Supplementary Material (ESI) for Chemical Communications

Supporting Information

High-Valent Manganese(V)-Oxo Porphyrin Complexes in Hydride Transfer Reactions

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Experimental Section

Materials. Commercially available reagents, such as Mn(Prop)Cl (Porp = TPFPP, TDFPP and TDCPP; Frontier Scientific Inc., Logan, UT, USA), 1-benzyl-1,4-dihydronicotinamide (BNAH), 9-phenyl-10-methylacridinium ion (Acr^+–Ph), 10-methylacridone, acridine, methyl iodide (MeI), $NaBH_4$, $LiAlD_4$ and $NaBD_4$, were the best available purity and were used without further purification unless otherwise noted. Acetonitrile (MeCN), dichloromethane, and ether were dried according to the literature procedures[1] and distilled under Ar prior to use. *m*-Chloroperbenzoic acid (*m*-CPBA) was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure.

9,10-Dihydro-10-methylacridine ($AcrH_2$) was prepared by reducing 10-methylacridinium iodide ($AcrH^+I^-$) with $NaBH_4$ in methanol and purified by recrystallization from ethanol.[2] For the preparation of $AcrH^+I^-$, acridine was treated with MeI in acetone, and then the mixture was refluxed for 7 days. 9-Alkyl-9,10-dihydro-10-methylacridine (AcrHR; R = Me, Et) was prepared by the reduction of $AcrH^+I^-$ with the corresponding Grignard reagents (RMgX) and purified by recrystallization from ethanol.[2] The dideuterated compound, [9,9'-$^2H_2$]-10-methylacridine ($AcrD_2$), was prepared from 10-methylacridone by reduction with $LiAlD_4$ in ether.[2] The dideuterated compound, 1-benzyl-1,4-dihydro[4,4'-$^2H_2$]-nicotinamide (BNAH-4,4'-d_2), was prepared from monodeuterated compound (BNAH-4-d_1) by three cycles of oxidation with *p*-chloranil in dimethylformamide and reduction with dithionite in deuterium oxide.[3,4]

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer equipped with a circulating water bath or a Hi-Tech Scientific SF-61 multimixing cryogenic stopped-flow instrument equipped with a Hi-Tech Scientific KinetaScan diode array rapid scanning unit. Product analysis was performed with a Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS). ^{1}H NMR was also measured with a Bruker 9503DPX-250 (250 MHz) FT-NMR spectrometer for the product analysis. ^{1}H-NMR measurements were carried out in $CDCl_3$ at 25 ^{o}C. Detailed experimental conditions are described in footnote of Fig. S3.

Kinetic and Reactivity Studies. All reactions were followed by monitoring UV-vis spectral changes of reaction solutions with a Hewlett Packard 8453 spectrophotometer equipped with an Optostat^{DN}

variable-temperature liquid nitrogen cryostat (Oxford instruments) or with a Hi-Tech Scientific SF-61 multimixing cryogenic stopped-flow instrument equipped with a Hi-Tech Scientific KinetaScan diode array rapid scanning unit at 25 ^{o}C. Manganese(V)-oxo porphyrin complexes, $[Mn^{V}(O)_2(TPFPP)]^{-}$ (**1**), $[Mn^{V}(O)_2(TDFPP)]^{-}$ (**2**), and $[Mn^{V}(O)_2(TDCPP)]^{-}$ (**3**), were prepared by reacting manganese(III) porphyrin chlorides (0.2 mM) with 6 equiv of *m*-CPBA in the presence of tetra-*n*-butylammonium hydroxide (20 equiv) in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) at 25 ^{o}C. Subsequently, appropriate amounts of substrates were added to the reaction solutions. After the completion of reactions, pseudo-first-order fitting of the kinetic data allowed us to determine k_{obs} values. Product analysis was performed with $[Mn^{V}(O)_2(TPFPP)]^{-}$ (1 mM) and substrates (50 mM), by injecting the reaction solutions directly into GC-MS. Products were identified by comparing retention times and mass patterns to those of known authentic samples. For NMR measurement, pure product of the completed reaction of $[Mn^{V}(O)_2(TPFPP)]^{-}$ and $AcrH_2$ at 25 ^{o}C was obtained after column chromatography, which was packed with silicagel 60.

References

[1] W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Butterworth-Heiemann, Oxford, **2003**.

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[3] a) A. G. Anderson, Jr. and G. Berkelhammer, *J. Am. Chem. Soc*., 1958, **80**, 992; b) D. Mauzerall and F. H. Westheimer, *J. Am. Chem. Soc.,* 1955, **77**, 2261.

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Table S1. Second-Order Rate Constants, k_2, Determined in Hydride Transfer from NADH Analogues to $[Mn^{V}(O)_2(Porp)]^{-}$ at 25 °C.

Entry	NADH analogue	k_2 ($[Mn^{V}(O)_2(Porp)]^{-}$), M^{-1} s^{-1}			k_2 (Cl_4Q),[a] M^{-1} s^{-1}	k_d,[b] s^{-1}
		Porp = TPFPP	Porp = TDFPP	Porp = TDCPP		
1	BNAH	1.3×10^{3}	6.2×10^{2}	5.9×10	1.0×10^{3}	2.4×10
2	BNAH-4,4'-d_2	1.3×10^{2}	7.7×10	1.0×10	1.9×10^{2}	1.8×10
3	$AcrH_2$	1.5×10	3.9	1.3	1.5×10	6.4
4	$AcrD_2$	1.0	2.0×10^{-1}	1.3×10^{-1}	1.7	7.1×10^{-1}
5	AcrHMe	2.7×10^{-1}	1.1×10^{-1}	6.4×10^{-2}	9.4×10^{-1}	1.1
6	AcrHPh	1.7×10^{-1}	6.5×10^{-2}	5.6×10^{-2}	6.6×10^{-1}	4.1
7	AcrHEt	9.3×10^{-2}	5.1×10^{-2}	5.4×10^{-2}	4.6×10^{-1}	4.9×10^{-1}

[a] Detailed discussion on the linear correlation observed in hydride-transfer reactions by high-valent metal-oxo species and Cl_4Q will be presented in elsewhere: S. Fukuzumi, H. Kotani, Y.-M. Lee, W. Nam, unpublished results. [b] Taken from reference 12 in the text.

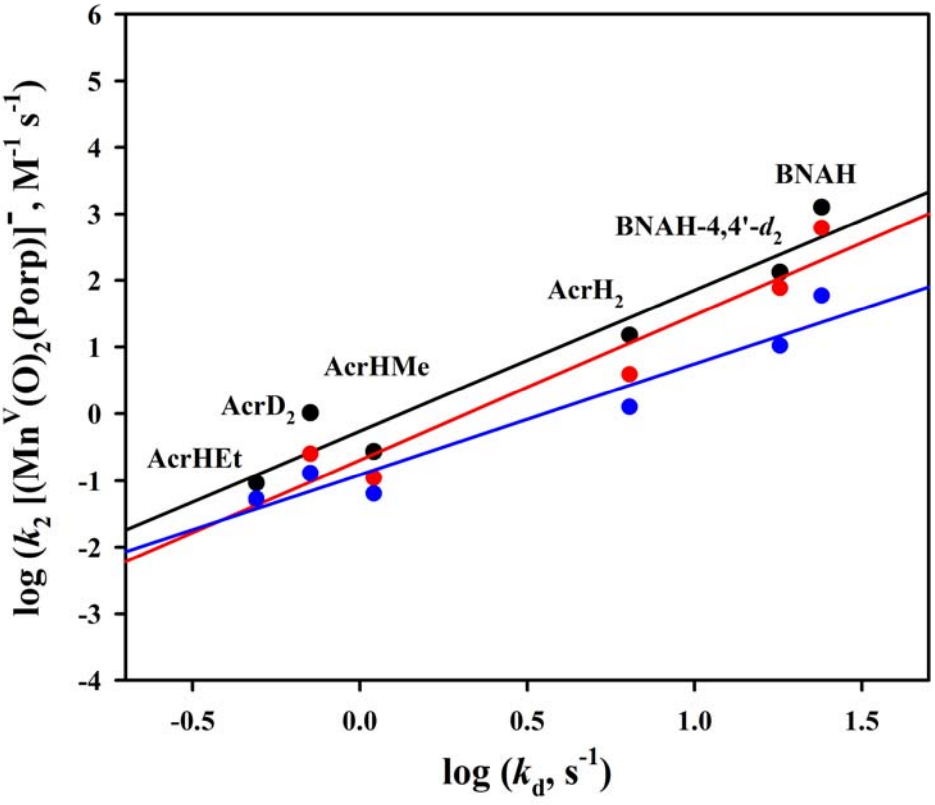

Fig. S1 Plot of log k_2 for the reactions of NADH analogues with $[Mn(V)(O)_2(TPFPP)]^-$ (**1**) (black circles), $[Mn(V)(O)_2(TDFPP)]^-$ (**2**) (red circles), and $[Mn(V)(O)_2(TDCPP)]^-$ (**3**) (blue circles) vs log k_d for the deprotonation of $AcrHR^{\bullet+}$ in MeCN at 298 K.

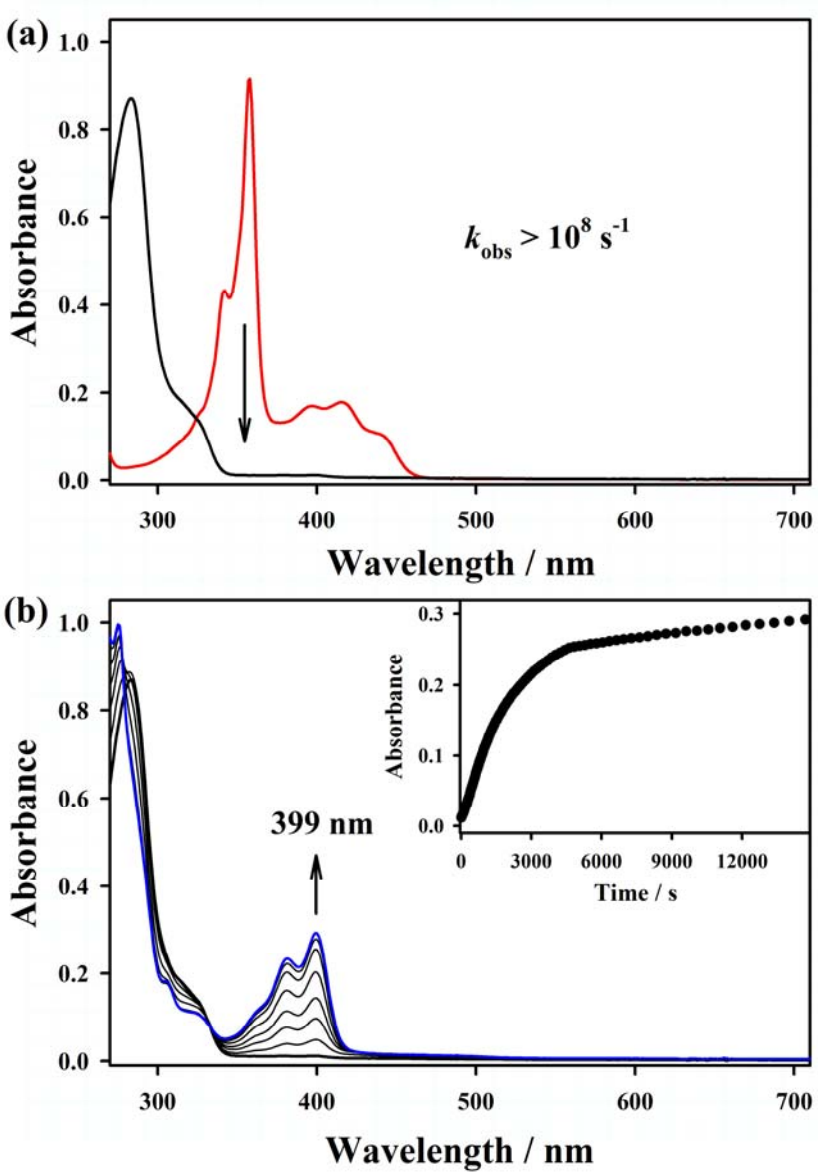

Fig. S2 (a) UV-vis spectral change of 10-methylacridinium [$AcrH^+$] (0.05 mM) (red line) to 9-hydroxy-9,10-dihydro-10-methylacridine [AcrH(OH)] (black line) upon addition of 20 equiv tetra-*n*-butylammonium hydroxide to a solution of $AcrH^+$ (0.05 mM) in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) at 25 ^oC. The disappearance of $AcrH^+$ was $k_{obs} > 10^8$ s^{-1}. (b) UV-vis spectral changes showing the conversion of AcrH(OH) (0.05 mM; black line) to 10-methylacridone [Acr(O)] (blue line) in a solvent mixture of CH_3CN and CH_2Cl_2 (1:1) at 25 ^oC. The AcrH(OH) species did not react with $[Mn^V(O)_2(Porp)]^-$, but were slowly converted to Acr(O) in air. Inset shows time course of the formation of Acr(O) monitored at 399 nm.

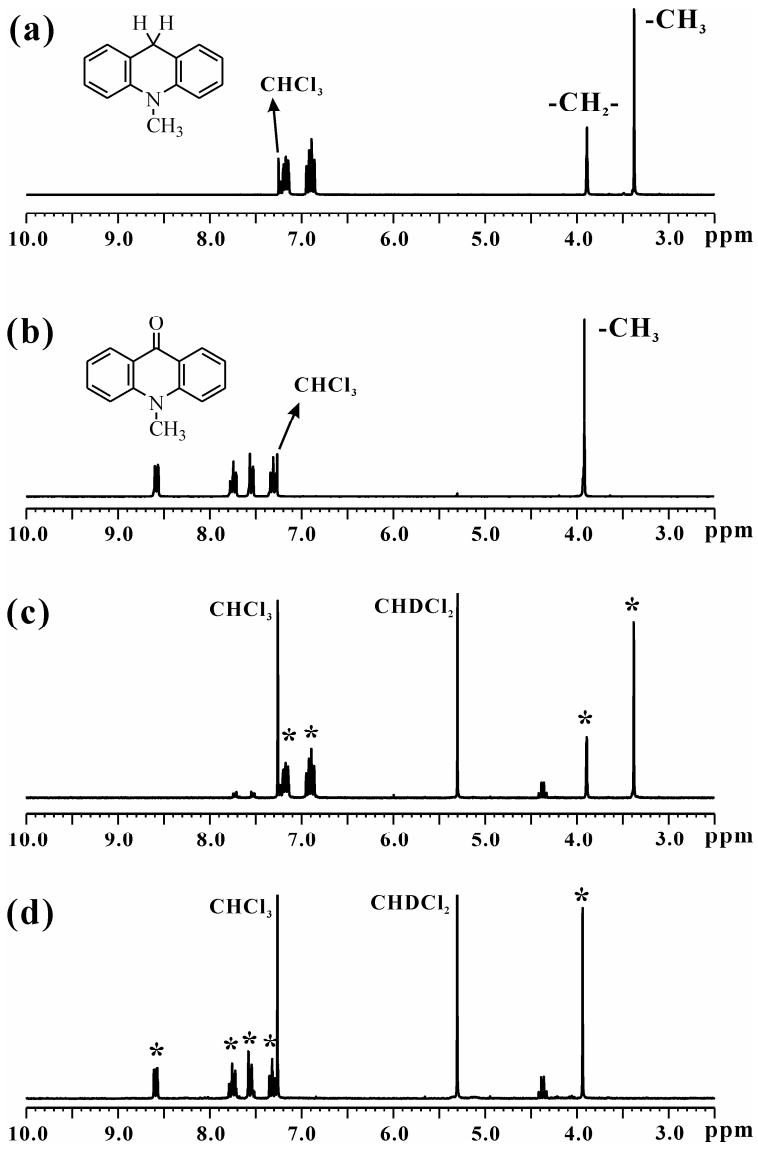

Fig. S3 ^{1}H-NMR spectra (250 MHz) of the authentic reference samples and the products obtained from the completed reaction of $[Mn^{V}(O)_2(TPFPP)]^{-}$ and 10-methyl-9,10-dihydroacridine ($AcrH_2$) in $CDCl_3$ at 25 ^{o}C. (a) and (b) show ^{1}H-NMR spectra of the authentic samples, $AcrH_2$ and 10-methyl-acridone (Acr(O)), respectively. Pure product of the completed reaction of $[Mn^{V}(O)_2(TPFPP)]^{-}$ and $AcrH_2$ at 25 ^{o}C was obtained after column chromatography, which was packed with silicagel 60. (c) shows ^{1}H-NMR spectrum of the unreacted $AcrH_2$ obtained from the first fraction, which was eluted by 100% CH_2Cl_2. (d) shows ^{1}H-NMR spectrum of the product obtained from the second fraction, which was eluted by 90% CH_2Cl_2 and 10% acetone. This spectrum is completely matched with that of Acr(O) authentic sample.