

Supporting Information

Generation of an Isolable, Monomeric Manganese(V)-Oxo Complex from O₂ and Visible Light

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General. The complexes $(\text{TBP}_8\text{Cz})\text{Mn}^{\text{III}}$ (**1**) and $[(\text{TBP}_8\text{Cz})\text{P}(\text{OH})]\text{OH}$ (TBP_8Cz = octakis(*p*-*tert*-butylphenyl)corrolazinato³⁻) were synthesized according to published methods.^{1,2} Toluene was purified via a Pure-Solv solvent purification system from Innovative Technologies, Inc. Dioxygen gas (2.6 grade) was purchased from BOC Gases and dried by passage through a column of Drierite. H_2^{18}O (97% ^{18}O) was purchased from Cambridge Isotopes, Inc., and $^{18}\text{O}_2$ (98% ^{18}O) was purchased from ICON (Isotope) Services, Inc. 9,10-dimethylantracene was purchased from TCI. Cyclohexane was purified by washing with concentrated H_2SO_4 , followed by water and 5% NaOH until neutral. It was then dried with MgSO_4 and distilled from CaH_2 . PPh_3 was recrystallized from hexanes as described in published procedures.³ All other solvents and reagents were purchased from commercial sources at the highest available purity and used as received, unless otherwise noted.

Instrumentation. UV-vis spectroscopy was performed on a Hewlett-Packard 8542 diode-array spectrophotometer equipped with HPChemstation software. The light source was a General Electric Sunlamp Model RSK6A equipped with a 275-Watt bulb. For monitoring by UV-vis, reactions were run in a quartz cuvette (3 mL, 1 cm path length). The light source was positioned ~15 cm from the reaction mixture, and a 400 nm long-pass filter was placed directly between the quartz cuvette and light source. LDI-TOF mass spectrometry was conducted on a Bruker Autoflex III TOF/TOF instrument equipped with a nitrogen laser at 335 nm using an MTP 384 ground steel target plate. ^1H -NMR and ^{31}P -NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer at 298 K. All spectra were recorded in 5-mm o.d. NMR tubes, and chemical shifts were reported as δ values from standard peaks.

Laser Desorption Ionization Mass Spectrometry. For a typical experiment, an aliquot of sample dissolved in a small amount of solvent was transferred quickly to the steel target plate and allowed to evaporate to dryness, until a thin layer of compound remained on the target plate. LDI-TOF mass spectra were obtained in positive ion reflectron mode. Spectra were accumulated in multiples of 250 laser shots at a frequency of 200 Hz to a sum of 1000 shots total. Samples were deposited neat without the use of matrix, as done previously for metallocorrolazines^{4,5} and for other metalloporphyrins⁶ that can be analyzed in neat form. All mass assignments were made via external calibration using peptide ions as calibrants.

Aerobic Oxidation of (TBP₈Cz)Mn^{III} (1) for UV-vis Spectroscopy. An aerobic solution of **1** (12 μ M) in cyclohexane or toluene (2.5 mL) in a quartz cuvette was continuously irradiated with visible light ($\lambda_{\text{irr}} > 400$ nm) at 23 °C for 20 min. A color change from green-brown to green occurred. The reaction was monitored by UV-vis spectroscopy and showed the complete isosbestic conversion of **1** ($\lambda_{\text{max}}(\text{C}_6\text{H}_{12}) = 432, 687$ nm, $\lambda_{\text{max}}(\text{toluene}) = 434, 689$ nm) to (TBP₈Cz)Mn^V(O) **2** ($\lambda_{\text{max}}(\text{C}_6\text{H}_{12}) = 419, 639$ nm, $\lambda_{\text{max}}(\text{toluene}) = 419, 634$ nm).

Aerobic Oxidation of (1) for Isolation as a Solid. An aerobic solution of **1** (12 μ M) in cyclohexane (25 mL) was continuously irradiated ($\lambda_{\text{irr}} > 400$ nm) 23 °C for 20 min. In this case, the reaction was run in a pyrex round-bottom flask, confirming that $\lambda_{\text{irr}} > 400$ nm is sufficient for the reaction to proceed. A color change from green-brown to green occurred. The reaction mixture was then dried under vacuum. The green solid was redissolved in CH₂Cl₂ and transferred onto a silica gel column (10 x 2 cm) and eluted as a green band with CH₂Cl₂. $R_f = 0.9$. ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm), 8.42-8.39 (m,

8H), 8.05 (d, $J = 8.4$ Hz, 4H), 7.75-7.70 (m, 8H), 7.61-7.52 (m, 8H), 7.25 (d, $J = 8.4$ Hz, 4H), 1.522 (s, 18H), 1.518 (s, 18H), 1.44 (s, 18H), 1.40 (s, 18H). UV-vis (CH_2Cl_2): λ_{max} (nm) ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) 418 (6.29) (soret), 634 (1.99) (Q band). LDI-TOF m/z isotopic cluster centered at 1426.8 (M^+).

Preparation of $(\text{TBP}_8\text{Cz})\text{Mn}^{\text{V}}(^{18}\text{O})$. To a solution of **1** (10 μM) in toluene (2.5 mL) under a N_2 atmosphere was added 10 mL of $^{18}\text{O}_2$ transferred via gas-tight syringe. The reaction was performed in a quartz cuvette and continuously irradiated ($\lambda_{\text{irr}} > 400$ nm) for 20 min at 23 $^\circ\text{C}$. The reaction was monitored by UV-vis spectroscopy to ensure full formation of **2**. The reaction mixture was then concentrated under vacuum to approx. 100 μL and transferred under a stream of Ar to the target plate. LDI-TOF: m/z isotopic cluster centered at 1427.7 (55% ^{18}O incorporation based on simulated spectral fitting to the observed isotopic pattern).

Aerobic Oxidation of (1) in the Presence of H_2^{18}O . To an aerobic solution of **1** (12 μM) in cyclohexane (2.5 mL) was added 25 μL of H_2^{18}O . The reaction was performed in a quartz cuvette and continuously irradiated ($\lambda_{\text{irr}} > 400$ nm) for 20 min. Isosbestic conversion of **1** ($\lambda_{\text{max}} = 432, 687$ nm) to **2** ($\lambda_{\text{max}} = 419, 639$ nm) was observed by UV-vis spectroscopy. LDI-TOF m/z (percent intensity): isotopic cluster centered at 1426.8 (M^+ , 100%, no ^{18}O incorporation).

Photocatalytic Oxidation of PPh_3 . In a typical reaction, to an aerobic solution of **1** (10 μM) in C_6H_{12} (3 mL) in a quartz cuvette was added excess PPh_3 (13 mM). The solution was stirred and continuously irradiated ($\lambda_{\text{irr}} > 400$ nm) for 20 – 60 min at 23 $^\circ\text{C}$. The reaction mixture was then concentrated to dryness under vacuum and redissolved in CDCl_3 . The yield of O=PPh_3 was analyzed by ^{31}P NMR spectroscopy by determining the

ratio of PPh_3 to OPPh_3 from spectral integrations. For solutions involving excess O_2 , a stream of dry dioxygen gas was purged through the solvent during irradiation.

Aerobic Oxidation of (1) in the Presence of the Singlet Oxygen Trap 9,10-Dimethylanthracene (DMA). To an aerobic solution of DMA (0.24 mM) in cyclohexane (3 mL) was added complex **1** (18 μM). The solution was continuously irradiated ($\lambda_{\text{irr}} > 400 \text{ nm}$) in a quartz cuvette at 23 °C. The reaction mixture was monitored by UV-vis spectroscopy in 10 min intervals, and complete conversion of **1** ($\lambda_{\text{max}} = 432, 687 \text{ nm}$) to **2** ($\lambda_{\text{max}} = 419, 639 \text{ nm}$) was observed after 20 min. The peaks corresponding to DMA (300 – 400 nm) were observed both before and after irradiation (Figure 3), indicating no significant loss of DMA.

Irradiation of [(TBP₈Cz)P(OH)]OH in the Presence of DMA. To an aerobic solution of 9,10-dimethylanthracene (DMA, 0.24 mM) in cyclohexane (3 mL) was added phosphorus corrolazine [(TBP₈Cz)P(OH)]OH, 6.2 μM). The solution was continuously irradiated ($\lambda_{\text{irr}} > 400 \text{ nm}$) in a quartz cuvette. The reaction mixture was monitored by UV-vis spectroscopy after 10 min. and showed complete loss of peaks for DMA (300 – 400 nm), indicating the generation and trapping of singlet O_2 (Figure S2).

Aerobic Oxidation of (1) with AIBN. To an aerobic solution of **1** (8 μM) in cyclohexane (2.5 mL) was added AIBN (12 mM). The reaction was carried out in the dark at 50 °C (heated to initiate radical formation from AIBN). The UV-vis spectrum of the reaction mixture was obtained after 20 min and showed complete conversion of **1** ($\lambda_{\text{max}} = 432, 687 \text{ nm}$) to **2** ($\lambda_{\text{max}} = 419, 639 \text{ nm}$) (Figure S4).

References.

- (1) Lansky, D. E.; Mandimutsira, B.; Ramdhanie, B.; Clausen, M.; Penner-Hahn, J.; Zvyagin, S. A.; Telser, J.; Krzystek, J.; Zhan, R.; Ou, Z.; Kadish, K. M.; Zakharov, L.; Rheingold, A. L.; Goldberg, D. P. *Inorg. Chem.* **2005**, *44*, 4485-4498.
- (2) Ramdhanie, B.; Stern, C. L.; Goldberg, D. P. *J. Am. Chem. Soc.* **2001**, *123*, 9447-9448.
- (3) Armarego, W. L. F., Perrin D. D. *Purification of Laboratory Chemicals*; 4th ed.; Butterworth-Heinemann: Oxford, UK, 1997.
- (4) Prokop, K. A.; de Visser, S. P.; Goldberg, D. P. *Angew. Chem. Int. Ed.* **2010**, *49*, 5091-5095.
- (5) Prokop, K. A.; Neu, H. M.; de Visser, S. P.; Goldberg, D. P. *J. Am. Chem. Soc.* **2011**, *133*, 15874-15877.
- (6) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W. Z.; Chait, B. T. *J Porphyrins Phthalocyanines* **1999**, *3*, 283-291.

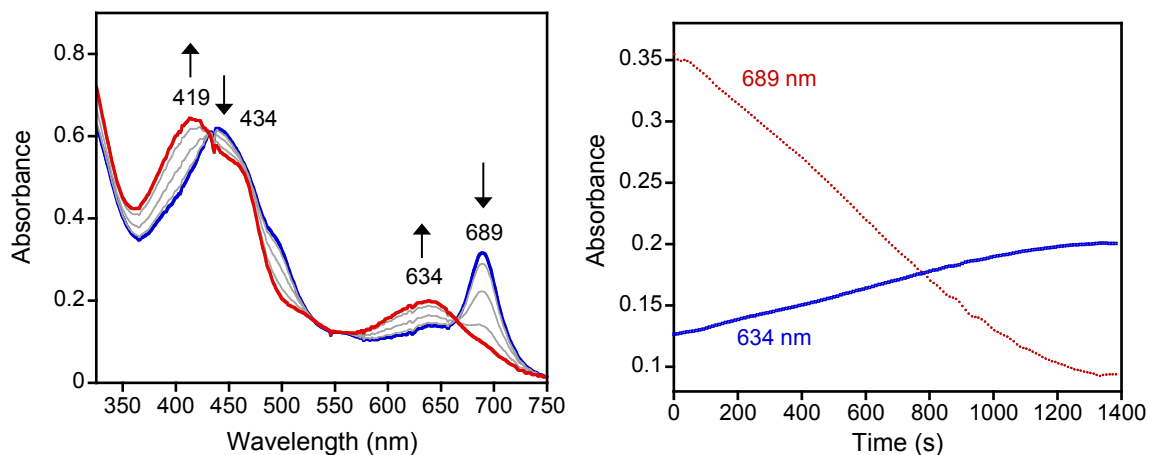


Figure S1. Time resolved UV-vis spectra of **1** (11 μM) in toluene (2.5 mL) continuously irradiated ($\lambda_{\text{irr}} > 400 \text{ nm}$) at 23 $^{\circ}\text{C}$ (left) with corresponding time profile (right) showing the loss of **1** (689 nm) and the formation of **2** (634 nm).

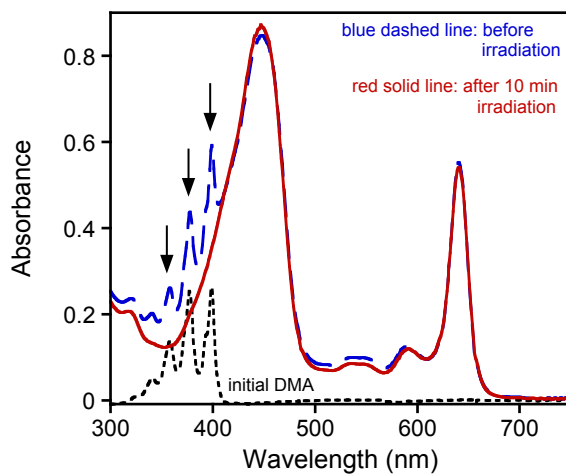


Figure S2. UV-vis spectra of $[(\text{TBP}_8\text{Cz})\text{P}(\text{OH})]\text{OH}$ (6.2 μM) and 9,10-dimethylantracene (0.24 mM) in cyclohexane (3 mL) (blue dashed line) and following irradiation ($\lambda_{\text{irr}} > 400 \text{ nm}$) for 10 min (red solid line).

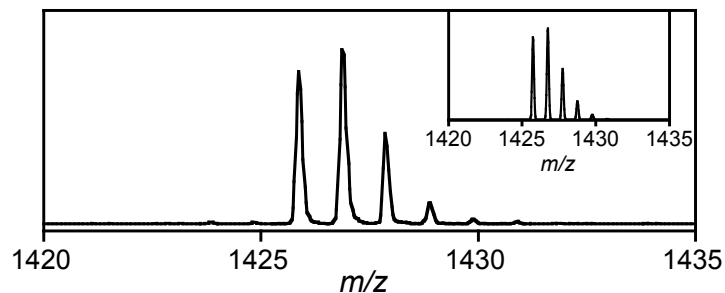


Figure S3. LDI-MS of **2** derived from the aerobic oxidation of **1** in a solution of toluene and H_2^{18}O . Calculated isotope pattern for **2** (insert) matches the experimental pattern, which shows no ^{18}O incorporation.

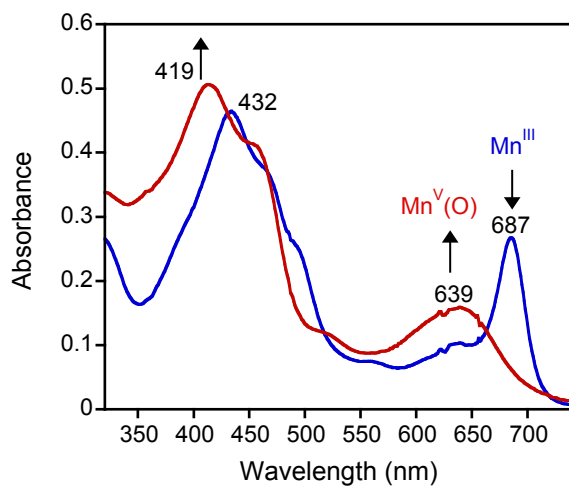


Figure S4. Initial (blue) and final (red) UV-vis spectra for the aerobic reaction between **1** ($8\ \mu\text{M}$) and AIBN ($12\ \text{mM}$) in cyclohexane ($2.5\ \text{mL}$).

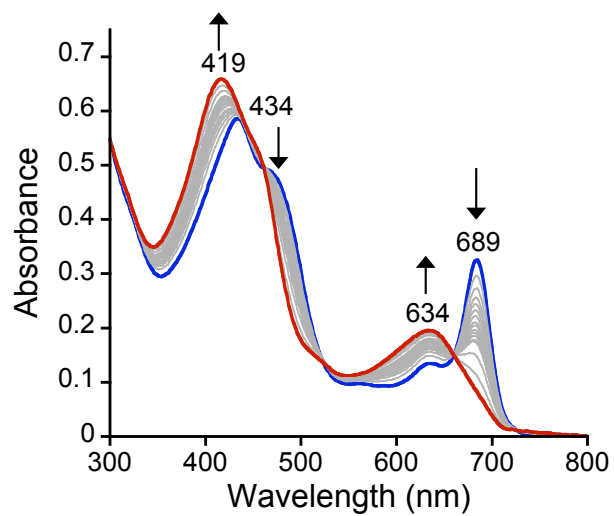


Figure S5. Time-resolved UV-vis spectra for the reaction between $(\text{TBP}_8\text{Cz})\text{Mn}^{\text{III}}$ (10 μM) and $t\text{-BuOOH}$ (50 mM) in CH_2Cl_2 at 23 $^\circ\text{C}$.

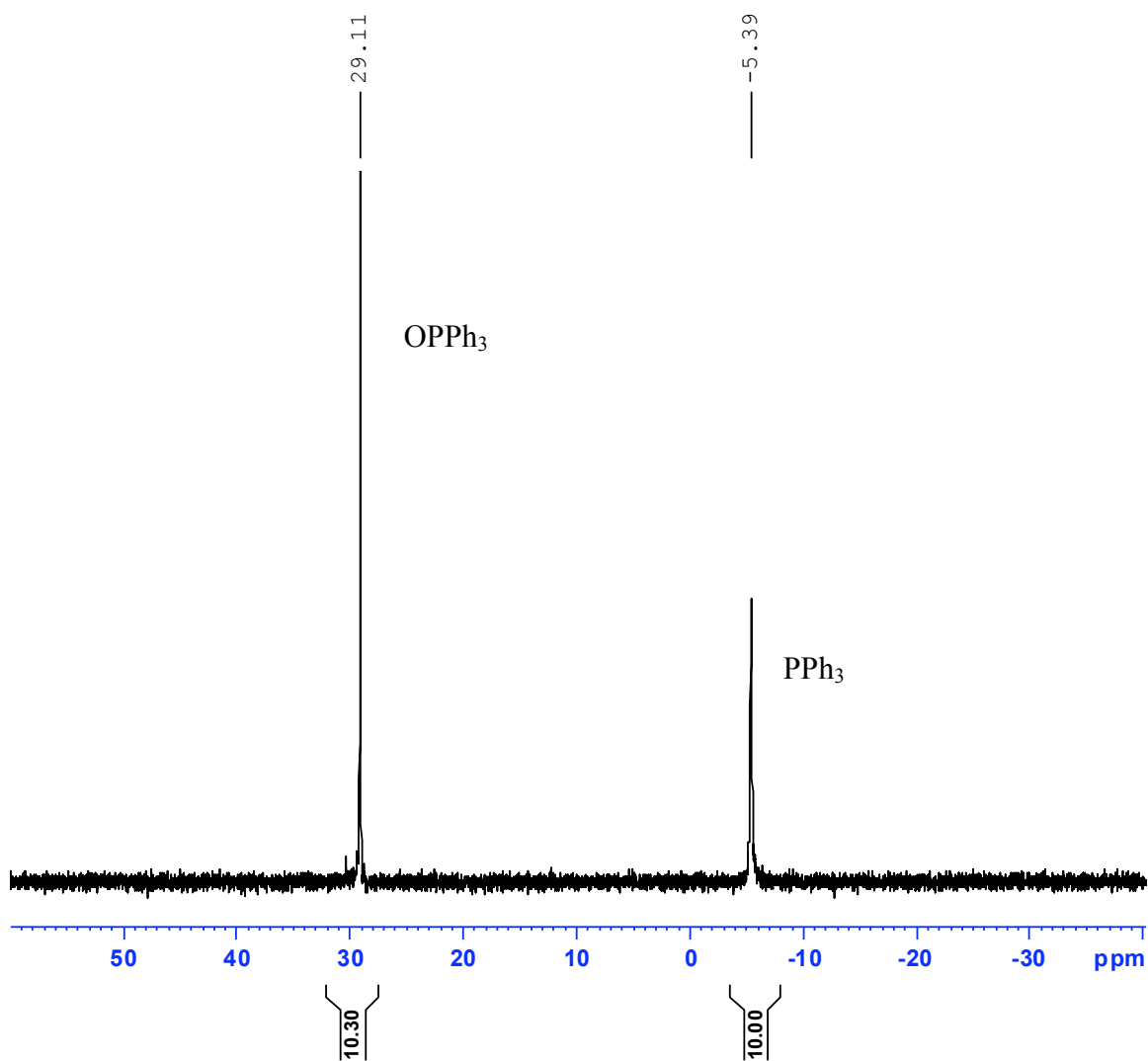


Figure S6. Representative ^{31}P NMR spectrum for the catalytic reaction mixture of **1** (10 μM) and PPh_3 (13 mM) following the addition of O_2 gas and continuous irradiation ($\lambda_{\text{irr}} > 400 \text{ nm}$) for 60 min in C_6H_{12} (3 mL). The reaction mixture was dried and redissolved in CDCl_3 prior to obtaining the spectrum.