Supporting Information

Spectroscopic Characterization and Reactivity Studies of a Mononuclear Nonheme Mn(III)-Hydroperoxo Complex

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**Materials and Instrumentation**

All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use. $^{31}$H$_2^{18}$O$_2$ (90% $^{18}$O-enriched, 2% H$_2^{18}$O$_2$ in water) was purchased from ICON Services Inc. (Summit, NJ, USA).

UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments or on a Hi-Tech Scientific (UK) SF-61 DX2 cryogenic stopped-flow spectrometer equipped with a Xe arc lamp and a KinetaScan diode array rapid scanning unit. CW-EPR spectra were taken at 5 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR spectra were as follows: Microwave frequency = 9.647 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = $1 \times 10^4$, time constant = 10.24 ms, conversion time = 81.96 ms. Resonance Raman spectra were obtained using a liquid nitrogen cooled CCD detector (CCD-1024×256-OPEN-1LS, HORIBA Jobin Yvon) attached to a 1-m single polychromator (MC-100DG, Ritsu Oyo Kogaku) with a 1200 grooves/mm holographic grating. An excitation wavelength of 406.7 nm was provided by a Kr$^+$ laser (Spectra Physics, BeamLok 2060-RM), with 20 mW power at the sample point. All measurements were carried out with a spinning cell (1000 rpm) at –40 °C. Raman shifts were calibrated with indene, and the accuracy of the peak positions of the rRaman bands was ±1 cm$^{-1}$.

$^1$H NMR spectra were measured with Bruker model digital AVANCE III 400 FT-NMR spectrometer.
Generation of \([\text{Mn}^{\text{III}}(\text{TMC})(\text{O}_2)]^+\) (1)

\([\text{Mn}^{\text{III}}(\text{TMC})(\text{O}_2)]^+\) (1) was prepared according to the literature methods.\(^{S2}\) 1 was generated by reacting \([\text{Mn}^{\text{II}}(\text{TMC})(\text{CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)\) (0.10 mM) with \(\text{H}_2\text{O}_2\) (5 equiv; 51 \(\mu\)L, 30% in water, 0.50 mmol) in the presence of 2 equiv of triethylamine (TEA; 28 \(\mu\)L, 0.20 mmol) in CH\(_3\)CN (2 mL) at –40 °C. Then, Et\(_2\)O (40 mL) was added to the solution of \([\text{Mn}^{\text{III}}(\text{TMC})(\text{O}_2)](\text{CF}_3\text{SO}_3)\) to yield a green precipitate at –40 °C. This green precipitate was washed with Et\(_2\)O and dried under Ar atmosphere. Similarly, \([\text{Mn}^{\text{III}}(\text{TMC})(\text{18O}_{18}\text{O})]^+\) (\(1\)-\(18\)O) was prepared by adding 5 equiv of \(\text{H}_2\text{O}_{18}\text{O}\) (90% \(18\)O-enriched, 2% \(\text{H}_2\text{O}_{18}\text{O}\) in water) to a solution containing \([\text{Mn}^{\text{II}}(\text{TMC})]^2^+\) and 2 equiv of TEA in CH\(_3\)CN at –40 °C.

Generation and Characterization of \([\text{Mn}^{\text{III}}(\text{TMC})(\text{OOH})]^2^+\) (2)

HClO\(_4\) (0.39 mM, 3 equiv.) was added to CH\(_3\)CN solution containing \([\text{Mn}^{\text{III}}(\text{TMC})(\text{O}_2)]^+\) (0.13 mM) at –40 °C, producing a yellow solution (\(\lambda_{\text{max}} = 324\) and 384 nm with \(\varepsilon = 6400, 8000\) M\(^{-1}\) cm\(^{-1}\), respectively). The \(18\)O-labeled Mn\(^{\text{III}}\)-hydroperoxo complex, \([\text{Mn}^{\text{III}}(\text{TMC})(\text{18O}_{18}\text{OH})]^2^+\) (\(2\)-\(18\)O), was prepared by reacting \([\text{Mn}^{\text{III}}(\text{TMC})(\text{18O}_{18}\text{O})]^+\) (\(1\)-\(18\)O) (0.13 mM) with 3 equiv of HClO\(_4\) in CH\(_3\)CN at –40 °C under Ar atmosphere. Upon excitation at 407 nm, the isotopic shifts of resonance-enhanced vibrations were observed (792 cm\(^{-1}\) for \(2\)-\(16\)O and 748 cm\(^{-1}\) for \(2\)-\(18\)O).

Reactivity Studies and Product Analysis

All reactions were run in a 1-cm UV cuvette and followed by monitoring UV-vis spectral changes of reaction solutions, and rate constants were determined under pseudo-first-order conditions by fitting the changes in absorbance at 384 nm for 2. The intermediate 2 (0.13mM) was used in oxygen atom transfer reactions of \textit{para}-substituted thioanisoles with different \(\rho\) value, such as –0.78 for 4-methoxythioanisole, –0.31 for 4-Methylthioanisole, –0.07 for 4-
fluorothioanisole, 0 for thioanisole and 0.15 for 4-bromothioanisole, in CH$_3$CN at $-40^\circ$C (Table S1; Figure S2). Reactions were run at least in triplicate, and the data reported represent the average of these reactions.

The Mn product in the reaction solution was analyzed with EPR and ESI-MS. X-band EPR and ESI-MS spectra of the Mn product obtained in the reaction of 2 and 4-methoxythioanisole indicate that Mn$^{II}$ species was the major product (Figures S3 and S4). Organic products formed in the oxidation of thioanisoles by 2 in CH$_3$CN at $-40^\circ$C were analyzed by HPLC. Phenyl methyl sulfoxide (>60%) was formed as a sole product in the oxidation of thioanisoles by 2.

**Spin-State Measurement by $^1$H NMR Spectroscopy**

The spin state of 2 was determined using the modified $^1$H NMR method of Evans at room temperature.$^{S3}$ A WILMAD® coaxial insert (sealed capillary) tube containing only the blank acetonitrile-$d_3$ solvent (with 1.0% TMS) was inserted into the normal NMR tubes containing the complex 2 (60 $\mu$L, 4.0 mM) dissolved in acetonitrile-$d_3$ (with 0.1% TMS). The chemical shift of the TMS peak in the presence of the paramagnetic metal complexes was compared to that of the TMS peak in the inner NMR tube. The magnetic moment was calculated using the following equation,

$$\mu = 0.0618(\Delta\nu T / 2fM)^{1/2}$$

where $f$ is the oscillator frequency (MHz) of the superconducting spectrometer, $T$ is the absolute temperature, $M$ is the molar concentration of the metal ion, and $\nu$ is the difference in frequency (Hz) between the two reference signals.$^{S3c}$ The $^1$H NMR Evans method allowed us to determine magnetic moment of 5.1 $\mu_B$ for 2 in CH$_3$CN at $-40^\circ$C, indicating that the 2 possesses an $S = 2$ spin state in CH$_3$CN solution.

**X-ray Absorption Spectroscopy**
The Mn K-edge X-ray absorption spectra of [Mn\textsuperscript{III}(TMC)(O\textsubscript{2})]\textsuperscript{+} (1), [Mn\textsuperscript{III}(TMC)(OOH)]\textsuperscript{2+} (2) and the starting [Mn\textsuperscript{II}(TMC)]\textsuperscript{2+} complex were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) on the unfocussed 20-pole 2 T wiggler side-station beam line 7-3 under standard ring conditions of 3 GeV and ~500 mA. A Si(220) double crystal monochromator was used for energy selection. A Rh-coated harmonic rejection mirror was used on beam line 7-3 to reject components of higher harmonics. The monochromator was further detuned by 30% to eliminate higher harmonic and to reduce beam damage on samples. All complexes were measured as solutions, which were transferred into 2 mm delrin XAS cells with 70 µm Kapton tape windows under synthesis conditions and were immediately frozen after preparation and stored under liquid N\textsubscript{2}. During data collection, samples were maintained at a constant temperature of ~10–15 K using an Oxford Instruments CF 1208 liquid helium cryostat. Data were measured to $k = 12$ Å\textsuperscript{-1} (fluorescence mode) using a Canberra Ge 30-element array detector. Internal energy calibration was accomplished by simultaneous measurement of the absorption of a Mn-foil placed between two ionization chambers situated after the sample. The first inflection point of the foil spectrum was fixed at 6539.0 eV. The samples were monitored for photoreduction; however, no visual change in the rising edge energy position was observed over successive scans, indicating that all the samples were resistant to photoreduction. Data presented here are 12-scan average for [Mn\textsuperscript{II}(TMC)]\textsuperscript{2+}, 21-scan average spectra for 1 and 28-scan average for 2. Data were processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as background. A four-region spline of orders 2, 3, 3 and 3 was used to model the smoothly decaying post-edge region. The data were normalized by subtracting the cubic spline and assigning the edge jump to 1.0 at 6555 eV using the Pyspline\textsuperscript{S4} program. Data were then renormalized in Kaleidagraph for comparison and quantification purposes.
Theoretical EXAFS signals $\chi(k)$ were calculated by using FEFF (Macintosh version 8.4). Starting structural models for 1 were obtained from the crystal structure and models for [Mn$^{II}$(TMC)]$^{2+}$, 2 was generated by modifying the crystal structure of 1 in Avogadro. The input structure was improved based on preliminary EXAFS fit parameters to generate more accurate theoretical EXAFS signals. Data fitting was performed in EXAFSPAK. The structural parameters varied during the fitting process were the bond distance ($R$) and the bond variance $\sigma^2$, which is related to the Debye-Waller factor resulting from thermal motion, and static disorder of the absorbing and scattering atoms. The non-structural parameter $E_0$ (the energy at which $k = 0$) was also allowed to vary but was restricted to a common value for every component in a given fit. Coordination numbers were systematically varied in the course of the fit but were fixed within a given fit.

Density Functional Theory

Calculations were done with Density Functional Theory (DFT) using the Gaussian 09 package and the B3LYP functional. Optimizations and single-point frequency calculations were done with the LACVP basis set (except for S, which required 6-311+G*), while a single-point energy evaluation was done using the LACV3P*+ basis set. All calculations (including the optimizations) were done in solvent (acetonitrile) using the CPCM scheme. Dispersion was calculated with DFT-D3 program. The quoted energy value in the text is B3LYP/LACV3P*/B3LYP/LACVP value, due to issues with the reliability of free energy values. In the calculation models described below, “syn” refers to the four TMC-methyl groups being on the same side of the TMC ligand plane as OOH, while “anti” refers to the opposite configuration.

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Table S1. Data for the Reactions of 2 and para-X-Ph-SCH₃ in CH₃CN at –40 °C.

| X      | σᵣ⁺ᵇ | Eₒₓ (V vs SCE)ᵇ | k₂ (M⁻¹ s⁻¹) |
|--------|-------|-----------------|--------------|
| OCH₃   | -0.78 | 1.13            | 2.9 × 10³    |
| CH₃    | -0.31 | 1.24            | 2.3 × 10¹    |
| F      | -0.07 | N.A.ᶜ          | 7.7 × 10⁻¹   |
| H      | 0     | 1.34            | 3.6 × 10⁻¹   |
| Br     | 0.15  | 1.41            | 7.9 × 10⁻²   |

ᵃ Taken from the reference: Hammett, L. P. *J. Am. Chem. Soc.* 1937, 59, 96.ᵇ Taken from the reference: Taki, M.; Itoh, S.; Fukuzumi, S. *J. Am. Chem. Soc.* 2002, 124, 998.ᶜ Not available.

Table S2. EXAFS Least Squares Fitting Results.

| Complex | Coordination/Path | R(Å)ᵇ | σ²(Å²)b | E₀ (eV) | Fᶜ |
|---------|------------------|-------|---------|---------|----|
| 1       | 2 Mn-O           | 1.88  | 236     | -6.92   | 0.21 |
|         | 4 Mn-N           | 2.24  | 695     |         |     |
|         | 6 Mn-C           | 2.99  | 827     | -3.39   | 0.21 |
|         | 18 Mn-C-N        | 3.25  | 126     |         |     |
|         | 4 Mn-C           | 3.58  | 611     |         |     |
| 2       | 1 Mn-O           | 1.93  | 765     |         |     |
|         | 4 Mn-N           | 2.17  | 458     |         |     |
|         | 6 Mn-C           | 2.94  | 1398    | -3.39   | 0.21 |
|         | 18 Mn-C-N        | 3.22  | 250     |         |     |
|         | 4 Mn-C           | 3.53  | 1162    |         |     |

ᵇ The estimated standard deviations for the distances are in the order of ± 0.02 Å.ᵇ The σ² values are multiplied by 10⁵.ᶜ Error is given by Σ[(χₜₒₜ – χₑₒₑ)²kᵦ]/[Σ(χₑₒₑ)²kᵦ]. The S₀² factor was set at 1. The same number of independent parameters was used for 1 and 2.
Table S3. Energies of \textit{syn}-[\text{Mn}^{III}(TMC)(O_2)]^+ (1) in kcal/mol.

|       | \(\Delta\text{lacvp}\) | \(\Delta\text{lacv3p}^+\) | \(\Delta E^a\) | \(\Delta Z_0\) | \(\Delta E_{\text{thermal}}^b\) | \(-T\Delta S^b\) | \(\Delta\text{Disp}\) | \(\Delta G^c\) |
|-------|----------------|----------------|----------------|-------------|----------------|----------------|----------------|--------------|
| \(S = 1\) | 20.46 | +1.83 | **22.29** | +1.91 | -0.70 | +2.23 | -2.73 | **23.00** |
| \(S = 2\) | 0.00 | +0.00 | **0.00** | +0.00 | +0.00 | +0.00 | +0.00 | **0.00** |

\(^a\) Sum of the two previous columns.  
\(^b\) \(T = 298.15\) K.  
\(^c\) \(\Delta G = \Delta E + \Delta Z_0 + \Delta E_{\text{thermal}} - T\Delta S + \Delta\text{Disp}\).  

This value is however deemed less reliable due to double counting of effects.

Table S4. Mulliken spin density distribution of \textit{syn}-[\text{Mn}^{III}(TMC)(O_2)]^+ (1).

|       | Mn    | O\(_2\) | 4 x N | Rest |
|-------|-------|---------|-------|------|
| \(S = 1\) | 2.27  | -0.08   | -0.22 | 0.03 |
| \(S = 2\) | 4.47  | -0.42   | -0.14 | 0.09 |

Table S5. Geometries of \textit{syn}-[\text{Mn}^{III}(TMC)(O_2)]^+ (1) in Å and degrees.

|       | Mn-O | O\(_{\text{proximal}}\)-O\(_{\text{distal}}\) | Mn-N\(_1\) | Mn-N\(_2\) | Mn-N\(_3\) | Mn-N\(_4\) | \(\angle\)Mn-O-O |
|-------|------|----------------|--------|--------|--------|--------|-------------|
| \(S = 1\) | 1.92/1.91 | 1.51         | 2.19   | 2.16   | 2.16   | 2.20   | 66.58       |
| \(S = 2\) | 1.97/1.97 | 1.47         | 2.24   | 2.34   | 2.34   | 2.26   | 68.01       |
Table S6. Energies of [Mn$^{III}$(TMC)(OOH)]$^{2+}$ (2) in kcal/mol.

| S = 1 | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
|       | Syn   | Anti  | Syn   | Anti  | Syn   | Anti  |
| Δlacvp| 17.21 | 17.72 | 0.00  | 2.50  | 17.21 | 17.72 |
| Δlacv3p$^+$| +1.09 | +4.60 | +0.00 | +2.84 | +1.09 | +4.60 |
| ΔE$^a$| 18.30 | 22.31 | 5.34  | 4.54  | 16.37 | 20.06 |
| ΔZ$_0$| +0.07 | +0.37 | +0.50 | -0.50 | +0.07 | +4.60 |
| ΔE$_{thermal}^b$| +0.14 | +0.05 | +0.36 | +0.36 | +0.14 | -2.55 |
| -TΔS$^b$| -0.52 | -0.12 | -1.24 | -1.24 | -0.52 | -2.55 |
| ΔDisp| -1.62 | -2.55 | -1.83 | -1.83 | -1.62 | -2.55 |
| ΔG$^c$| 16.37 | 20.06 | 2.13  | 2.13  | 16.37 | 20.06 |

$^a$ Sum of the two previous columns. $^b$ T = 298.15 K. $^c$ ΔG = ΔE + ΔZ$_0$ + ΔE$_{thermal}$ - TΔS + ΔDisp.

This value is however deemed less reliable due to double counting of effects.

Table S7. Mulliken spin density distribution of [Mn$^{III}$(TMC)(OOH)]$^{2+}$ (2).

|       | Mn | O$_{proximal}$ | HO$_{distal}$ | 4 x N | Rest |
|-------|----|----------------|---------------|-------|------|
| S = 1 | Syn| 2.10           | -0.02         | 0.03  | -0.17| 0.05 |
|      | Anti| 2.09          | 0.03          | -0.01 | -0.20| 0.08 |
| S = 2 | Syn| 4.06           | 0.08          | 0.03  | -0.29| 0.12 |
|      | Anti| 3.62           | 0.14          | 0.04  | -0.07| 0.27 |

Table S8. Geometries of [Mn$^{III}$(TMC)(OOH)]$^{2+}$ (2) in Å and degrees.

|       | Mn-O$_{proximal}$ | O$_{proximal}$-O$_{distal}$ | H-O$_{distal}$ | Mn-N$_1$ | Mn-N$_2$ | Mn-N$_3$ | Mn-N$_4$ | ∠Mn-O-O |
|-------|-------------------|-----------------------------|---------------|----------|----------|----------|----------|----------|
| S = 1 | Syn               | 1.82                        | 1.50          | 0.99     | 2.12     | 2.15     | 2.11     | 2.14     | 110.09   |
|       | Anti              | 1.82                        | 1.53          | 0.99     | 2.12     | 2.09     | 2.10     | 2.10     | 121.17   |
| S = 2 | Syn               | 1.93                        | 1.52          | 0.98     | 2.13     | 2.13     | 2.26     | 2.20     | 110.22   |
|       | Anti              | 1.99                        | 1.51          | 0.98     | 2.16     | 2.15     | 2.10     | 2.10     | 123.04   |

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### Table S9. Energies of thioanisole sulfoxidation by [Mn^{III}(TMC)(OOH)]^{2+} (2) in kcal/mol.

|      | $\Delta$acvp | $\Delta$acv3p$^+$ | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}^b$ | $-T\Delta S^b$ | $\Delta$Disp | $\Delta G^c$ |
|------|--------------|-------------------|--------------|--------------|------------------------|----------------|------------|------------|
| **$S = 1$** |  |  |  |  |  |  |  |  |
| Syn Reactant | 16.23  | +1.78  | **18.01**  | +0.22  | -0.05  | +0.45 | -1.52 | **17.10** |
| TS | 26.70 | +5.17  | **31.86**  | -0.44  | -0.39  | +2.20 | -2.18 | **31.05** |
| Product | -26.61 | -6.01  | **-32.62** | +1.10  | -1.31  | +4.91 | -2.68 | **-30.60** |
| Anti Reactant | 17.37  | +4.37  | **21.74**  | +0.88  | -0.28  | +0.48 | -1.58 | **21.25** |
| TS | 28.60 | +6.57  | **35.18**  | -0.22  | -0.50  | +2.42 | -3.55 | **33.33** |
| Product | -24.74 | -4.46  | **-29.20** | +1.22  | -0.86  | +3.37 | -6.05 | **-31.52** |
| **$S = 2$** |  |  |  |  |  |  |  |  |
| Syn Reactant | 0.00  | +0.00  | 0.00  | +0.00  | +0.00  | +0.00 | +0.00 | 0.00 |
| TS | 14.45 | +2.10  | **16.55**  | -1.50 | -0.12 | +1.15 | -0.20 | **15.88** |
| Product | -41.64 | -7.31  | **-48.95** | +0.40 | -0.42 | +2.19 | -2.74 | **-49.52** |
| Anti Reactant | 2.45  | +2.84  | **5.28**  | +0.28 | -0.02 | +0.13 | -2.73 | **2.94** |
| TS | 20.12 | +4.86  | **24.98**  | -1.64 | -0.13 | +1.33 | -2.00 | **22.54** |
| Product | -37.18 | -5.85  | **-43.03** | +0.13 | -0.29 | +1.23 | -4.56 | **-46.51** |

$^a$ Sum of the two previous columns. $^b$ T = 298.15 K. $^c$ $\Delta G = \Delta E + \Delta Z_0 + \Delta E_{thermal} - T\Delta S + \Delta$Disp.

This value is however deemed less reliable due to double counting of effects.
Table S10. Mulliken spin density distributions of thioanisole sulfoxidation by 2 in kcal/mol.

|      | Mn  | O_{proximal} | O_{distal} | 4 x N | S         | Substrate excl. S | Rest  |
|------|-----|--------------|-----------|-------|-----------|-------------------|-------|
| $S = 1$ Syn Reactant | 2.06 | -0.02 | 0.03 | -0.14 | 0.01 | 0.00 | 0.06 |
|      | TS  | 1.84 | -0.13 | 0.15 | -0.12 | 0.20 | 0.03 | 0.04 |
|      | Product | 1.96 | 0.14 | 0.01 | -0.14 | 0.00 | 0.00 | 0.04 |
|      | Anti Reactant | 2.24 | 0.02 | -0.01 | -0.30 | 0.00 | 0.00 | 0.04 |
|      | TS  | 1.73 | -0.13 | 0.15 | -0.08 | 0.20 | 0.03 | 0.09 |
|      | Product | 2.03 | 0.14 | 0.00 | -0.22 | 0.00 | 0.00 | 0.04 |
| $S = 2$ Syn Reactant | 4.05 | 0.05 | -0.01 | -0.22 | 0.00 | 0.00 | 0.12 |
|      | TS  | 3.88 | -0.16 | 0.07 | -0.12 | 0.19 | 0.04 | 0.11 |
|      | Product | 4.09 | 0.18 | 0.00 | -0.33 | 0.00 | 0.00 | 0.06 |
|      | Anti Reactant | 4.19 | 0.15 | 0.04 | -0.45 | 0.00 | 0.00 | 0.07 |
|      | TS  | 3.60 | -0.09 | 0.10 | -0.06 | 0.22 | 0.04 | 0.20 |
|      | Product | 4.10 | 0.20 | 0.01 | -0.37 | 0.00 | 0.00 | 0.07 |
Table S11. Geometries of thioanisole sulfoxidation by 2 in Å and degrees.

|   |   | Mn-Oproximal | Oproximal-Odistal | Odistal-S | H-Odistal | H-Oproximal | ∠Mn-O-O |
|---|---|--------------|-----------------|----------|-----------|-------------|--------|
| $S = 1$ | Syn Reactant | 1.82          | 1.50            | 3.18     | 1.01      | 1.99        | 107.71 |
|       | TS            | 1.72          | 1.80            | 2.39     | 0.99      | 2.01        | 125.16 |
|       | Product       | 1.75          | 2.63            | 1.57     | 1.62      | 1.01        | 124.97 |
| Anti Reactant | 1.82          | 1.52            | 3.23    | 1.00     | 1.97      | 121.25      |
|       | TS            | 1.73          | 1.80            | 2.39     | 0.99      | 2.02        | 127.44 |
|       | Product       | 1.77          | 2.62            | 1.56     | 1.61      | 1.01        | 130.06 |
| $S = 2$ | Syn Reactant | 1.91          | 1.52            | 3.20     | 1.01      | 2.01        | 97.13  |
|       | TS            | 1.76          | 1.89            | 2.23     | 0.99      | 2.02        | 105.98 |
|       | Product       | 1.83          | 2.67            | 1.56     | 1.68      | 1.00        | 121.65 |
| Anti Reactant | 1.98          | 1.51            | 3.26    | 1.00     | 1.96      | 121.37      |
|       | TS            | 1.79          | 1.92            | 2.21     | 0.99      | 2.01        | 128.43 |
|       | Product       | 1.87          | 2.70            | 1.56     | 1.71      | 1.00        | 128.87 |
Figure S1. UV-vis spectral changes showing the interconversion between $[{\text{Mn}^{\text{III}}(\text{TMC})-(\text{OOH})}]^{2-}$ (2) (black line) (0.13 mM in CH$_3$CN) and $[{\text{Mn}^{\text{III}}(\text{TMC})(\text{O}_2)}]$ (1) (red line) (a) upon addition of 5 equiv of TEA to the solution of 2 in CH$_3$CN at −40 °C and then (b) addition of 3 equiv of HClO$_4$ to the resulting solution of (a) in CH$_3$CN at −40°C.
Figure S2. Plots of $k_{obs}$ against the concentration of substrate to determine second-order rate constants in the reactions of $[\text{Mn}^{III}(\text{TMC})(\text{OOH})]^{2+}$ (2) with para-substituted thioanisoles, such as (a) 4-methoxythioanisole, (b) 4-methylthioanisole, (c) 4-fluorothioanisole, (d) thioanisole and (e) 4-bromothioanisole in CH$_3$CN at $-40^\circ$C (see Table S1).
**Figure S3.** X-band EPR spectrum recorded at 5 K, after the completion of the reaction of [Mn$^{III}$(TMC)(OOH)]$^{2+}$ (2) with 50 equiv of 4-methoxythioanisole in CH$_3$CN at –40 °C.
**Figure S4.** ESI-MS spectrum recorded after the completion of the reaction of \([\text{Mn}^{III}(\text{TMC})-(\text{OOH})]^{2+}\) (2) with 50 equiv of 4-methoxythioanisole in CH\(_3\)CN at –40 °C. Peaks were assigned as follows: \(m/z = 175.93\) (major, relative intensity 100%) for \([\text{Mn}^{II}(\text{TMC})(\text{CH}_3\text{CN})]^{2+}\), \(m/z = 410.3\) for \([\text{Mn}^{II}(\text{TMC})(\text{ClO}_4)]^{+}\) and \(m/z = 460.2\) (relative intensity *ca.* 10%) for \([\text{Mn}^{II}(\text{TMC})(\text{CF}_3\text{SO}_3)]^{+}\).
Figure S5. The sulfoxidation reaction mechanism of thioanisole by 2 calculated with DFT at B3LYP/LACV3P*/B3LYP/LACVP level. The lowest transition state is reached when 2 is in its high-spin syn state over a barrier of 16.5 kcal/mol, which is also the ground state at the reactant complex stage.
Coordinates

Coordinates are given in x-y-z file format with charge/multiplicity given in parenthesis on the comment line.

S21
C -6.88622 -1.59744 -2.43336
C -7.34032 -0.72062 -3.42688
C -6.67277 0.48946 -3.65235
C -5.54803 0.82982 -2.88680
C -5.08854 -0.03356 -1.88647
H -7.39184 -2.54277 -2.26278
H -8.20435 -0.98749 -4.02543
H -7.02319 1.16365 -4.42648
H -5.02949 1.76504 -3.06893
H -4.20960 0.21968 -1.30223