Supporting Information

Mechanistic Insights into Hydride-Transfer and Electron-Transfer Reactions by a Manganese(IV)-Oxo Porphyrin Complex

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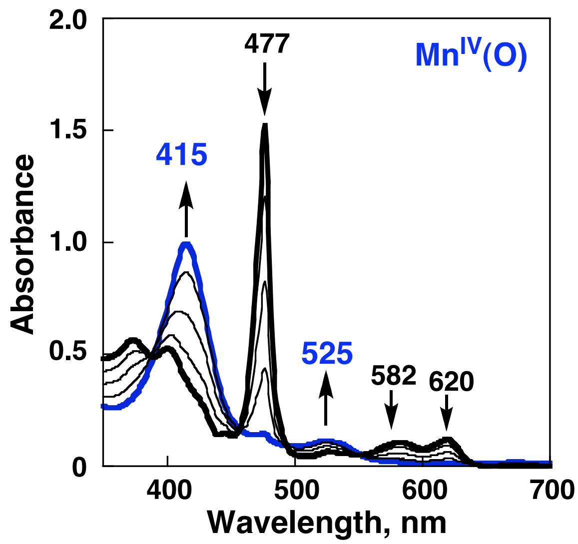

Figure S1. Spectral change for formation of (TMP)Mn^{IV}(O) by the reaction of (TMP)Mn^{III}(Cl) (1.0×10^{-5} M) with *m*-CPBA (5.0×10^{-5} M) in MeCN at 233 K.

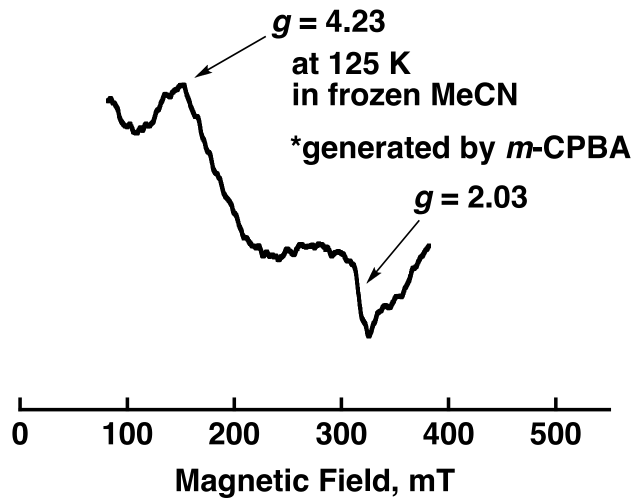

Figure S2. ESR spectrum of (TMP)Mn^{IV}(O) produced by the reaction of (TMP)Mn^{III}(Cl) (1.0×10^{-5} M) with *m*-CPBA (5.0×10^{-5} M) in MeCN and measured at 125 K.

The detailed derivation of eq 5 from eq 2 and eq 4 is given by eq 4', which is obtained by the substitution of the term [C] (eq 4) into eq 2.

$$d[(TMP)Mn^{III}(OH)]/dt = k_2[C][AcrH_2] + k_1[(TMP)Mn^{IV}(O)]^2 - k_{-1}[C] \quad (2)$$

$$d[C]/dt = k_1[(TMP)Mn^{IV}(O)]^2 - k_{-1}[C] - k_2[C][AcrH_2] \quad (3)$$

$$[C] = k_1[(TMP)Mn^{IV}(O)]^2/(k_{-1} + k_2[AcrH_2]) \quad (4)$$

$$\frac{d[(TMP)Mn^{III}(OH)]}{dt} = \left(k_2[AcrH_2] - k_{-1}\right)\left(\frac{k_1[(TMP)Mn^{IV}(O)]^2}{k_{-1} + k_2[AcrH_2]}\right) + k_1[(TMP)Mn^{IV}(O)]^2 \quad (4')$$

$$= \frac{\left(k_2[AcrH_2] - k_{-1}\right) k_1[(TMP)Mn^{IV}(O)]^2 + k_1[(TMP)Mn^{IV}(O)]^2 \left(k_{-1} + k_2[AcrH_2]\right)}{k_{-1} + k_2[AcrH_2]}$$

$$= \frac{2k_1k_2[(TMP)Mn^{IV}(O)]^2[AcrH_2]}{k_{-1} + k_2[AcrH_2]}$$

$$d[(TMP)Mn^{III}(OH)]/dt = 2k_1k_2[(TMP)Mn^{IV}(O)]^2[AcrH_2]/(k_{-1} + k_2[AcrH_2]) \quad (5)$$

Table S1. Oxidation Potentials (E_{ox}) of NADH Analogues, Rate Constants (k_H) for Hydride Transfer from NADH Analogues to Cl_4Q and Rate Constants (k_2K_1) for Hydride Transfer from NADH Analogues to $(TMP)Mn^{IV}(O)$ in Deaerated MeCN at 298 K

no.	NADH analog	E_{ox} (V vs SCE)	k_H (Cl_4Q) (M^{-1} s^{-1})	k_2K_1, M^{-2} s^{-1} $(TMP)Mn^{IV}(O)$
1	BNAH	0.57	1.0×10^3	$(2.3 \pm 0.2) \times 10^9$
2	BNAH-4,4'-d_2	0.57	1.9×10^2	
3	$AcrH_2$	0.81	1.5×10	$(4.2 \pm 0.3) \times 10^8$
4	$AcrD_2$	0.81	1.7	$(1.8 \pm 0.1) \times 10^8$
5	AcrHMe	0.84	9.4×10^{-1}	$(3.3 \pm 0.2) \times 10^8$
6	AcrHPh	0.88	6.6×10^{-1}	$(9.0 \pm 1.0) \times 10^7$
7	AcrHEt	0.84	4.6×10^{-1}	
8	AcrDPh	0.88	1.3×10^{-1}	

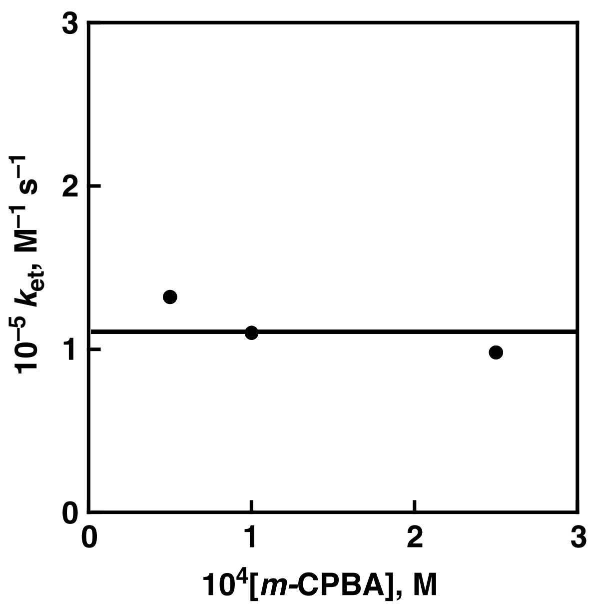

Figure S3. Plot of k_{et} for electron transfer from ferrocene to (TMP)Mn^{IV}(O) vs concentration of *m*-CPBA in MeCN at 298 K.

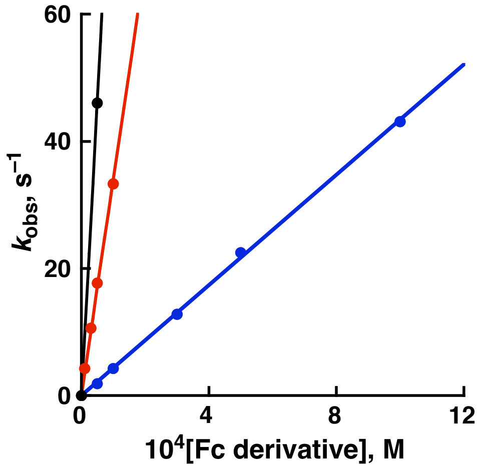

Figure S4. (a) Plots of the observed pseudo-first rate constant (k_{obs}) of electron transfer from ferrocene derivatives to (TMP)Mn^{IV}(O) (black: Me_2Fc, red: Fc, blue: BrFc) vs concentrations of ferrocene derivatives in MeCN at 298 K.

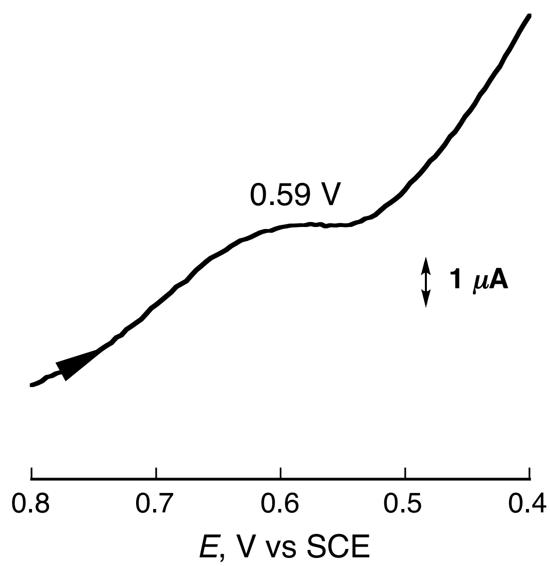

Figure S5. Differential pulse voltammogram (DPV) of (TMP)Mn^{IV}(O) (3.0×10^{-4} M) after the addition of *m*-CPBA (3.0×10^{-3} M) to the solution of (TMP)Mn^{III}(Cl) (3.0×10^{-4} M) in MeCN containing 0.1 M $TBAPF_6$ at 233 K.