

Supporting Information

A Highly Efficient Non-Heme Manganese Complex in Oxygenation Reactions

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Experimental Conditions.

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 [1]. H₂¹⁸O (95% ¹⁸O-enriched) and ¹⁸O₂ (95% ¹⁸O-enriched) were purchased from ICON Services Inc. (Summit, NJ, USA). Iodosylbenzene (PhIO) was prepared by a literature method [2]. Peracetic acid (CH₃CO₃H, 32 wt. % solution containing <6% H₂O₂) was obtained from Aldrich Chemical Co. Ligands such as BQEN, BPMEN, and BPMCN were synthesized by published procedures [3-5]. Manganese(II) complexes, such as Mn(BQEN)(CF₃SO₃)₂, Mn(BPMEN)(CF₃SO₃)₂, and Mn(BPMCN)(CF₃SO₃)₂, were prepared in a glovebox by literature methods [6].

Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 μL/min using a syringe pump. The spray voltage was set at 4.7 kV and the capillary temperature at 220 °C. Product analysis for the oxidation products were performed with an Agilent Technologies 6890N gas chromatograph (GC) and Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS). Product analyses for the epoxidation of *cis*- and *trans*-stilbenes were performed on DIONEX Summit Pump Series P580 equipped with a variable wavelength UV-200 detector (HPLC). Products were separated on Waters Symmetry C18 reverse phase column (4.6 x 250 mm), and detection was made at 215 and/or 254 nm. Elemental Analysis was done on a Thermo Finnigan Italia SpA (Flash EA[®] 1112) CHN analyzer. 2,5-Bis(5' *tert*-butyl-2-benzoxazol-2-yl)thiophene (BBOT) was used as a reference standard. EPR spectra were obtained on a JEOL JES-FA200 spectrometer. ¹H NMR spectra were measured with Bruker DPX-250 spectrometer. Crystallographic analysis was conducted with an SMART APEX CCD equipped with a Mo X-ray tube at the Crystallographic Laboratory of Ewha Womans University.

Characterization of Mn(BQEN)(CF₃SO₃)₂ (1). The purity of **1** was checked with positive ESI MS prior to use; m/z of 546.2 for [Mn(II)(BQEN)(CF₃SO₃)⁺] (calculated m/z of 546.1) and m/z of 218.9 for [Mn(II)(BQEN)(CH₃CN)]²⁺ (calculated m/z of 219.1) (Figure S1). Elemental analysis (%) calcd for C₂₄H₂₂F₆MnN₄O₆S₂: C 41.45, H 3.19, N 8.06; found: C 41.34, H 3.25, N 8.12.

Colorless needle crystals suitable for crystallographic analysis were obtained from CH₃CN/diethyl ether. The diffraction data for **1** were collected at 170 K on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo K α ($\lambda = 0.71073$ Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V6.12 [7]. Hydrogen atoms were located in the calculated positions. Crystal data of [(BQEN)Mn^{II}(CF₃SO₃)₂] (**1**): *Orthorhombic*, $P2_12_12_1$ (No. 19), $Z = 4$, $a = 9.677(6)$ Å, $b = 13.617(10)$ Å, $c = 21.660(15)$ Å, $V = 2854(3)$ Å³, $\mu = 0.695$ mm⁻¹, $d_{\text{calc}} = 1.619$ g/cm³, $R1 = 0.049$, $wR_2 = 0.076$ for 5588 unique reflections, 390 variables. The absolute structure parameter is 0.20(3). The crystallographic data for **1** are listed in Table S1, and Table S2 lists the selected bond distances and angles.

The spin state of **1** was determined using the modified ¹H NMR method of Evans at room temperature [8]. A WILMAD[®] coaxial insert (sealed capillary) tubes containing **1** (60 μ L, 10 mM) in acetonitrile-*d*₃ (with 1.0% TMS) was inserted into a normal NMR tube containing blank acetonitrile-*d*₃ solvent (with 0.1% TMS). The chemical shift of the TMS peak in the presence of **1** was compared to that of the TMS peak in the outer NMR tube. The effective magnetic moment was calculated using the following equation, where f is

$$\mu = 0.0618(\Delta f \cdot T / 2f \cdot M)^{1/2}$$

the oscillator frequency (MHz) of the superconducting spectrometer, T is the absolute temperature, M is the molar concentration of the metal ion, and Δf is the difference in frequency (Hz) between the two reference signals [8].

Catalytic olefin epoxidation by PhIO. All Reactions were run at least in triplicate, and the data reported represent the average of these reactions. In general, PhIO (100 equiv to manganese catalyst) was added to a reaction solution containing Mn(II) complex (1 mM),

alkene (0.5 M), and decane (0.2 M) as an internal standard in CH₃CN (2 mL) at 25 °C. The reaction solution was stirred for 30 min, followed by filtering through a 0.45- μ M filter. The resulting solution was directly analyzed by GC, HPLC, or GC/MS. Products yields were determined by comparison of peak area with those of known authentic samples.

Catalytic oxygenation with peracetic acid. In a typical reaction, 100 equiv of peracetic acid (0.1 M, diluted in 100 μ L of CH₃CN) was added to a reaction solution containing a manganese complex (1 mM), substrate (0.5 M) and decane (0.2 M) as an internal standard in CH₃CN (2 mL) through syringe pump for 20 min at 25 °C. The reaction mixture was stirred for 10 min, and then directly injected into GC, HPLC or GC/MS for analysis. Product yields were determined by comparison against standard curves prepared with known authentic samples.

Competitive oxidation reactions. Peracetic acid (50 equiv per manganese; 50 mM, diluted in 100 μ L of MeCN) was added to a reaction solution containing a manganese catalyst (1 mM), substrates (0.25 M each) and decane (0.2 M) as an internal standard in CH₃CN (2 mL) through syringe pump for 20 min at 25 °C. The reaction mixture was stirred for 10 min prior to product analysis. In the reaction of PhIO, solid PhIO (50 equiv per manganese) was added to a reaction solution containing a manganese catalyst (1 mM) and substrates (0.25 M each) in CH₃CN (2 mL) at 25 °C. The reaction mixture was stirred for 30 min and then filtered through a 0.45- μ M filter. Products were analyzed by GC, HPLC or GC/MS, and product yields were calculated by comparison against standard curves prepared with known authentic samples.

Determination of KIE values. In general, 25 equiv of peracetic acid (25 mM, diluted in 100 μ L of MeCN) was added to a reaction solution containing Mn(II) complex (1 mM), substrates (0.25 M each), decane (0.2 M) as an internal standard in CH₃CN (2 mL) through syringe pump for 20 min at 25 °C. The reaction solution was analyzed by GC and GC/MS.

References

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Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C ₂₄ H ₂₂ F ₆ MnN ₄ O ₆ S ₂	
Formula weight	695.52	
Temperature	170(2) K	
Wavelength	0.71073	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 9.677(6) Å	α = 90.00°
	b = 13.617(10) Å	β = 90.00°
	c = 21.660(15) Å	γ = 90.00°
Volume	2854(3) Å ³	
Z	4	
Density (calculated)	1.619 Mg/m ³	
Absorption coefficient	0.695 mm ⁻¹	
F(000)	1412	
Crystal size	0.15 x 0.03 x 0.03 mm ³	
Reflections collected	14719	
Independent reflections	5588 [R(int) = 0.2424]	
Data / restraints / parameters	5588 / 0 / 390	
Goodness-of-fit on F ²	0.812	
Final R indices [I > 2σ(I)]	R ₁ = 0.0490, wR ₂ = 0.0760	
R indices (all data)	R ₁ = 0.1479, wR ₂ = 0.0992	
Absolute structure parameter	0.20(3)	
Largest diff. peak and hole	0.655 and -0.744 e.Å ⁻³	

Table S2. Selected bond lengths [\AA] and angles [deg] for **1**.

Mn(1)-O(11)	2.141(4)
Mn(1)-O(21)	2.174(4)
Mn(1)-N(4)	2.198(5)
Mn(1)-N(1)	2.199(5)
Mn(1)-N(2)	2.328(5)
Mn(1)-N(3)	2.360(5)
O(11)-Mn(1)-O(21)	91.60(16)
O(11)-Mn(1)-N(4)	98.19(18)
O(21)-Mn(1)-N(4)	90.68(18)
O(11)-Mn(1)-N(1)	91.02(18)
O(21)-Mn(1)-N(1)	99.06(18)
N(4)-Mn(1)-N(1)	166.42(18)
O(11)-Mn(1)-N(2)	163.77(17)
O(21)-Mn(1)-N(2)	98.80(16)
N(4)-Mn(1)-N(2)	94.13(18)
N(1)-Mn(1)-N(2)	75.13(18)
O(11)-Mn(1)-N(3)	93.37(16)
O(21)-Mn(1)-N(3)	165.84(17)
N(4)-Mn(1)-N(3)	75.49(18)
N(1)-Mn(1)-N(3)	94.10(18)
N(2)-Mn(1)-N(3)	79.50(16)

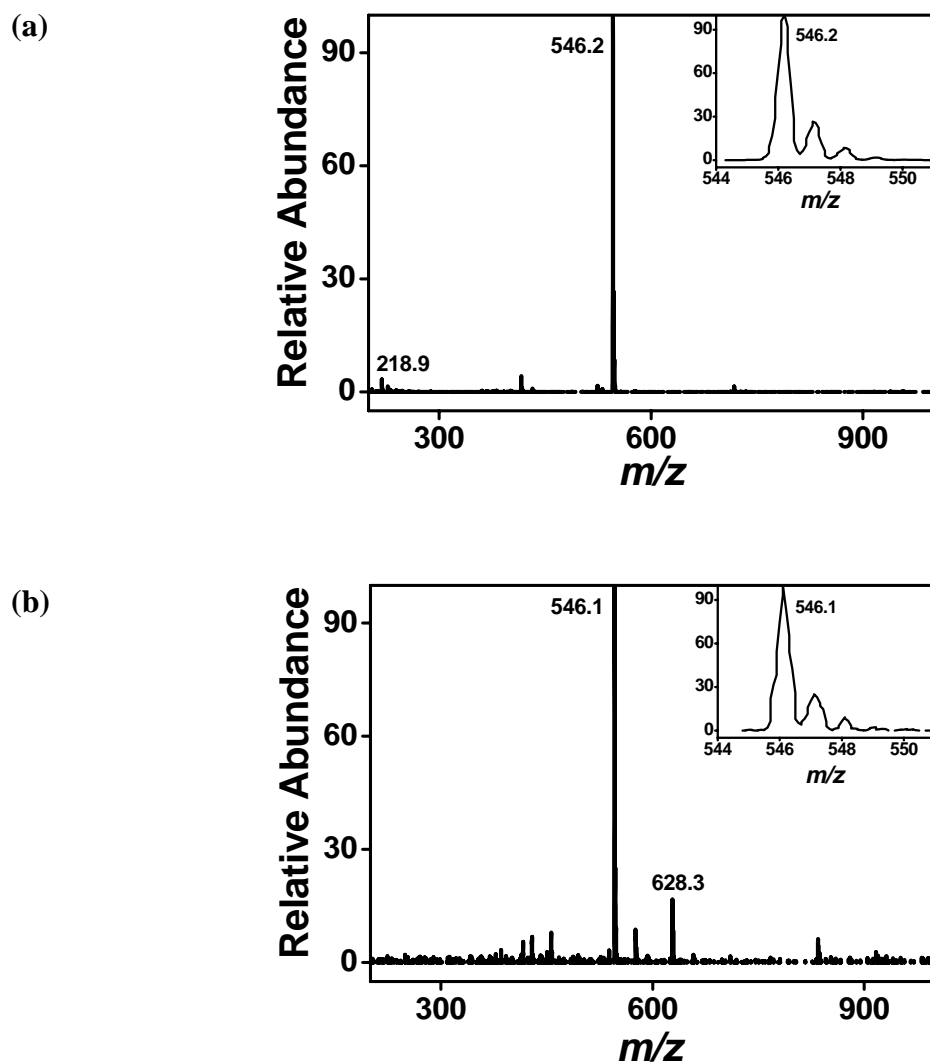


Figure S1. ESI MS spectra of (a) $\text{Mn}(\text{BQEN})(\text{CF}_3\text{SO}_3)_2$ (**1**) (1 mM) and (b) after the completion of a catalytic reaction with cyclohexane and peracetic acid.

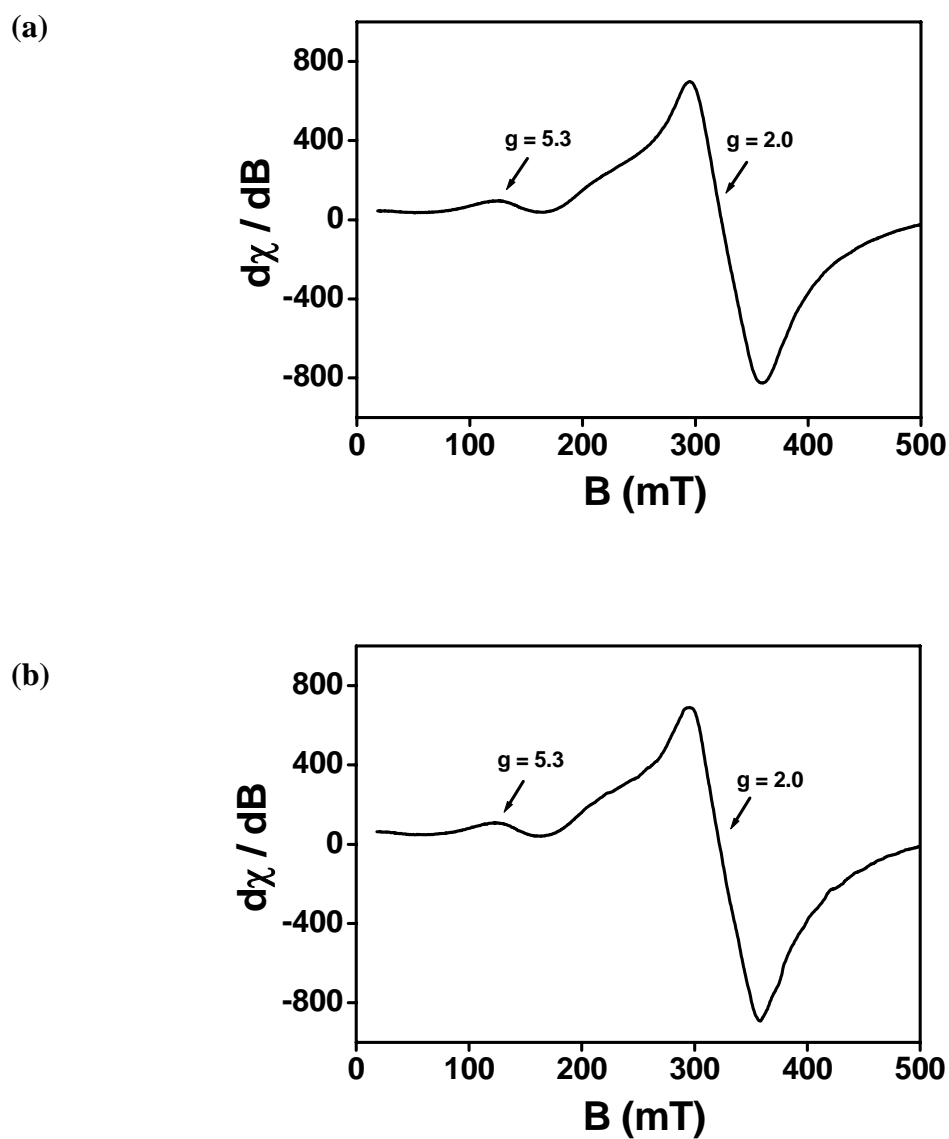


Figure S2. EPR spectra of (a) $\text{Mn}(\text{BQEN})(\text{CF}_3\text{SO}_3)_2$ (2 mM) and (b) after the completion of a catalytic reaction with cyclohexane and peracetic acid. Instrumental parameters: temp. 4 K; microwaves, 9.05 GHz at 1 mW; modulation 100 KHz.