**Photochemical generation of manganese(IV)-oxo porphyrins by visible light
photolysis of dimanganese(III) μ -oxo *bis*-porphyrins**

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Abstract

Visible light photolysis of dimanganese(III) μ -oxo *bis*-porphyrins, $[\text{Mn}^{\text{III}}(\text{Por})]_2\text{O}$, was studied in three porphyrin systems with different electronic structures. Direct conversion of manganese (III) μ -oxo dimers to manganese(IV)-oxo porphyrins plus manganese(III) products has been observed in benzene solution upon light irradiation. The spectral signature of $\text{Mn}^{\text{IV}}(\text{Por})(\text{O})$ was further confirmed by production of the same species in the known experiment of the $\text{Mn}^{\text{III}}(\text{Por})\text{Cl}$ with $\text{PhI}(\text{OAc})_2$. Continuous irradiation of dimanganese(III) μ -oxo *bis*-porphyrins in the presence of pyridine or triphenylphosphine gave rise to the formation of $\text{Mn}^{\text{II}}(\text{Por})(\text{Py})$ or $\text{Mn}^{\text{II}}(\text{Por})(\text{PPh}_3)$ which were stable to be detected. A photo-disproportionation mechanism similar to that for diiron(III) μ -oxo *bis*-porphyrins was proposed to explain above photochemical behaviors of the three dimanganese(III) μ -oxo *bis*-porphyrins.

Key Words

Dimanganese(III) μ -oxo *bis*-porphyrins; manganese(IV)-oxo porphyrin; disproportionation; visible light

1. Introduction

Catalytic oxidation is a pivotal transformation for chemical synthesis in organic laboratories and petrochemical industries.[1, 2] In Nature, the ubiquitous cytochrome P450 enzymes (P450s) can catalyze a wide variety of oxidation reactions with exceptionally high reactivity and selectivity.[3, 4] In the past decades, many transition metal catalysts bearing a core structure resembling the iron porphyrin core of P450s, have been synthesized as models to probe the sophisticated mechanism of molecular oxygen activation as well as to invent enzyme-like oxidation catalysts.[5-8] In general, high-valent transition metal-oxo species have been implicated as the active oxidizing species.[9, 10] In particular, manganese-oxo intermediates are among the more reactive oxidizing transition metal derivatives. A variety of these species are employed catalytically in applied syntheses,[5, 6] and Nature uses Mn-oxo species in the production of oxygen in photosynthesis II.[11] Highly reactive porphyrin-manganese(V)-oxo derivatives[12, 13] are proposed intermediates in catalytic processes that have been known for decades.[14, 15] In contrast, the well-characterized manganese(IV)-oxo derivatives are less reactive than manganese(V)-oxo species in manganese porphyrin-catalyzed oxidations.[16-18]

Photochemistry is particularly intriguing to explore the metal-oxo chemistry.[19, 20] With photochemical production of reactive metal-oxo transients, one has access to time scales that are much shorter than the fastest mixing experiments. Furthermore, kinetics of oxidation reactions of transients of interest are not convoluted with the kinetics of reactions that form the transients. In this regard, laser flash photolysis (LFP) techniques have been successfully developed for generation and direct kinetic studies of a variety of high-valent transition metal-oxo species supported by porphyrin and corrole ligands.[21-26] In so-called photo-induced ligand cleavage reactions, both porphyrin-manganese(IV)-oxo species and porphyrin-manganese(V)-oxo species can be produced as a function of the identity of the axial ligands. For examples, irradiation of porphyrin-manganese(III) nitrates and chlorates resulted in homolytic cleavage of the O-X bonds in the ligands to afford porphyrin-manganese(IV)-oxo species, whereas irradiation of porphyrin-manganese(III) perchlorates resulted in heterolytic cleavage of O-Cl bonds to give porphyrin-manganese(V)-oxo cations.[27]

Notably, the chemistry of cofacial metal-*bis*-porphyrins has drawn increased attention owing to the ability of these systems to utilize molecular oxygen and visible light (sunlight) for organic oxidations.[28, 29] One example is the catalytic aerobic oxidation by high-valent

iron(IV)-oxo species in a process that involves photo-disproportionation of a diiron(III)- μ -oxo *bis*-porphyrin complex.[30, 31] The catalytic efficiency of diiron(III)- μ -oxo systems was improved by employing “Pacman” ligand designs with organic spacer-hinges, which can pre-organize two iron centers in a favorable co-facial arrangement.[32-35] In a similar fashion, we discovered that photolysis of a *bis*-corrole-iron(IV) μ -oxo dimer apparently proceeded by the same type of photo-disproportionation mechanism to give corrole-iron(V)-oxo transient.[36, 37] In addition, we reported a putative porphyrin-ruthenium(V)-oxo species generated in a similar photo-disproportionation process that has shown great potential for aerobic photocatalytic oxidations.[38, 39] Herein, we report direct spectroscopic observation of photochemical generation of porphyrin-manganese(IV)-oxo complexes by visible light irradiation of *bis*-porphyrin-manganese(III) μ -oxo dimers. The results in the current study support the conclusion that *bis*-porphyrin-manganese(III) μ -oxo dimers undergo photo-disproportionation reaction upon light irradiation to generate a germinal porphyrin-manganese(II)/manganese(IV)-oxo pair that can be detected and studied in real time (Scheme 1).

Scheme 1. Visible light photolysis of *bis*-porphyrin-manganese(III) μ -oxo dimers to produce a germinal porphyrin-manganese(II)/manganese(IV)-oxo pair in three porphyrin systems

2 Results and discussions

2.1. Synthesis and spectral studies of bis-porphyrin-dimanganese(III) μ -oxo complexes (**1**)

As shown in Scheme 1, three porphyrin systems, 5,10,15,20-tetrakis(4-trifluoromethylphenyl)porphyrin (4-CF₃TPP, **a**), 5,10,15,20-tetrakis(4-fluorophenyl)porphyrin (4-FTPP, **b**) and 5,10,15,20-tetraphenylporphyrin (TPP, **c**), were studied in this work. Abbreviations used here follow those conventionally established. All ligands **a-c** are generally considered as a sterically non-encumbered porphyrin due to the absence of substituents on the *ortho* positions of the *meso*-phenyl groups. The different aromatic groups on the porphyrins also result in varying electron demands with the trifluoromethylphenyl system being the most electron withdrawing.

Following a known procedure,[40] three *bis*-porphyrin-dimanganese(III) μ -oxo complexes (**1**) were synthesized by reacting a corresponding Mn^{III}(Por)Cl with NaOH in benzene solutions. The formed products in three porphyrin systems are characterized by UV–visible and ¹H-NMR spectra. The representative spectra of **1a** are shown Fig. 1 and other spectra for **1b** and **1c** are shown in Fig S1 and S2 in the Supplementary Information. All *bis*-porphyrin-dimanganese(III) μ -oxo complexes show distinct UV-vis absorption characterized by split Soret bands at approximate 425 nm and 474 nm, respectively, consistent with reported values in the literature.[40] Interestingly, the non-oxidative transformation of manganese(III) monomer to its μ -oxo dimer **1** was also identified by featuring paramagnetically shifted pyrrolic protons, which was slightly more downfield than that of manganese(III) monomer of Mn^{III}(Por)Cl (Fig. 1B). Attempts to prepare some sterically hindered porphyrin μ -oxo dimers which contain relatively large electron-donating substituents (including methyl and methoxy) at *ortho* position of the *meso*-phenyl rings were not successful, apparently due to the steric hindrance. As noticed in earlier reports,[37, 41] it was found that electron-withdrawing substituents such as CF₃ and F on porphyrin ligand favor μ -oxo dimer formation. Presumably, the electron-withdrawing groups could stabilize the metal complexes in a dimer form by reducing the electron density of metal atoms. It is noteworthy that compound **1** is significantly stable in non-polar solvents such as benzene or cyclohexane; however, in CH₂Cl₂ or acetonitrile solution, complex **1** is not stable and gradually returns to the monomeric Mn^{III} complex (Fig S3 in the Supplementary Information). Apparently, the relatively weak Mn-O-Mn bond in dimeric complexes can be readily dissociated by these polar solvents.

Fig. 1. (A) UV-vis spectra of manganese(III) chloro precursor $\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})\text{Cl}$ (dashed line) and *bis*-porphyrins dimanganese(III) μ -oxo complex $[\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})]_2\text{O}$ (**1a**) (solid line) in benzene (B) ^1H -NMR spectrum of $\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})\text{Cl}$ (top) and $[\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})]_2\text{O}$ (**1a**, bottom) in CDCl_3 .

2.2 Visible light photolysis of *bis*-porphyrin-dimanganese(III) μ -oxo dimers

Visible light irradiation of μ -oxo complex **1a** in anaerobic benzene from a SOLA engine (120 W) gave rise to the formation of a transient species **2a** with a slightly blue-shifted Soret band at 420 nm. The absorption spectral changes shows that the twin peaks of **1a** located at 425 and 472 nm gradually decreased and a new peak at 420 nm appeared during the course of irradiation up to 3.5 min (Fig. 2A). Judging from the spectral changes and kinetic behavior, the transient species that formed at 420 nm could be ascribed to the manganese(IV)-oxo porphyrin, i.e. $\text{Mn}^{\text{IV}}(4\text{-CF}_3\text{TPP})(\text{O})$. Note that the absorption spectra of **2a** overlap with that of another Mn^{III} porphyrin which apparently gave a Soret band at 472 nm and partial absorption in the range of 370 to 415 nm. The spectra signature of the photo-generated **2a** as $\text{Mn}^{\text{IV}}(4\text{-CF}_3\text{TPP})(\text{O})$ was further confirmed by production of the same species from chemical oxidation of manganese(III) with $\text{PhI}(\text{OAc})_2$ as a mild oxidant (Fig. 2B).[42] When excess amounts of organic reductants such as cyclohexene or styrene were added to above solutions of **2a**, the UV-visible spectrum of **2a** returned to that of manganese(III) porphyrin, which was recovered in > 90% yield (Fig. 3). The overall reaction sequence is consistent for the behavior expected for porphyrin-

manganese(IV)-oxo species.[42] In a similar fashion, irradiation of **1b** with visible light also produced **2b** in another porphyrin system (Fig. S4 in Supplementary Information). Although the complex **1c** showed relatively low solubility in benzene solution, visible light irradiation of **1c** gave similar results (data not shown) as compared to that of **1a** and **1b**.

Fig. 2. (A) Time-resolved spectrum of **2a** upon irradiation of **1a** with a 120-W visible lamp in anaerobic benzene over 3.5 min. at 23 ± 2 °C; (B) UV-visible spectrum of **2a** (solid line) generated by reacting $\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})\text{Cl}$ (dash line) with $\text{PhI}(\text{OAc})_2$ (25 equiv.) in benzene at ambient temperature.

Fig. 3. Time-resolved spectra over 220 s for reaction of photo-generated **2a** with 0.5 M cyclohexene in benzene at 23 ± 2 °C; the inset shows the kinetic trace at 420 nm in the absence (self-decay) and presence of cyclohexene (0.5 M).

2.3 Proposed mechanism

Visible light photolysis of dimer **1** to produce manganese(IV)-oxo porphyrin **2** can be explained by a photo-disproportionation mechanism similar to that previously established for the photolysis of *bis*-porphyrin-diiron(III) μ -oxo complexes.[30] As outlined in Scheme 2, photo-disproportionation of dimer **1** gives the reactive manganese(IV)-oxo transient **2** in addition to one molecule of a porphyrin-manganese(II) species **3** and oxidation of an organic reductant by **2** gives a second molecule of **3**. Species **3** was known to be unstable in aerobic media and tends to be rapidly oxidized to the manganese(III) complex (**4**).[20] Clearly, photolyses of dimanganese(III) μ -oxo *bis*-porphyrins **1** appear to present a reaction manifold similar to that of diiron(III) μ -oxo *bis*-porphyrins,[30] diruthenium(IV)- μ -oxo *bis*-porphyrins[38] and diiron(IV)- μ -oxo *bis*-corroles.[37] In light of the current interest in photo-disproportionation reaction, the effects of electronic structure on the photolysis of manganese (III) μ -oxo bisporphyrins and insights into the detailed intramolecular electron transfer process involved deserves further study

including the theoretic support from computational calculations. These studies are expected to further our understanding of photo-disproportionation reactions in different systems.

Scheme 2. A proposed photo-disproportionation mechanism (square represents the porphyrin ring)

2.4 Photolysis of bis-porphyrin-dimanganese(III) μ -oxo dimers in the presence of pyridine and triphenylphosphine

To accentuate the proposed photo-disproportionation mechanism, irradiation of the thermally stable complex **1a** in the presence of excess pyridine was conducted. Similar to the well-known photo-disproportionation of diiron(III)- μ -oxo *bis*-porphyrin complexes,[30] the μ -oxo precursor **1a** gradually converted to a stable product **5a** with well-anchored isosbestic points (Figure 4A). According to previous studies by Hoshino and coworkers,[43] the product **5a** formed with λ_{max} at 440 nm was assigned as $\text{Mn}^{\text{II}}(4\text{-CF}_3\text{TPP})(\text{Py})$, which was further confirmed by production of the same species in the known experiment of the $\text{Mn}^{\text{III}}(4\text{-CF}_3\text{TPP})(\text{NO}_2)$ with excess pyridine.[43] The reactants and products of the overall photoreaction are matched to their respective absorption profiles. This photochemical observation of a clean reduction of $[\text{Mn}^{\text{III}}(\text{Por})]_2\text{O}$ to $\text{Mn}^{\text{II}}(\text{Por})(\text{Py})$ further supports a photo-disproportionation pathway that allows for the generation of the manganese(IV)-oxo porphyrin. Of note, similar spectral changes were also observed upon the photo-disproportionation of dimanganese(III)- μ -oxo *bis*-porphyrin (**1a**) in the presence of excess Ph_3P that gave another stable $\text{Mn}^{\text{II}}(4\text{-CF}_3\text{TPP})(\text{PPh}_3)$ (Fig 4B).

Fig. 4 (A) Time-resolved spectra of $\text{Mn}^{\text{II}}(4\text{-CF}_3\text{TPP})(\text{Py})$ generated by visible light irradiation of **1a** in the presence of excess amount of pyridine (3 mM) over 50 min in benzene; (B) Time-resolved spectra of $\text{Mn}^{\text{II}}(4\text{-CF}_3\text{TPP})(\text{PPh}_3)$ generated by irradiation of **1a** in the presence of excess amount of triphenylphosphine (3 mM) over 8 min in benzene. Visible light was produced from a 120-W solar lamp.

3. Conclusions

In conclusion, photo-cleavage of *bis*-porphyrin-manganese(III) μ -oxo dimers using visible light proceeds by homolysis of an Mn-O bond to give manganese(IV)-oxo porphyrins that are spectroscopically indistinguishable from the species formed by chemical oxidation of the corresponding porphyrin-manganese(III) chlorides. In addition, continuous irradiation of dimanganese(III) μ -oxo *bis*-porphyrins in the presence of pyridine or triphenylphosphine gave rise to the formation of $\text{Mn}^{\text{II}}(\text{Por})(\text{Py})$ or $\text{Mn}^{\text{II}}(\text{Por})(\text{PPh}_3)$ that was also directly observed. The photochemical behavior of dimanganese(III) μ -oxo *bis*-porphyrins upon irradiation is ascribed to a photo-disproportionation mechanism similar to that for diiron(III) μ -oxo *bis*-porphyrins. Further studies to characterize the observed transients spectroscopically more fully are ongoing in our laboratory.

4 Experimental

4.1 General considerations

All commercial reagents were of the best available purity and were used as supplied unless otherwise specified. HPLC grade benzene (> 99.9%) was purified by passing through a dry Al₂O₃ (Grade I neutral) column prior to use. Free porphyrin ligand including H₂(4-CF₃TPP) (**a**), H₂(4-FTPP)(**b**) and H₂TPP(**c**) were prepared according to the known methods. [44] The corresponding manganese(III) chloride complexes Mn^{III}(Por)Cl (Por = **a-c**) used for generation of [Mn^{III}(Por)]₂O (**1**) were prepared by literature methods and characterized fully, matching those reported.[45] UV-vis spectra were recorded on an Agilent 8453 diode array spectrophotometer. ¹H-NMR was performed on a JEOL ECA-500 MHz spectrometer at 298 K with tetramethylsilane (TMS) as internal standard. Chemical shifts (ppm) are reported relative to TMS. Visible light was produced from a SOLA SE II light engine (Lumencor) configured with a liquid light guide. The output power is 120 W.

4.2. Preparation of dimanganese(III) bis-porphyrins [Mn^{III}(Por)]₂O.

In a typical run, [Mn^{III}(Por)]₂O (**1**) was prepared by vigorously stirring Mn^{III}(Por)Cl complex (100 mg) with 20% aqueous NaOH (5 mL) in benzene (25 mL) monitored by ¹H-NMR spectroscopy. The stirring time ranged from 3 h (**1a**) to overnight (**1c**), depending on the porphyrin system employed. When the chemical shifts of the paramagnetic pyrrolic protons at -24 ppm in ¹H-NMR disappeared, 30 mL water was added into the reaction to precipitate desired dimanganese(III)- μ -oxo compounds. The μ -oxo-dimer products were collected by vacuum filtration and washed with water, and dried in air. The [Mn^{III}(Por)]₂O products were further purified by recrystallization in benzene and cyclohexane, then fully dried in vacuum.

4.3. General procedure for photolysis of dimanganese(III) bis-porphyrin $[Mn^{III}(Por)]_2O$.

When the benzene solution of **1** at desired concentration (*ca.* 1.5×10^{-5} M) was irradiated with a 120 W of visible light at ambient temperature, the formation of porphyrin-manganese(IV)-oxo species **2** was complete in *ca.* 3 to 4 min monitored by UV-visible spectroscopy. Reactions of oxo-species **2** with excess cyclohexene (0.5 M) were conducted in a solution at 23 ± 2 °C, and the observed rates were monitored by the decay of the Soret absorption band of the oxo-species **2**. The identity of **2** as $Mn^{IV}(Por)(O)$ was confirmed by producing the same species from chemical oxidation of corresponding manganese(III) chloride precursor with 25-fold excess of $PhI(OAc)_2$ in benzene. When the solution of **1** in the presence of excess pyridine or triphenyl phosphine (3 mM) was irradiated with visible light at ambient temperature, the time-resolved formation of manganese(II) products (**3**) was monitored by UV-visible spectroscopy during the course of irradiation up to 50 min.

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Abbreviations of porphyrin ligands used in this work: Por = porphyrin; 4-CF₃TPP = 5,10,15,20-tetra(4-trifluoromethylphenyl)porphyrin dianion; 4-FTPP = 5,10,15,20-tetra(4-fluorophenyl)porphyrin dianion TPP = 5,10,15,20-tetraphenylporphyrin dianion;

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Graphic Abstract:

Visible light photolysis of *bis*-porphyrin-manganese(III) μ -oxo dimers gave porphyrin-manganese(II) and manganese(IV)-oxo species that can be directly observed.