Supporting Information for

O–H Bond Oxidation by a Monomeric Mn^{III}–OMe Complex

Gayan B. Wijeratne, Victor W. Day, and Timothy A. Jackson*

†*Department of Chemistry and Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66045*

RECEIVED DATE

*To whom correspondence should be addressed:

Timothy A. Jackson
1251 Wescoe Hall Drive
Lawrence, KS 66045
Phone: (785) 864-3968
Fax: (785) 864-5396
taj@ku.edu

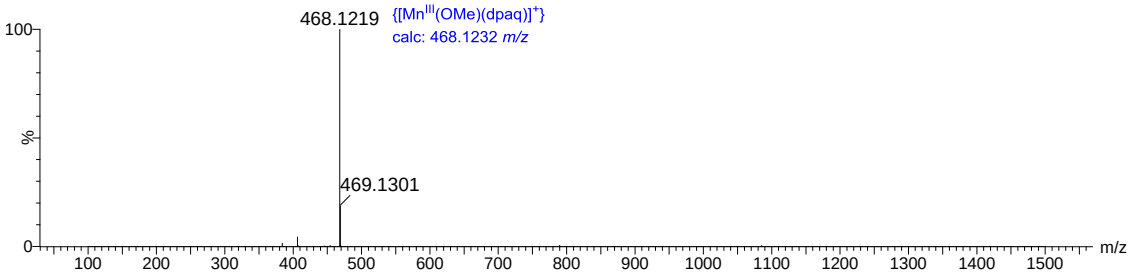
Table S1. Crystal Data and Structure Refinement for [Mn^{III}(OMe)(dpaq)](OTf).

Empirical formula	C50 H46 F6 Mn2 N10 O10.73 S2	
Formula weight	1246.73	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 13.6388(4) Å	a= 90°.
	b = 26.1547(7) Å	b= 90°.
	c = 15.1412(4) Å	g = 90°.
Volume	5401.1(3) $Å^3$	
Z	4	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	5.306 mm^{-1}	
F(000)	2552	
Crystal size	0.20 x 0.09 x 0.06 mm^3	
Theta range for data collection	3.37 to 70.01°.	
Index ranges	-16<=h<=16, -30<=k<=29, -15<=l<=17	
Reflections collected	50470	
Independent reflections	8511 [R(int) = 0.0247]	
Completeness to theta = 66.00°	97.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.715	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8511 / 211 / 826	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.2117	
R indices (all data)	R1 = 0.0757, wR2 = 0.2131	
Absolute structure parameter	0(3)	
Largest diff. peak and hole	1.177 and -0.773 $e.Å^{-3}$	

$R_1 = \Sigma \, ||F_O| - |F_C|| \, / \, \Sigma \, |F_O|$

$wR_2 = \{ \, \Sigma \, [w(F_O^2 - F_C^2)^2] \, / \, \Sigma \, [w(F_O^2)^2] \, \}^{1/2}$

A)



B)

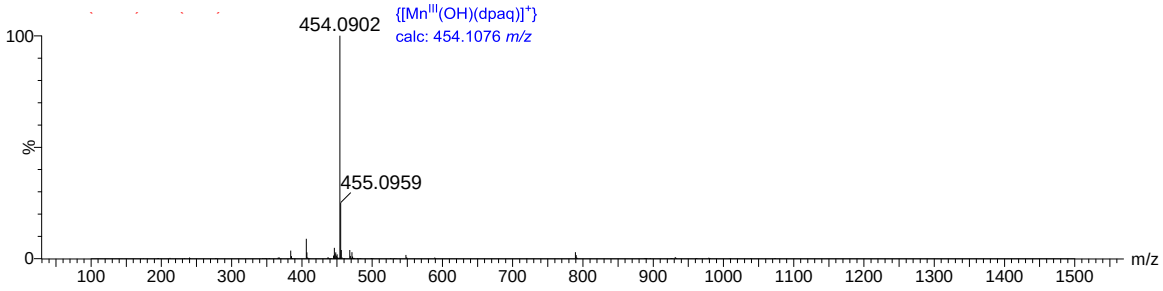


Figure S1. ESI mass spectra of A) $[Mn^{III}(OMe)(dpaq)]^+$ in MeOH and B) $[Mn^{III}(OMe)(dpaq)]^+$ dissolved in H_2O, showing full conversion to $[Mn^{III}(OH)(dpaq)]^+$.

Table S2. Selected Bond Lengths (Å) and Angles (deg) for One of the Two $[Mn^{III}(OMe)(dpaq)]^+$ Cations in the X-ray Diffraction Structure of $[Mn^{III}(OMe)(dpaq)]^+$.

$[Mn^{III}(OMe)(dpaq)]^+$ (B)			
Mn–O2	1.814(5)	O2–Mn–N2	178.0(3)
Mn–N2	1.982(6)	N4–Mn–N5	153.8(2)
Mn–N1	2.086(11)	N1–Mn–N3	156.5(4)
Mn–N3	2.169(6)	N4–Mn–N2	86.8(2)
Mn–N4	2.154(7)	N1–Mn–N2	74.5(2)
Mn–N5	2.195(6)	N3–Mn–N2	82.1(3)

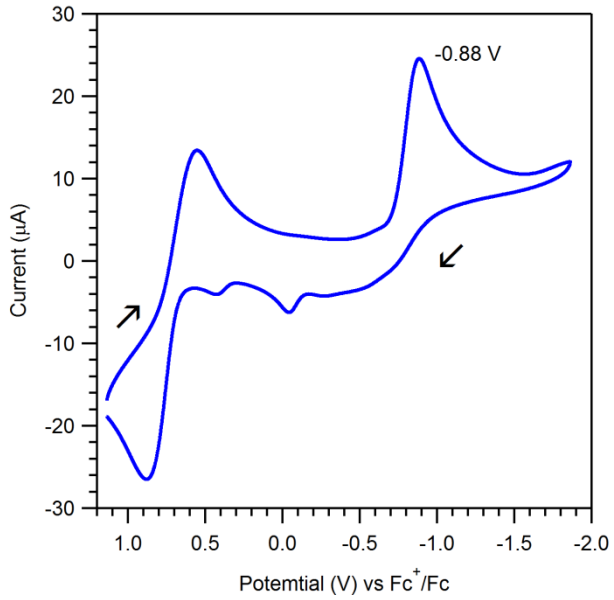


Figure S2. Cyclic voltammogram of $[Mn^{III}(OMe)(dpaq)]^+$ in acetonitrile (12.89 mg in 10 ml) at 298 K (Scan rate = 100 mV s^{-1}; starting potential = 1.13 V) under an argon atmosphere. The electrochemical cell consisted of a glassy carbon working electrode, a platinum auxiliary electrode, and a AgCl/Ag reference electrode along with a 0.1 M acetonitrile solution of $Bu_4N(PF_6)$ as the supporting electrolyte.

NOTE: The irreversible redox event at $E_{p,c}$ = -0.88 V is attributed to the Mn^{III}/Mn^{II} couple which is 0.22 V lower than that of $[Mn^{III}(OH)(dpaq)]^+$ (-0.6 V vs Fc^+/Fc).[1] The multiple oxidation events between E_{pa} = +0.5 and -0.4 V are possibly due to the redox activity of the 8-aminoquinolinyl moiety of the supporting ligand, as previously observed for ruthenium(II) complexes supported by 8-aminoquinoline.[2]

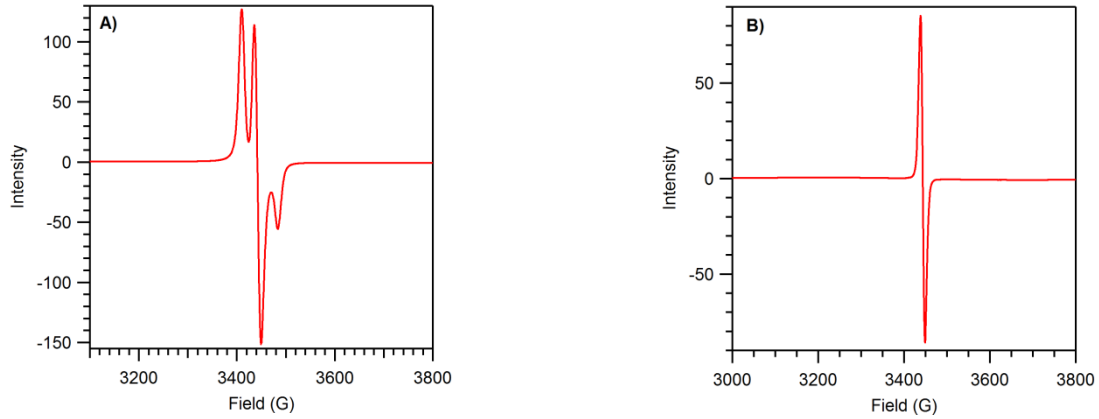


Figure S3. A) 5 K EPR spectra of the final products of A) TEMPOH and B) $^{4\text{-}t\text{-butyl}}$ArOH oxidation by $[Mn^{III}(OMe)(dpaq)]^{+}$ in MeCN. The intense features centered at g = 2.04 has been previously observed for both TEMPO and $^{4\text{-}t\text{-butyl}}$ArO· radicals.[3, 4] Parallel-mode EPR experiments were performed on both of these samples, but no features were observed.

Table S3. Yields of $^{4\text{-}t\text{-butyl}}ArO^{\bullet}$ from the Oxidation of $^{4\text{-}t\text{-butyl}}$ArOH by $[Mn^{III}(OMe)(dpaq)]^{+}$ at 50 ºC in MeCN at Variable Concentrations of the Phenol.

$[Mn^{III}(OMe)(dpaq)]^{+}_0$ (mM) [a]	$[^{4\text{-}t\text{-butyl}}ArOH]_0$ (mM) [a]	AU_{628} (final)	$[^{4\text{-}t\text{-butyl}}ArO\cdot]_f$ (mM) [b]	Percent conversion [c]
1.25	12.5	0.36	0.90	72%
1.25	62.5	0.38	0.95	76%
1.25	93.8	0.36	0.90	72%
1.25	125	0.38	0.95	76%
1.25	156	0.39	0.98	79%

[a] Initial concentration at t = 0 s. [b] Final concentration of phenoxyl radical determined using the extinction coefficient of $^{4\text{-}t\text{-butyl}}$ArO· at 25 ºC in MeCN.[5] [c] Percent conversion of phenoxyl radical relative to initial concentration of $[Mn^{III}(OMe)(dpaq)]^{+}$.

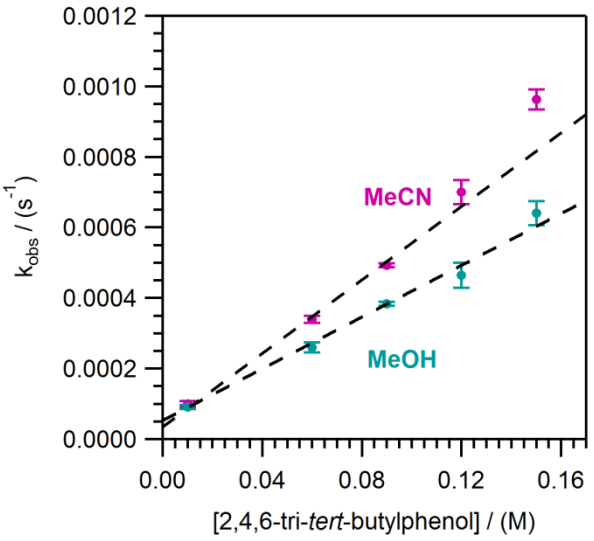


Figure S4. Observed pseudo-first order rate constants (k_{obs}) as a function of substrate concentration for the oxidation of $^{4\text{-}t\text{-butyl}}$ArOH by $[Mn^{III}(OMe)(dpaq)]^{+}$ in MeCN and in MeOH at 50 ºC.

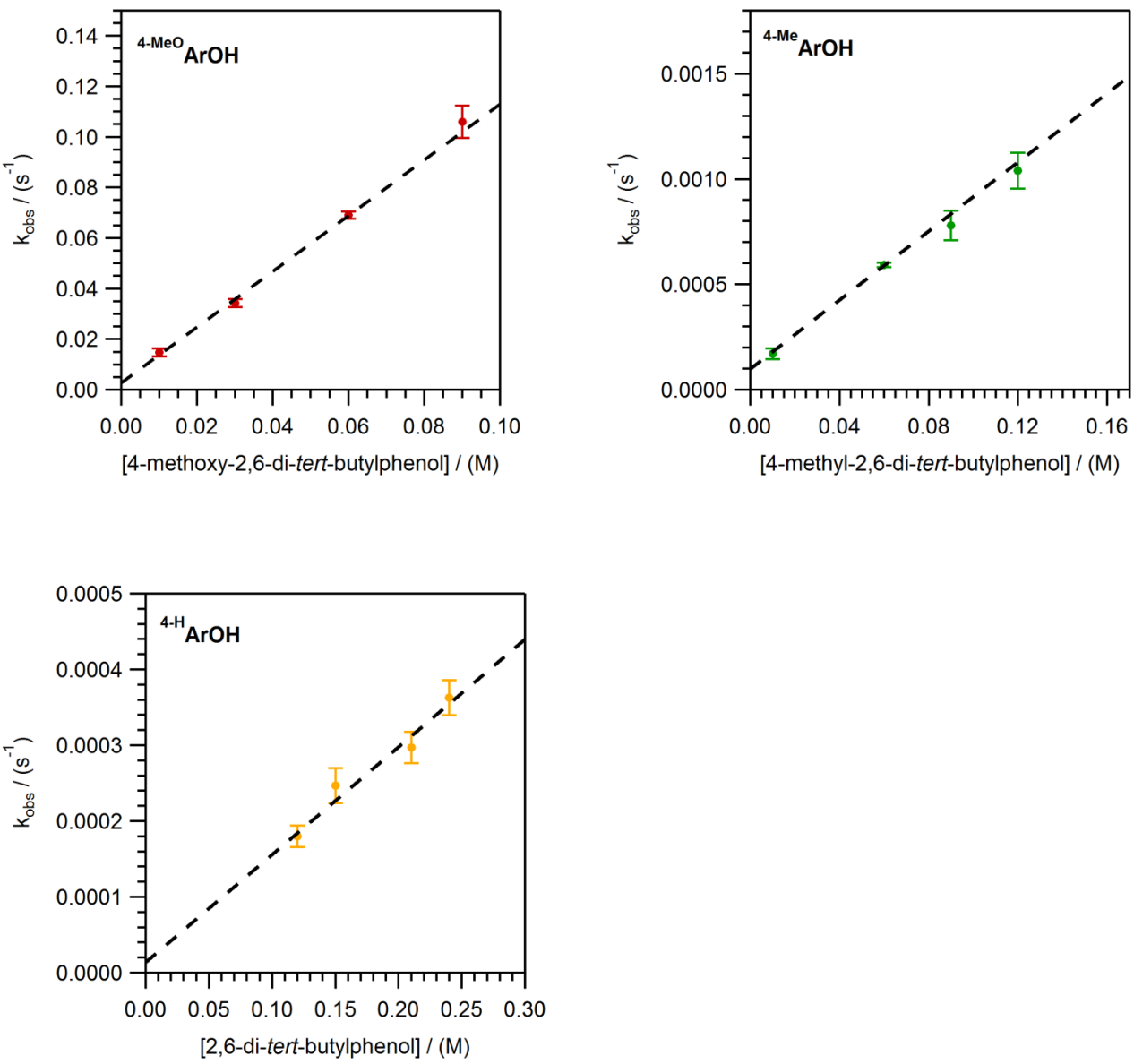


Figure S5. Observed pseudo-first order rate constants (k_{obs}) as a function of phenol concentration for reactions of $^{4\text{-OMe}}$ArOH, $^{4\text{-Me}}$ArOH, and $^{4\text{-H}}$ArOH with $[Mn^{III}(OMe)(dpaq)]^+$ in MeCN at 50 °C.

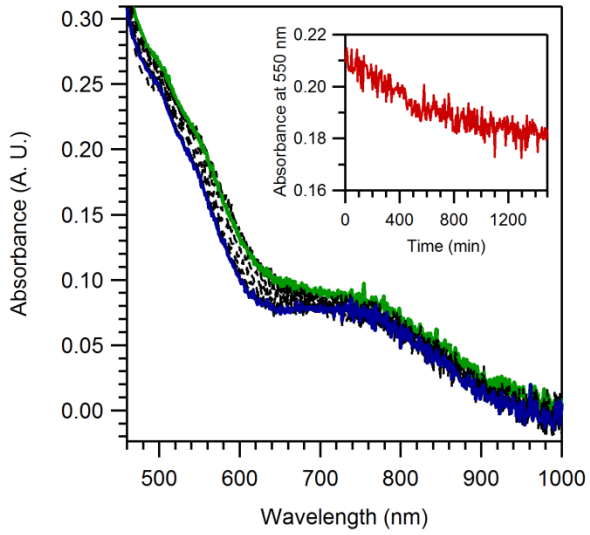


Figure S6. The decay of electronic absorption features of a 1.25 mM MeCN solution of $[Mn^{III}(OMe)(dpaq)]^{+}$ upon the addition of 250 equiv. xanthene at 50 ºC under argon. Inset: Time evolution of the absorption signal at 550 nm. The pseudo-first order rate constant for this reaction was determined using the method of initial rates.

References

1. G. B. Wijeratne, B. Corzine, V. W. Day and T. A. Jackson, *Inorg. Chem.*, 2014, **53**, 7622-7634.
2. M. K. O'Neill, A. F. Trappey, P. Battle, C. L. Boswell and D. N. Blauch, *Dalton Trans.*, 2009, 3391-3394.
3. M. F. Ottaviani, M. Garcia-Garibay and N. J. Turro, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1993, **72**, 321-332.
4. A. T. Fiedler and L. Que, *Inorg. Chem.*, 2009, **48**, 11038-11047.
5. V. W. Manner, T. F. Markle, J. H. Freudenthal, J. P. Roth and J. M. Mayer, *Chem. Commun. (Cambridge, U. K.)*, 2008, 256-258.