to identify the possible intermediates during the first 100 ps because the relative low intensities of some of the bands and the fact that they are changing at different rates. We find that after 100 ps the spectra became more uniform, which suggests that they may represent intermediate species. The most likely species are (1) $PFe^{II}$ and $PFe^{IV}{=}O$ (disproportionation), (2) $PFe^{II}$ and $P^{\bullet}Fe^{III}{=}O$ ($\pi$ cation radical), and (3) $PFe^{III+}$ and $PFe^{III}\text{–}O^-$ (ion pair).

There is disagreement in the literature on the products of electrochemical oxidation of the $[Fe^{III}TPP]_2O$. Felton et al.[28]

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**Table II.** Comparison of the Position and Integrity of the Main Absorption Bands of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ with Possible Photoproducts: $\mathrm{Fe^{II}TPP}$, $\mathrm{Fe^{IV}{=}OTPP}$, and $\mathrm{Fe^{III}TPP^+}$

| $\lambda$ ($\epsilon \times 10^{-4}$) | | | |
|---|---|---|---|
| $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$[a] | $\mathrm{Fe^{II}TPP}$[b] | $\mathrm{Fe^{IV}{=}OTPP}$[c] | $\mathrm{Fe^{III}TPPCl}$[a] |
| | 421 (7.5) | 419 (3.6) | 378.0 (5.8) |
| | | | 415.0 (10.8) |
| 408 (12) | 447 (4.7) | | 509.5 (1.3) |
| | | 557 (0.185) | 577.5 (.33) |
| 571.5 (1.07) | 540 (0.83) | | 656.5 (.28) |
| | | 591 (0.11) | 690.5 (0.31) |
| 612 (0.48) | | | |

[a] Fleischer and Srivastava.[23] [b] Gouterman in *Porphyrins*.[4] [c] Chin et al.[31]

originally assigned the electrochemical oxidation of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ in the presence of $O_2$ to the formation of the $\mathrm{Fe^{IV}{=}O}$ species; however, others[29] have assigned oxidation products to $\mathrm{Fe^{III}{-}P^{\bullet}}$ with strong antiferomagnetic coupling between the $\pi$ cation radical at the Fe(III). Recent chemical oxidation of $\mathrm{Fe^{III}TPP}$ has also resulted in stable complexes, which are likely to be $\pi$ cation radicals of the porphyrins rather than a higher oxidation state of the iron.[30]

In Table II are presented the main absorption bands of the starting compound $[\mathrm{TPP\ Fe^{III}}]_2\mathrm{O}$, $\mathrm{Fe^{III}TPPCl}$, and the possible disproportionation products $\mathrm{Fe^{II}TPP}$ and $\mathrm{Fe^{IV}{=}OTPP}$. We have used the data for absorption spectra of $\mathrm{Fe^{IV}{=}OTPP}$ from the base-catalyzed decomposition of the peroxo-bridged $\mathrm{TTPFe^{III}{-}O{-}O{-}Fe^{III}TPP}$ at -80 °C.[31] Since NMR does not indicate an axial ligand in the $\mathrm{TPPFe^{IV}{=}O}$ by the base *N*-methylimidazole, the spectrum of $\mathrm{TPPFe^{IV}{=}O}$ is probably very close to postulated unligated five-coordinate ferryl complex.

For the photodisproportionation of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ in benzene into the ferrous and ferryl species, new absorption bands should appear at about 420 nm and in the 540–557-nm region with perhaps a low band at 591 nm. Examination of the 100-ps spectra of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ after excitation with a 532-nm pulse shows the formation of bands with maxima at 420, 515, and 600 nm. It is possible that the broad absorption band centered at 515 nm is the result of disproportionation where a band at 540–557 nm (Table I), assigned to photoproduction of ferrous and ferryl TPP, has been masked by the large bleach of the Q band. This assignment is reinforced by the fact that the 515-nm band grows in a 1:1 ratio with the peak at 420 nm over the first 25 ps, also in agreement with the results of Richman and Peterson.[18] Unfortunately, the growth of the band at 590 nm, which also should be seen in disproportionation (Table I), cannot be monitored clearly in the $\Delta A$ spectra reported here because the bleach of the Q band has a very large effect on the spectra in this wavelength region. However, the difference spectrum at 100 ps is much more similar to the absorption spectra of ferric TPP. While it is probable that the $\mathrm{Fe^{III}TPP^+}$ and $\mathrm{Fe^{III}TPPO^-}$ will have spectra different from $\mathrm{Fe^{III}TPPCl}$ and therefore no unambiguous assignment of absorption bands can be made, the observed 510-nm absorption assigned to $\mathrm{Fe^{III}TPPCl}$ is also seen in the photoexcited $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ at 100 ps. In addition, $\mathrm{Fe^{III}TPPCl}$ also has Soret bands at 415 and 378 nm (hyper spectrum). We observe both these bands at 100 ps after photoexcitation. While there is a Q band in the $\mathrm{Fe^{III}TPPCl}$ at 577 nm, it has only about $^1/_3$ the extinction coefficient of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$. Therefore, the 571-nm bleaching over this area should predominate, and indeed, the spectra show a strong bleaching at 571 nm. Finally, there should be two absorption bands at 656 and 690.5 nm if the ferric form is generated. Two peaks are observed in this range; one at 635 nm the other at 665 nm. Although speculative, it is possible that these transitions in the $\mu$-oxo and ferric ion state are in-plane metal-to-pyrrole charge-transfer bands.[26] It is possible that these bands are blue-shifted due to the change in energy levels of the low lying $b_2$ orbitals as the iron ion out-of-plane displacement decreases and the symmetry approaches $D_{4h}$.

In the absence of published spectra, there is considerable uncertainty in the assignment of the $\mathrm{TPPFe^{III}O^-}$ 100-ps spectrum. Even though there is a resemblance to Fe(II) and $\mathrm{Fe^{IV}{=}O}$ spectra in the Soret and 515-nm region, these spectra are not identical. Similarly, ionic compounds of $\mathrm{TPPFe^{III}}$ have some resemblance to the 100-ps spectra; however, there is no direct correlation of all bands to warrant assignment. In addition, disproportionation products would be expected to have a long enough lifetime to be observed in the 4.3-ns difference spectrum and to yield visible differences in experiments with pyridine as the solvent. This does not mean, however, that there is no photodisproportionation. The geminate recombination process may be very efficient due to diffusion limitations upon the large porphyrin, and therefore, the disproportionation is not seen at long times. The photochemical oxidation of $\mathrm{Ph_3P}$ and alkenes observed by Richman et al.[18,19] are reported to have low quantum yields, $\phi < 10^{-4}$, such a small disproportionation reaction could be a side photoreaction in our experiments that is beyond our sensitivity limits to be clearly detected. There is evidence for the photoproduction of the ferryl TPP at 15K in a pure $O_2$ matrix during Raman spectroscopic examination of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ at 406.7 nm. The presence of a very strong 852-cm$^{-1}$ band is indicative of $\mathrm{Fe^{IV}{=}O}$ vibration. In addition, the spectra with oxygen and iron isotope substituted compounds suggest that there is high probability of ferryl TPP presence although $\mathrm{Fe^{III}{-}O^-}$ cannot be completely ruled out.[32] The usual ferric porphyrins do not oxidize $\mathrm{Ph_3P}$,[33] and therefore, the previously observed photocatalytic oxidation of $\mathrm{Ph_3P}$ by $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ is probably via a ferryl species. It has already been shown that the oxidation of $\mathrm{Ph_3P}$ can be accomplished by the ferryl complex generated by decomposition of the $\mu$-peroxo-$\mathrm{Fe^{III}TPP}$.[33] We therefore conclude that the photoexcitation of $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ results in an excited state, which can undergo either photoionization $\mathrm{TPPFe^{III+}}$ + $\mathrm{TPPFe^{III}{-}O^-}$ (>80%) or photodisproportionation $\mathrm{TPPFe^{II}}$ + $\mathrm{TPPFe^{IV}{=}O}$. It is likely that the combined quantum yield of both reactions is no more than about $10^{-4}$.

We find that with use of pyridine as a solvent, the spectra of photoexcited $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$ are the same as the ones observed with benzene. We must conclude that base coordination is a much slower process than the recombination of products into the starting compound. We are proceeding to study the proposed dissociation, recombination, and the possibility of radical ion formation by means of polar solvents and radical scavengers. This applies to the expected strong coordination of $\mathrm{Fe^{II}TPP}$ or the weaker coordination of the ferryl species in photodisproportionation or the weak coordination of the ferric compounds in photodissociation.

Recent studies by Hendrickson et al.[12] have clearly shown that the photoreduction of iron in the $\mathrm{Fe^{III}TPP}$ halides is due to an initial excitation into an intense halide-to-metal charge-transfer band in the near-UV (355 nm). While Peterson et al.[19] have shown that an absorption band exists at 316 nm for the $[\mathrm{Fe^{III}TPP}]_2\mathrm{O}$, it is unclear whether or not such a band is photoactive in the photodisproportionation reaction. In our experiments, no difference in kinetics or spectra of the excited state was observed between excitation at 355 and 532 nm.

There has been uncertainty as to whether the first oxidation product of ferric porphyrins is a ferryl species of the iron or a $\pi$ cation radical of the porphyrin. In the initial electrochemical studies,[34] the oxidation of iron TPP gives broadened and blue-shifted Soret bands with a broad featureless absorption band between 500 and 700 nm. PMR resonances also indicated that the hole resides in the iron rather than on the porphyrin ring.[28] Goff and co-workers[35] have found a larger than expected meso

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shift on the phenyl protons of oxidized $Fe^{III}TPPCl$ and suggest that it could arise from $A_{2u}$ symmetry of a $\pi$ cation radical species. In addition, they have shown that the near-IR bands are quite similar to ZnTPP radical species and that the first wave electrochemical potential for oxidation is independent of axial ligands for $Fe^{III}TPP^{+}$. If this radical is formed, it must be strongly antiferromagnetically coupled to the Fe(III) iron.[30] In general, the formation of simple $\pi$ cation radicals of metalloporphyrins of TTP result in a weaker, broadened, and blue-shifted Soret band with increased absorbance over the 600–700-nm range.[36] Peterson et al.[19] reported an excited-state band at 370 nm of $[Fe^{III}TPP]_2O$ in both benzene and pyridine. These transient absorption studies were attributed to formation of a Fe(III) porphyrin radical. In the absence of a good coordinating base, it was proposed that a $\pi$ cation radical species was observed rather than an Fe(IV) disproportionation complex. The appearance of a band at ~370 nm was also seen in the present studies, but we do not observe a clear change in the difference spectra of the $[Fe^{III}TPP]_2O$ in the 600–700-nm range; however, it is possible that a strongly coupled Fe(III) high spin state to a $\pi$ cation radical may alter the expected shifts. It may be pointed out, however, that coupling between copper and the $\pi$ cation radical of $Cu^{II}TPP$ in electrochemical oxidation still gives the features of a $\pi$ cation radical.[36]

## Conclusion

The photoexcitation of $[Fe^{III}TPP]_2O$ at either 532 or 355 nm results in an intermediate state with a lifetime of <100 ps that may be an excited state localized to a monomer unit and that forms the photodissociated pair $TPPFe^{II+}$ + $TPPFe^{III}$–$O^-$ with smaller yield photodisproportionation reaction, which generates $Fe^{II}TPP$ and $TPPFe^{IV}$=O. In the absence of easily oxidizable substrates, the photoproducts recombine into $[Fe^{III}TPP]_2O$ within 4.3 ns.

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**Registry No.** $[Fe^{III}TPP]_2O$, 12582-61-5; $TPPFe^{II+}$, 29484-63-7; TPP-$Fe^{III}$—$O^-$, 115162-51-1; $Fe^{II}TPP$, 16591-56-3; $TPPFe^{IV}$=O, 84152-32-9.

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# Trends in the Optical Signatures for Transition-Metal Oxide Carbonyl Complexes. Evaluation of Transition-Metal Carbonyl, $M(CO)_x$, Binding Energies

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**Abstract:** Transition-metal atoms entrained in argon, helium, and CO are oxidized with ozone ($O_3$) and nitrogen dioxide ($NO_2$) to study the nature of the metal atom complexation with CO. We establish a method for evaluating M–CO binding energies through comparison of the chemiluminescent emission from the oxidation of argon- and CO-entrained transition-metal atoms. These studies have thus far yielded $E_{\mathrm{binding}}(\mathrm{Ti(CO)}_x) \approx 1.75$ eV and $E_{\mathrm{binding}}(\mathrm{NiCO}) \approx 1.10$ eV, the latter in excellent agreement with previous experimental and theoretical evaluations of the Ni–CO bond energy. We identify the optical signatures for transition-metal oxide carbonyl (MOCO) complexes formed in the oxidation of M(CO) complexes. We outline trends in the nature of the observed metal oxide complex emissions. The current study suggests a method for obtaining the spectra of transition-metal carbonyl ($M(CO)_x$, $x = 1, 2$) complexes.

The volatile metal carbonyls ligated with several carbonyl groups exhibit a variety of molecular structures. These structures have created much previous interest, and the vibrational spectroscopy of the multiply ligated species, primarily those of the transition metals, which play an extremely important role in chemistry, have been the subject of considerable investigation. Both M–C and C–O stretching modes have been well studied.[1] While there has been considerable research in the volatile multiply ligated metal carbonyls, relatively little experimental work has focused on the basic metal monocarbonyl, M–CO, binding energies and MCO spectroscopy is sparse.[2] This gap in understanding is significant, for, without doubt, the most celebrated and studied gas–surface interaction is that of carbon monoxide on metal surfaces.[3]

The metal surface–CO interaction has been the subject of innumerable studies employing a wide variety of experimental[2] and theoretical methods.[3-5] These studies have been, in large part, a response to the industrial versatility of methods running the gamut from methanol formation[6] to the Fisher–Tröpsch synthesis.[7] MCO molecules, where M is a transition-metal element, have been of considerable interest as prototypes for CO chemisorption on metal surfaces. There are now a large number of theoretical papers concerning the electronic and bonding properties of these species, the proliferation of approaches to the study of NiCO being especially notable.[8] Much less experimental

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