

# Supporting Information

## Manganese(V)-Oxo Corroles in Hydride-Transfer Reactions

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## Experimental Section

**Materials.** Commercially available reagents, such as 10-methylacridone, acridine, 10-methylacridinium iodide ( $\text{AcrH}^+\text{I}^-$ ), methyl iodide (MeI),  $\text{NaBH}_4$ ,  $\text{LiAlD}_4$  and  $\text{NaBD}_4$ , were the best available purity and were used without further purification unless otherwise noted. Acetonitrile (MeCN) and ether were dried according to the literature procedures and distilled under Ar prior to use.<sup>1</sup> Iodosylbenzene (PhIO) was prepared by a literature method.<sup>2</sup>

9,10-Dihydro-10-methylacridine ( $\text{AcrH}_2$ ) was prepared by reducing 10-methylacridinium iodide ( $\text{AcrH}^+\text{I}^-$ ) with  $\text{NaBH}_4$  in methanol and purified by recrystallization from ethanol.<sup>3</sup> For the preparation of  $\text{AcrH}^+\text{I}^-$ , acridine was treated with MeI in acetone, and then the mixture was refluxed for 7 days. 9-Alkyl-9,10-dihydro-10-methylacridine ( $\text{AcrHR}$ ; R = Me, Et) was prepared by the reduction of  $\text{AcrH}^+\text{I}^-$  with the corresponding Grignard reagents ( $\text{RMgX}$ ) and purified by recrystallization from ethanol.<sup>3</sup> The dideuterated compound, [9,9'- $^2\text{H}_2$ ]-10-methylacridine ( $\text{AcrD}_2$ ), was prepared from 10-methylacridone by reduction with  $\text{LiAlD}_4$  in ether.<sup>3</sup> Corrole ligands [5,10,15-tris(4-nitrophenyl)corrole ( $\text{H}_3\text{TNPC}$ ), 5,10,15-tris(3,5-trifluoromethylphenyl)corrole ( $\text{H}_3\text{TFMPC}$ ) and 5,10,15-tris(pentafluorophenyl)corrole ( $\text{H}_3\text{TPFC}$ )], manganese(III) corrole complexes [ $\text{Mn}^{\text{III}}(\text{TPNC})$ ,  $\text{Mn}^{\text{III}}(\text{TFMPC})$  and  $\text{Mn}^{\text{III}}(\text{TPFC})$ ] and manganese(V)-oxo corroles [ $\text{Mn}^{\text{V}}(\text{O})(\text{TNPC})$  (**1**),  $\text{Mn}^{\text{V}}(\text{O})(\text{TFMPC})$  (**2**) and  $\text{Mn}^{\text{V}}(\text{O})(\text{TPFC})$  (**3**)] were prepared by the published method.<sup>4</sup>

**Instrumentation.** UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with a Hewlett Packard 8453 spectrophotometer equipped with an Optostat<sup>DN</sup> variable-temperature liquid nitrogen cryostat (Oxford instruments).  $^1\text{H}$  NMR spectra were measured with Bruker model digital AVANCE III 400 FT-NMR spectrometer.

**Kinetic and Reactivity Studies and Product Analyses.** All reactions were followed by monitoring UV-vis spectral changes of reaction solutions with a Hewlett Packard 8453 spectrophotometer equipped with a UNISOKU Scientific Instrument. Manganese(V)-oxo corrole complexes,  $\text{Mn}^{\text{V}}(\text{O})(\text{TNPC})$  (**1**),  $\text{Mn}^{\text{V}}(\text{O})(\text{TFMPC})$  (**2**) and  $\text{Mn}^{\text{V}}(\text{O})(\text{TPFC})$  (**3**), were prepared by reacting manganese(III) corroles ( $3.0 \times 10^{-5}$  M) with 2 equiv of PhIO in  $\text{CH}_3\text{CN}$  at  $10^\circ\text{C}$ . Subsequently, appropriate amounts of substrates were added to the reaction solutions. After the completion of reactions,  $k_{\text{obs}}$  values were calculated by pseudo-

first-order fitting of the kinetic data. By using dideuterated compound, AcrD<sub>2</sub>, kinetic isotope effect (KIE) value was determined.

Products formed in the oxidation of AcrHR (R = H, Me and Et) by Mn<sup>V</sup>(O)(Cor) *in the absence of* HClO<sub>4</sub> were analyzed by <sup>1</sup>H NMR spectroscopy. Products were isolated by column chromatography, which was packed with silicagel 60. Remaining AcrHR (R = H, Me and Et) was obtained in the first fraction, which was eluted by 100% CH<sub>2</sub>Cl<sub>2</sub>, and then the product was obtained in the second fraction, which was eluted by 70% CH<sub>2</sub>Cl<sub>2</sub> and 30% acetone. The final products in the oxidation of AcrHR (R = H, Me and Et) by Mn<sup>V</sup>(O)(Cor) were AcrR(OH) with >90% yield by <sup>1</sup>H NMR analysis. *In the presence of* HClO<sub>4</sub>, the final products in the oxidation of AcrHR (R = H, Me and Et) by Mn<sup>V</sup>(O)(Cor) were AcrR<sup>+</sup> by analyzing UV-vis spectra, and yields were quantitative based on the amount of **1** (see Fig. S4).

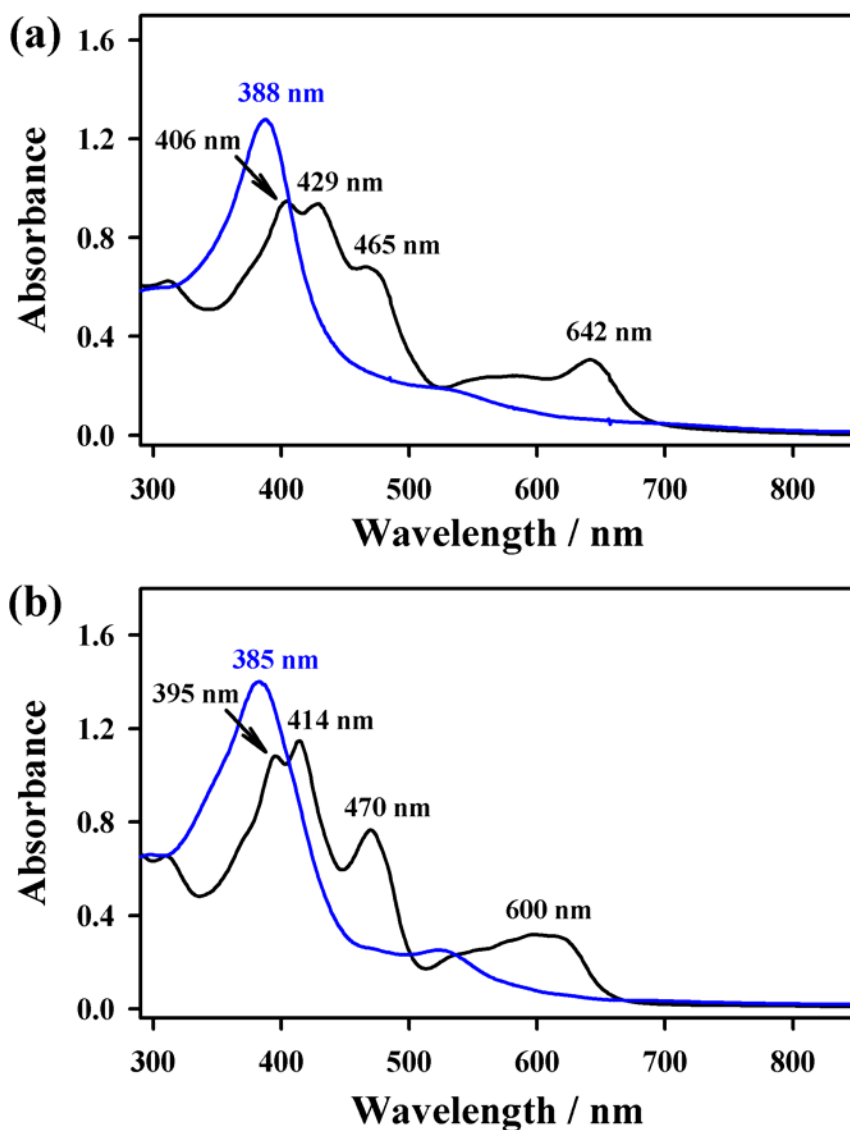
## References

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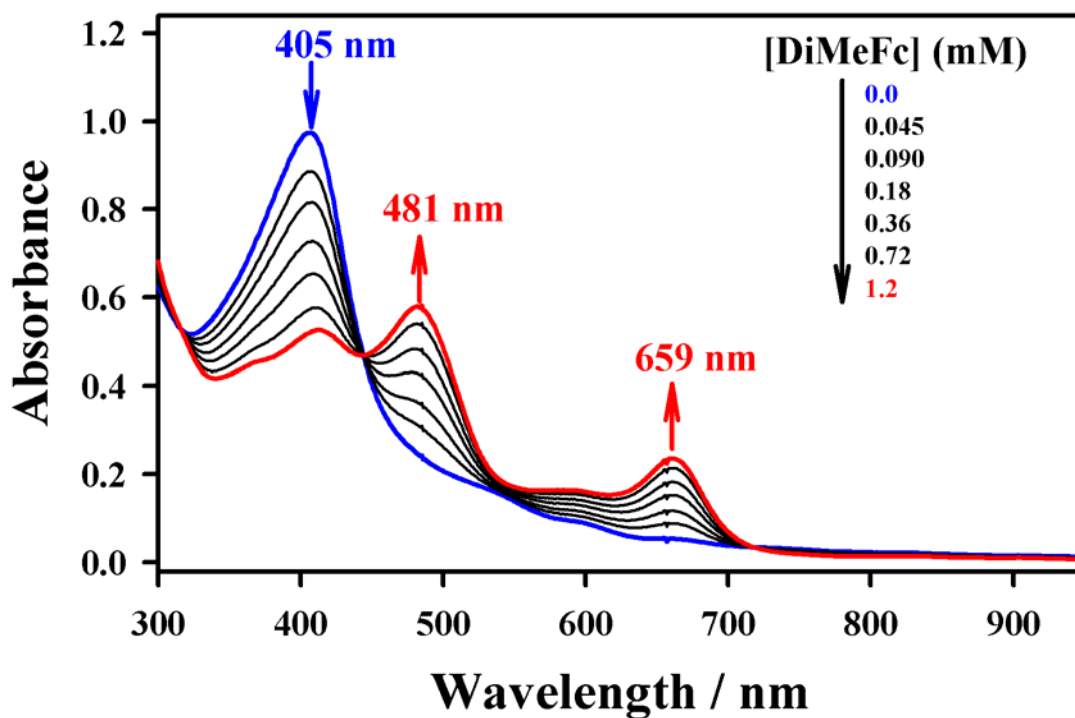
**Table S1.** Second-Order Rate Constants,  $k_2$ , Determined in Hydride Transfer from NADH Analogues to  $\text{Mn}^{\text{V}}(\text{O})(\text{Cor})$  at 10 °C.

Entry	NADH analogue	$k_2 (\text{Mn}^{\text{V}}(\text{O})(\text{Cor})), \text{M}^{-1} \text{s}^{-1}$			$k_2 ([\text{Mn}^{\text{V}}(\text{O})_2(\text{TPFPP})]^-),^a$ $\text{M}^{-1} \text{s}^{-1}$
		Cor = TNPC (1)	Cor = TFMPC (2)	Cor = TPFC (3)	
1	AcrH <sub>2</sub>	$8.2 \times 10$	$4.9 \times 10$	$8.8 \times 10^2$	$1.5 \times 10$
2	AcrD <sub>2</sub>	8.2	4.5	$1.2 \times 10^2$	1.0
3	AcrHMe	2.6	1.6	$3.2 \times 10$	$2.7 \times 10^{-1}$
4	AcrHEt	$9.4 \times 10^{-1}$	$5.7 \times 10^{-1}$	$1.7 \times 10$	$9.3 \times 10^{-2}$

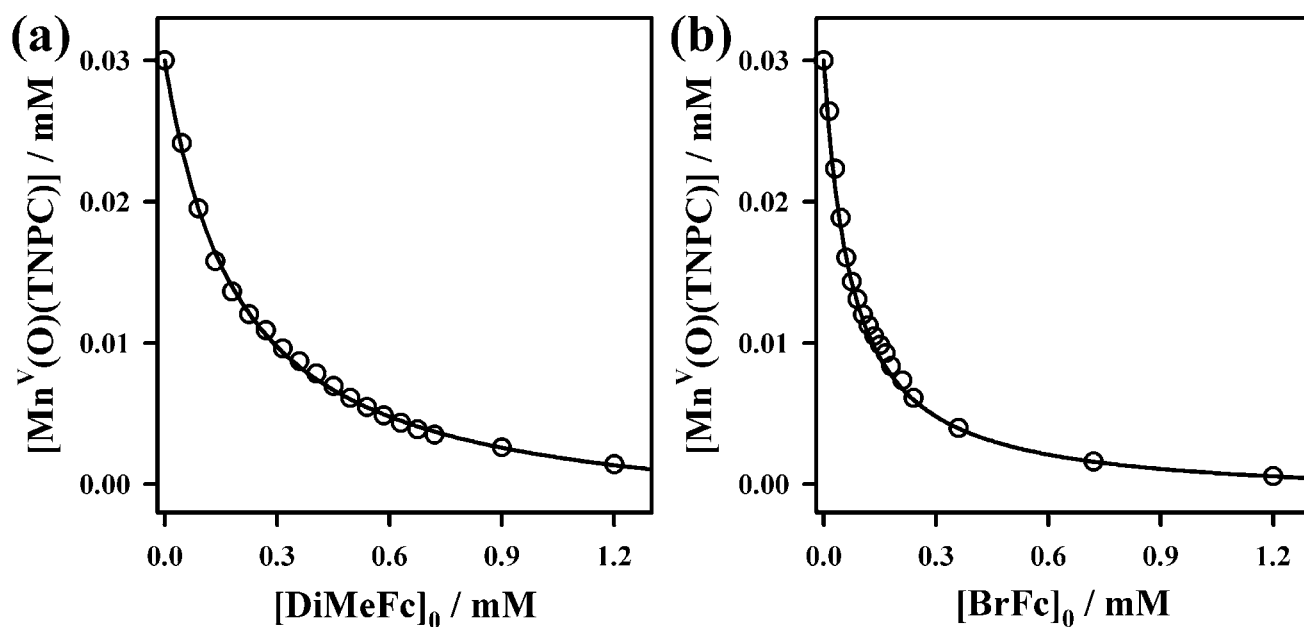
<sup>a</sup> Data are taken from reference 5c in text.



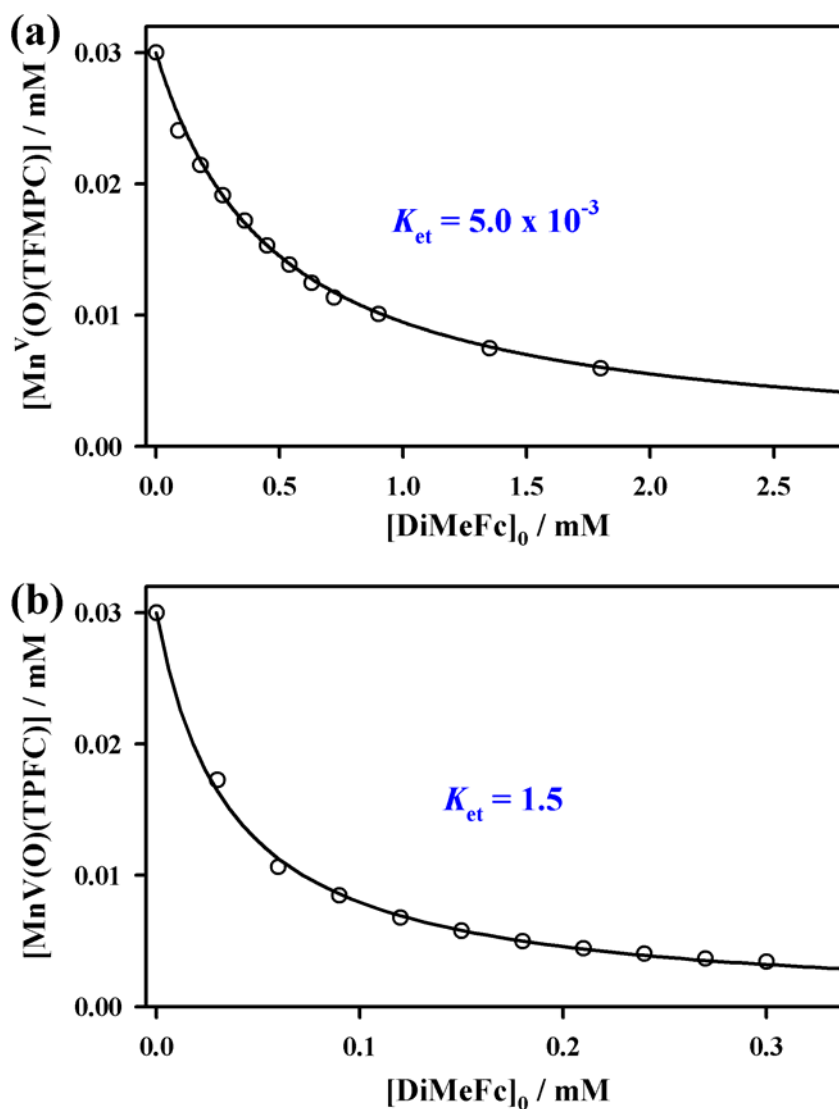
**Fig. S1** (a) UV-vis spectra of Mn<sup>III</sup>(TFMPC) ( $3.0 \times 10^{-5}$  M) (black line) and **2** (blue line) in CH<sub>3</sub>CN at 10 °C. **2** was generated in the reaction of Mn<sup>III</sup>(TFMPC) ( $3.0 \times 10^{-5}$  M) with 2.0 equiv PhIO in CH<sub>3</sub>CN at 10 °C. (b) UV-vis spectra of Mn<sup>III</sup>(TPFC) ( $3.0 \times 10^{-5}$  M) (black line) and **3** (blue line) in CH<sub>3</sub>CN at 10 °C. **3** was generated in the reaction of Mn<sup>III</sup>(TPFC) ( $3.0 \times 10^{-5}$  M) with 2.0 equiv PhIO in CH<sub>3</sub>CN at 10 °C.



**Fig. S2** UV-vis spectral change of **1** ( $3.0 \times 10^{-5}$  M) (blue line) to Mn<sup>III</sup>(TNPC) (red line) upon sequential addition of DiMeFc (0, 1.5, 3.0, 6.0, 12, 24 and 40 equiv) to a solution of **1** ( $3.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN at 10 °C. The absorption band at 405 nm due to **1** decreases, accompanied by an increase in the absorption bands at 481 and 659 nm due to Mn<sup>III</sup>(TNPC). The spectral data indicate the existence of equilibrium as shown in eqn. (1) in text, where the final concentration of Mn<sup>III</sup>(TNPC) produced in the ET reduction of **1** increases with an increase in the initial concentration of DiMeFc, [DiMeFc]<sub>0</sub>.

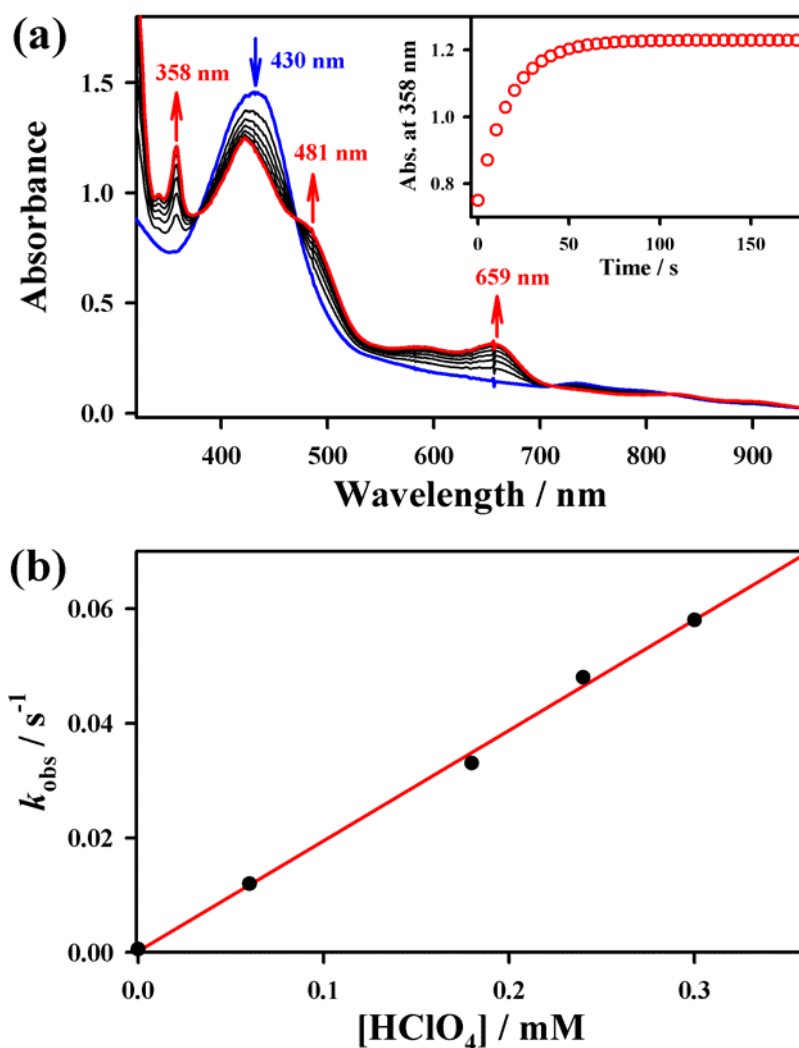


**Fig. S3** (a) Plot of concentration of **1** versus initial concentration of DiMeFc,  $[\text{DiMeFc}]_0$ , in electron transfer from DiMeFc to **1** ( $3 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}$  at  $10^\circ\text{C}$ . (b) Plot of concentration of **1** versus initial concentration of BrFc,  $[\text{BrFc}]_0$ , in electron transfer from BrFc to **1** ( $3 \times 10^{-5}$  M) in the presence of  $\text{HClO}_4$  (10 equiv,  $3 \times 10^{-4}$  M) in  $\text{CH}_3\text{CN}$  at  $10^\circ\text{C}$ .



**Fig. S4** (a) Plot of concentration of **2** vs initial concentration of DiMeFc,  $[\text{DiMeFc}]_0$ , in the reaction of electron transfer from DiMeFc to **2** ( $3.0 \times 10^{-5}$  M) in deaerated  $\text{CH}_3\text{CN}$  at  $10^\circ\text{C}$ . The equilibrium constant ( $K_{\text{et}}$ ) is calculated to be  $5.0 \times 10^{-3}$  at  $10^\circ\text{C}$  by fitting the plot, and the determined  $E_{\text{red}}$  of **2** is 0.19 V vs SCE. (b) Plot of concentration of **3** vs initial concentration of DiMeFc,  $[\text{DiMeFc}]_0$ , in the reaction of electron transfer from DiMeFc to **3** ( $3.0 \times 10^{-5}$  M) in deaerated  $\text{CH}_3\text{CN}$  at  $10^\circ\text{C}$ . The equilibrium constant ( $K_{\text{et}}$ ) is determined to be 1.5 at  $10^\circ\text{C}$  by fitting the plot, and the determined  $E_{\text{red}}$  of **3** is 0.27 V vs SCE.





**Fig. S5** (a) UV-vis spectral change of **1** (blue line) upon addition of AcrHEt (20 equiv,  $6.0 \times 10^{-4}$  M) to a solution of **1** ( $3.0 \times 10^{-5}$  M) in the presence of HClO<sub>4</sub> (10 equiv,  $3.0 \times 10^{-4}$  M) in CH<sub>3</sub>CN at 10 °C. Inset shows time course of the formation of AcrEt<sup>+</sup> ion monitored at 358 nm (red line). (b) Plot of  $k_{\text{obs}}$  against the concentration of HClO<sub>4</sub> in the hydride-transfer reaction of **1** ( $3.0 \times 10^{-5}$  M) and AcrHEt (20 equiv,  $6.0 \times 10^{-4}$  M) in the presence of HClO<sub>4</sub> (0, 2, 6, 8 and 10 equiv) in CH<sub>3</sub>CN at 10 °C.