Supplementary material

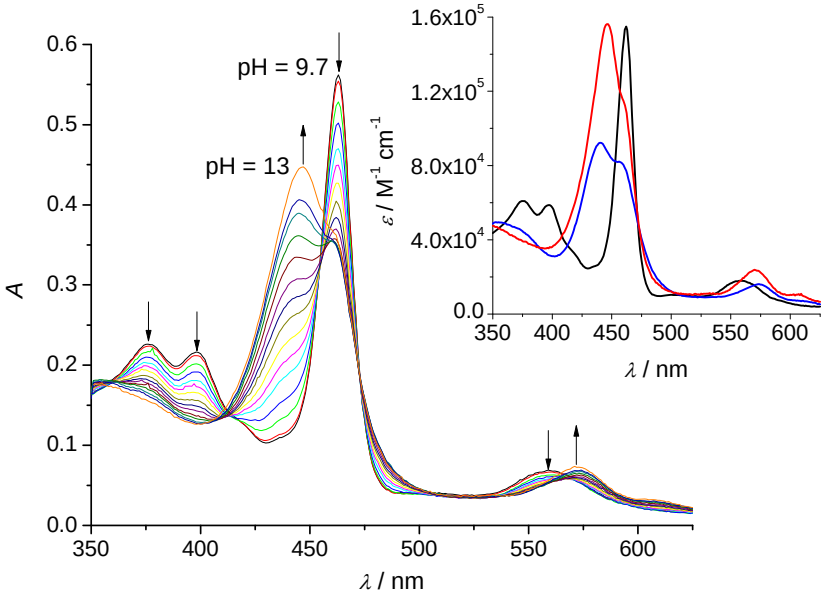

Figure S1. A typical titration profile of 3.6 μM Mn^{III}TE-3-PyP in 2 M $NaClO_4$ with 0.2 M NaOH (θ = 25 °C, l = 1 cm). The pH values of the solution were varied within the pH-range 9.7-13 (for the sake of clarity not all measured spectra are shown). **Inset:** The theoretical spectra of the protonated, (——), mono-deprotonated (——), and double deprotonated (——) species.

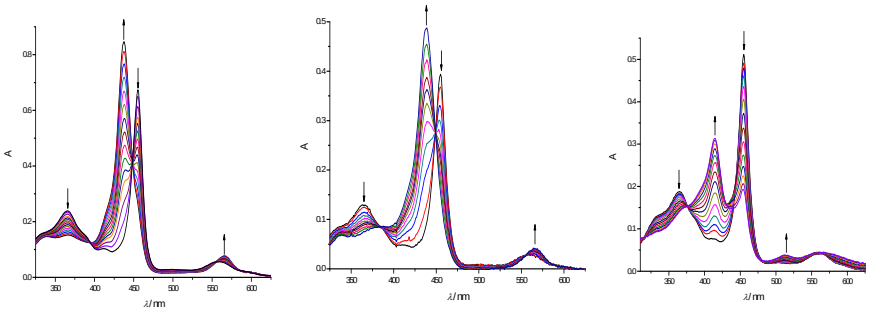

Figure S2. Time-dependent spectral changes of Mn^{III}TE-2-PyP in an anaerobic cell. **Left:** Condition: [Mn^{III}TE-2-PyP] = 49 μM, **pH = 8** (0.05 M NaH_2PO_4), I = 0.1 M (NaCl), θ = 25 °C, l = 0.1 cm, E_{cell} = -450 mV *vs.* Ag/AgCl. **Middle:** Condition: [Mn^{III}TE-2-PyP] = 29 μM, **pH = 4** (0.05M CH_3COONa), I = 0.1 M (NaCl), θ = 25 °C, l = 0.1 cm, E_{cell} = -450 mV *vs.* Ag/AgCl. **Right:** Condition: [Mn^{III}TE-2-PyP] = 37 μM, **pH = 1.5**, I = 0.1 M (NaCl), θ = 25 °C, l = 0.1 cm, E_{cell} = -450 mV *vs.* Ag/AgCl

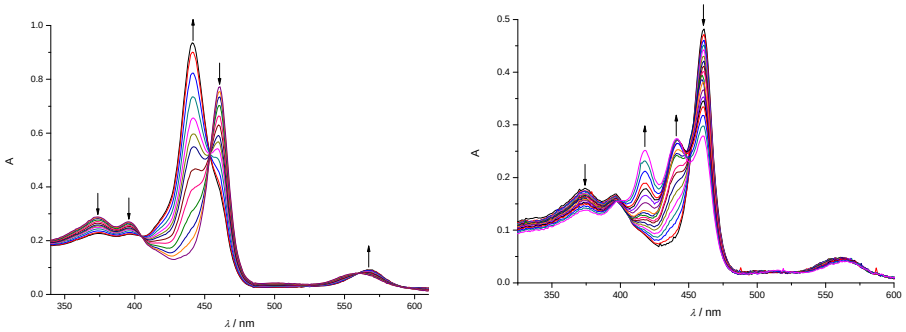

Figure S3. Time dependent spectral changes of Mn^{III}TE-3-PyP in an anaerobic cell. **Left:** Condition: [Mn^{III}TE-3-PyP] = 50 μM, **pH = 9** (0.025M $Na_2B_4O_7$), I = 0.1 M (NaCl), θ = 25 °C, l = 0.1 cm, E_{cell} = -600 mV *vs.* Ag/AgCl. **Right:** Condition: [Mn^{III}TE-3-PyP] = 31 μM, **pH = 4** (0.05M CH_3COONa), I = 0.1 M (NaCl), θ = 25 °C, l = 0.1 cm, E_{cell} = -600 mV *vs.* Ag/AgCl.

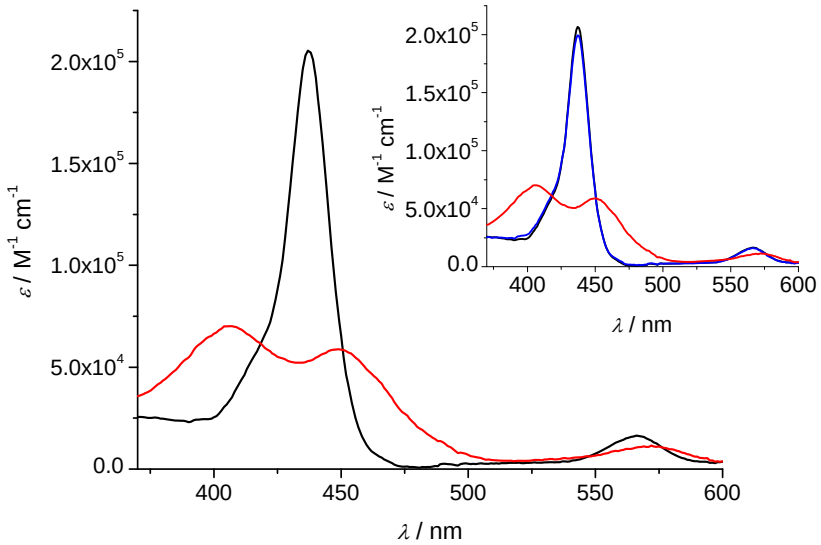

Figure S4. The theoretical spectra of the protonated (——) and deprotonated (——) species of Mn^{III}TE-2-PyP predicted according to the 2-species model. **Inset**: The theoretical spectra of the fully protonated (——), monodeprotonated (——), and fully deprotonated (——) species predicted according to the 3-species model.

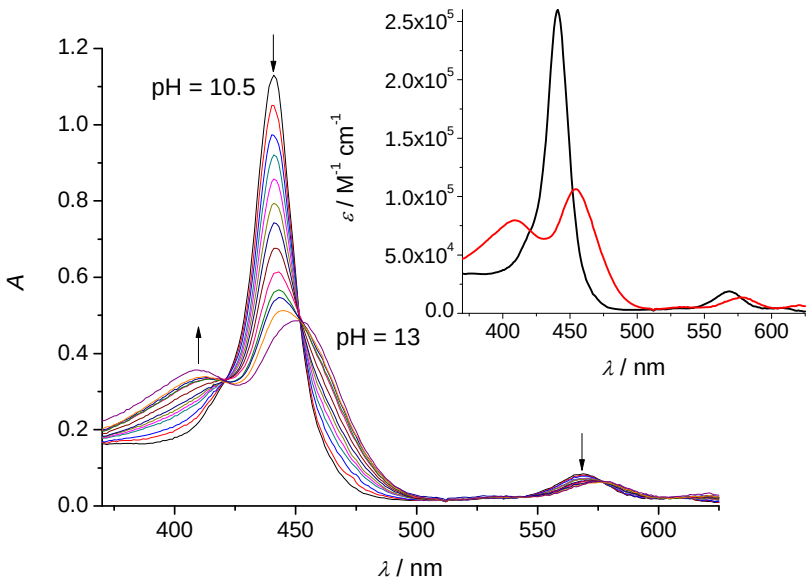

Figure S5. A typical titration profile of 4 μM Mn^{II}TE-3-PyP in 2 M $NaClO_4$ with 0.2 M NaOH (θ = 25 °C, l = 1 cm). The pH values of solution were varied within the pH-range 10.5-13.0 (for the sake of clarity not all measured spectra are shown). **Inset:** The theoretical spectra of the protonated (——) and deprotonated (——) species predicted according to the 2-species model. Spectra obtained at pH < 10.5 are shown in Figure S8.

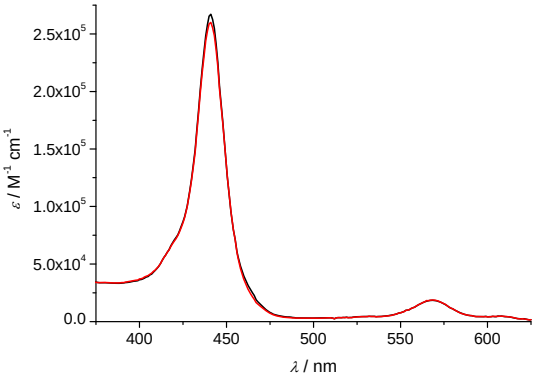

Figure S6. The theoretical spectra of Mn^{II}TE-3-PyP species obtained from the spectral changes observed in the spectroelectrochemical experiment at pH 9 (——) and in the pH-titration of Mn^{III}TE-3-PyP^{5+} in the presence of ascorbic acid recorded at pH 10.5. (——).

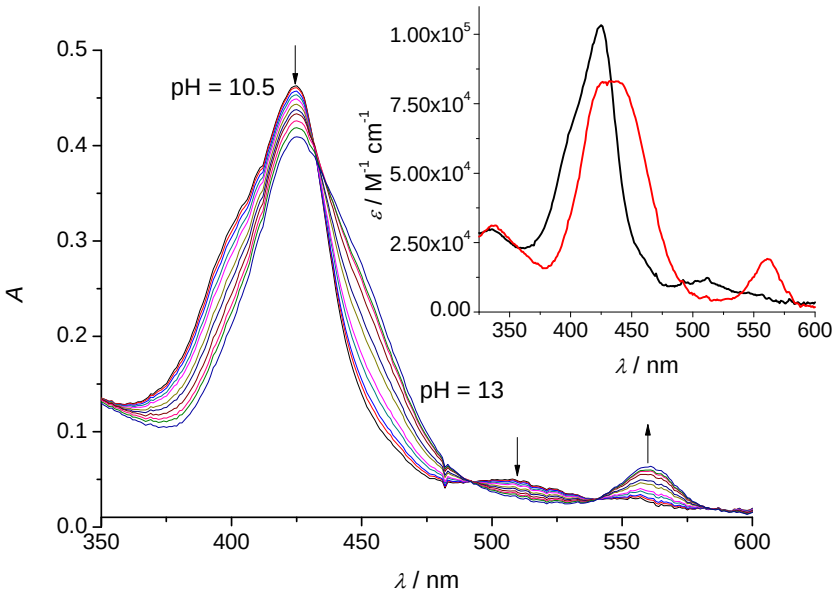

Figure S7. A typical titration profile of 4.8 μM Mn^{IV}TE-3-PyP in 2 M $NaClO_4$with 0.2 M NaOH (θ = 25 °C, l = 1 cm) in the presence of 0.1 mM $[Mo(CN)_8]^{3-}$. The pH values of the solution were varied within the pH-range 10.5-13. (for the sake of clarity not all measured spectra are shown). **Inset:** The theoretical spectra of the protonated (—) and deprotonated (—) species.

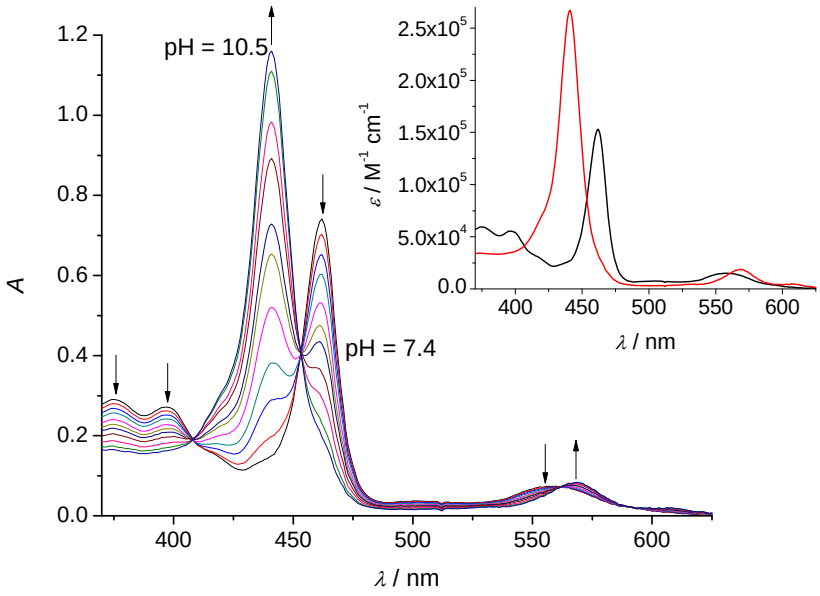

Figure S8. A typical titration profile of (4 μM Mn^{III}TE-3-PyP + 20 mM ascorbic acid + 0.5 mM $[Fe(CN)_6]^{3-}$) in 2 M $NaClO_4$with 0.2 M NaOH (θ = 25 °C, l = 1 cm). The pH values were varied within the pH-range 7.4-10.5 (for the sake of clarity not all measured spectra are shown). **Inset:** The theoretical spectra of $(H_2O)_2Mn^{III}$TE-3-PyP^{5+} (—) and $(H_2O)_2Mn^{II}$TE-3-PyP^{4+} (—).

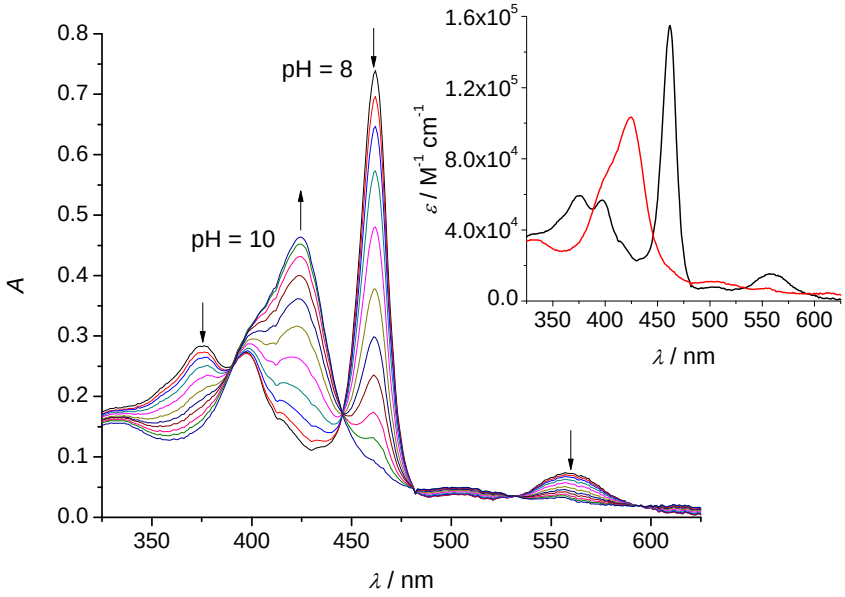

Figure S9. A typical titration profile of 4.8 μM Mn^{III}TE-3-PyP in 2 M $NaClO_4$ with 0.2 M NaOH (θ = 25 °C, l = 1 cm) in the presence of 0.1 mM $[Mo(CN)_8]^{3-}$ and 0.1 mM $[Mo(CN)_8]^{4-}$. The pH values of the solution were varied within the pH-range 8-10 (for the sake of clarity not all measured spectra are shown). **Inset:** The theoretical spectra of the reduced (——) and oxidized forms of MnTE-3-PyP (——).

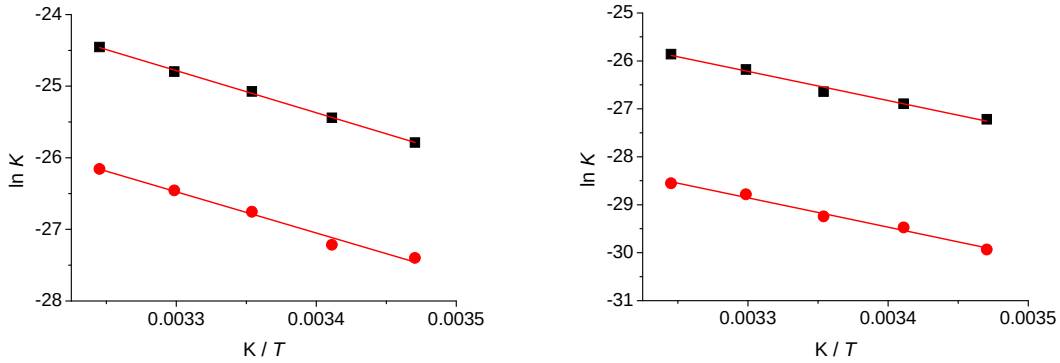

Figure S10. van't Hoff plots for deprotonation constants of Mn^{III}Ps, K_{a1} (■) and K_{a2} (●), I = 2 M ($NaClO_4$): **left:** Mn^{III}TE-2-PyP, **right:** Mn^{III}TE-3-PyP.

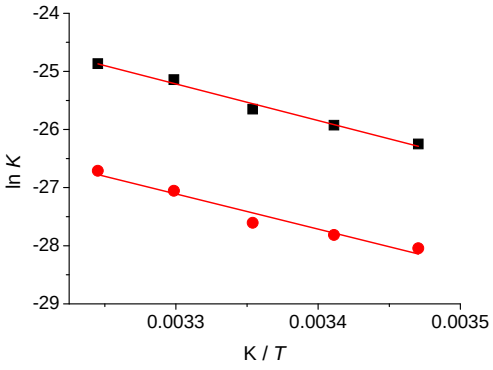

Figure S11. van't Hoff plots for deprotonation constants K''_{a1} of Mn^{IV}Ps, I = 2 M ($NaClO_4$): Mn^{IV}TE-2-Pyp (■),Mn^{IV}TE-3-Pyp (●).

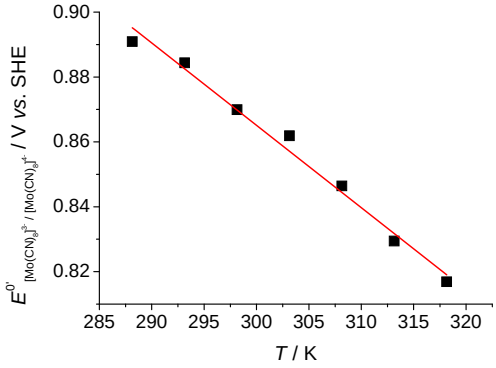

Figure S12. Temperature dependence of the formal potential for the reduction of 1 mM octacyanomolybdate, I = 2 M ($NaClO_4$).

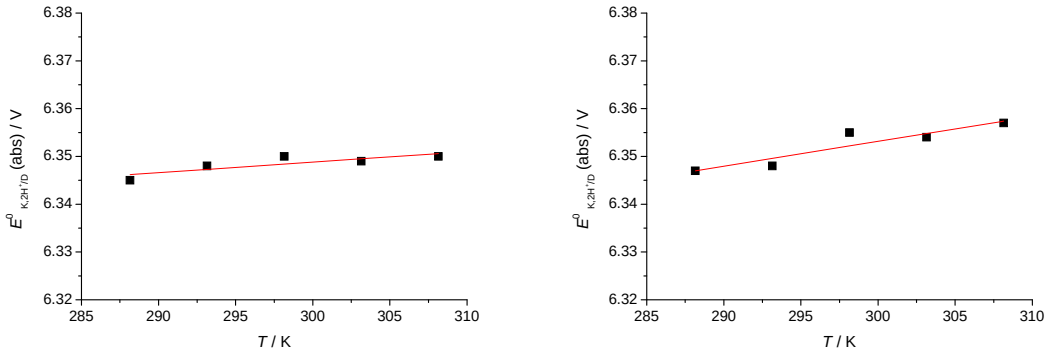

Figure S13. Temperature dependence of the formal potential for the redox couple K,2H$^+$/D, as assigned in Scheme 1, I = 2 M ($NaClO_4$): **left:** MnTE-2-PyP, **right:** MnTE-3-PyP.

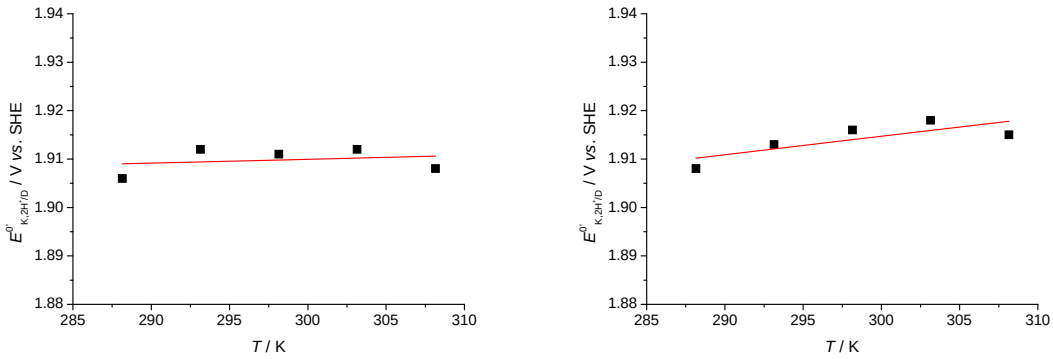

Figure S14. Temperature dependence of the formal potential for the redox couple K,2H$^+$/D *vs*. SHE, as assigned in Scheme 1, I = 2 M ($NaClO_4$): **left:** MnTE-2-PyP, **right:** MnTE-3-PyP.

Table S1. Thermodynamic data for the accessible redox couples of the studied manganese porphyrin complexes obtained in 2 M $NaClO_4$. The values were calculated from absolute redox potentials.

Couple	Parameter	
	$\Delta H \pm \sigma$[a]	$\Delta S \pm \sigma$[b]
$(O)(H_2O)Mn^{IV}TE\text{-}2\text{-}PyP^{4+} + 2H^+ + e^- \rightarrow (H_2O)_2Mn^{III}TE\text{-}2\text{-}PyP^{5+}$	-606 ± 2	21 ± 7
$(O)(H_2O)Mn^{IV}TE\text{-}2\text{-}PyP^{4+} + H^+ + e^- \rightarrow (OH)(H_2O)Mn^{III}TE\text{-}2\text{-}PyP^{4+}$	-557 ± 5	-23 ± 10
$(O)(H_2O)Mn^{IV}TE\text{-}2\text{-}PyP^{4+} + e^- \rightarrow (O)(H_2O)Mn^{III}TE\text{-}2\text{-}PyP^{3+}$	-509 ± 8	-85 ± 21
$(O)(OH)Mn^{IV}TE\text{-}2\text{-}PyP^{4+} + 2H^+ + e^- \rightarrow (OH)(H_2O)Mn^{III}TE\text{-}2\text{-}PyP^{5+}$	-609 ± 8	14 ± 21
$(O)(H_2O)Mn^{IV}TE\text{-}3\text{-}PyP^{4+} + 2H^+ + e^- \rightarrow (H_2O)_2Mn^{III}TE\text{-}3\text{-}PyP^{5+}$	-598 ± 4	50 ± 12
$(O)(H_2O)Mn^{IV}TE\text{-}3\text{-}PyP^{4+} + H^+ + e^- \rightarrow (OH)(H_2O)Mn^{III}TE\text{-}3\text{-}PyP^{4+}$	-547 ± 7	-1 ± 21
$(O)(H_2O)Mn^{IV}TE\text{-}3\text{-}PyP^{4+} + e^- \rightarrow (O)(H_2O)Mn^{III}TE\text{-}3\text{-}PyP^{3+}$	-496 ± 10	-73 ± 32
$(O)(OH)Mn^{IV}TE\text{-}3\text{-}PyP^{4+} + 2H^+ + e^- \rightarrow (OH)(H_2O)Mn^{III}TE\text{-}3\text{-}PyP^{5+}$	-597 ± 13	58 ± 40

[a] Reaction enthalpies are given in kJ mol^{-1}. [b] Reaction entropies are given in J K^{-1} mol^{-1}.

Table S2. The formal reduction potentials vs. SHE for all experimentally available redox couples assigned as in Scheme 1, obtained by the spectrophotometric pH titrations at θ = 25 °C, I = 2 M ($NaClO_4$).

Mn^X/Mn^{X-1}	Redox couple	$E^{0'}$ / V		
		MnTE-2-PyP	**MnTE-3-PyP**	**MnTnBu-2-PyP**[a]
Mn(III)/Mn(II)	$D/B,H^+$	–0.550	–0.764	–0.506
	$E,H^+/A$	+0.789	+0.632	+0.875
	$F,2H^+/A$	+1.477	+1.384	+1.604
	$F,H^+/B$	+0.782	+0.671	+0.895
Mn(IV)/Mn(III)	$K,2H^+/D$	+1.910	+1.915	+1.800
	$K,H^+/E$	+1.266	+1.231	+1.128
	$L,3H^+/D$	+2.569	+2.624	+2.497
	$L,2H^+/E$	+1.925	+1.940	+1.825
	$L,H^+/F$	+1.237	+1.189	+1.095
Mn(IV)/Mn(II)	$K/A,2H^+$	+1.028	+0.932	+1.002
	$L/A,3H^+$	+0.680	+0.575	+0.647
	$K/B,H^+$	+1.357	+1.286	+1.350
	$K/B,2H^+$	+1.009	+0.930	+0.995

[a] Values taken from Reference 13.