Supporting Information

Mn(V)(O) versus Cr(V)(O) Porphyrinoid Complexes: Structural Characterization and Implications for Basicity Controlling H-Atom Abstraction

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Materials. Compounds TBP_8CzH_3 and $Mn^V(O)(TBP_8Cz)$ (**2**) were synthesized according to published procedures.[1,2] The commercially available reagents triphenylphosphine (PPh_3), chromium hexacarbonyl, and tetrabutylammonium hexafluorophosphate were obtained from Sigma-Aldrich at the best available purity and used as received. The H-atom donor 2,2,6,6-tetramethylpiperidine hydroxylamine (TEMPOH) and its deuterated analogue TEMPOD were synthesized according to published procedures.[3] Deuterated chloroform ($CDCl_3$, 0.03% v/v TMS) for NMR was purchased from Cambridge Isotopes, Inc. Toluene was purified via a Pure-Solv solvent purification system from Innovative Technologies, Inc, and all other solvents were purchased and used as received.

Instrumentation. UV-vis spectroscopy was performed on a Hewlett-Packard 8452 diode-array spectrophotometer equipped with HPChemstation software. ^1H-NMR spectra were recorded on a Bruker Avance 400 NMR instrument at 400 MHz. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX spectrometer equipped with a Bruker ER 041 X G microwave bridge and a continuous-flow liquid helium cryostat (ESR900) coupled to an Oxford Instruments TC503 temperature controller. Cyclic voltammetry measurements were undertaken in methylene chloride using a BAS 100B electrochemical analyzer with a glassy carbon working electrode and a platinum wire auxiliary electrode. Potentials were recorded versus an $Ag/AgNO_3$ electrode. Scans were run at 25 mV/s under an Ar atmosphere using $[Bu_4N][PF_6]$ (0.1 M) as the supporting electrolyte.

Single Crystal X-ray Crystallography. All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Versions 1.171.36.32 or

1.171.37.31, Agilent Technologies, 2013-2014). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 (Sheldrick, 2013) and was refined on F^2 with SHELXL-2013 (Sheldrick, 2013). Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms.

Structure of $\mathrm{Mn^V(O)(TBP_8Cz)}$. One of the eight tert-butylphenyl (TBP) groups is found to be disordered over two orientations. The occupancy factor of the major component of the disorder refines to 0.910(4). The $\mathrm{Mn^V{\equiv}O}$ fragment is also slightly disordered, with the oxo ligand coordinated on either side of the plane of the corrolazine ligand. The occupancy factor of the major component of the disorder refines to 0.8671(7). The crystal lattice contains some amount of ordered and disordered lattice MeCN solvent molecules. The occupancy factors of the ordered lattice MeCN solvent molecules were refined using free variables, and there are *ca.* 1.94 ordered MeCN molecules per Mn complex. Some electron density in the asymmetric unit – i.e., some amount of very disordered solvent MeCN molecules with partial occupancy – has been taken out in the final refinement using the SQUEEZE procedure (SQUEEZE details are provided in the CIF file, Spek, 2003).

$\mathrm{Mn^V(O)(TBP_8Cz)}$: Fw = 1506.43, dark thin brown-purple lath, $0.62 \times 0.06 \times 0.02$ mm^3, triclinic, *P*-1 (no. 2), $a = 13.2613(4)$, $b = 16.7068(5)$, $c = 22.4780(8)$ Å, $\alpha = 75.669(3)$, $\beta = 75.927(3)$, $\gamma = 78.815(3)°$, $V = 4632.6(3)$ Å^3, $Z = 2$, $D_x = 1.080$ g cm^{-3}, $\mu = 1.533$ mm^{-1}, abs. corr. range: 0.674–0.972. 55653 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.62$ Å^{-1}. 18021 Reflections were unique ($R_{\text{int}} = 0.0611$), of which 12850 were observed [$I > 2\sigma(I)$]. 1120 Parameters were refined using 357 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0580/0.1339. $R1/wR2$ [all refl.]: 0.0878/ 0.1490. S = 1.009. Residual electron density found between −0.51 and 0.41 e Å^{-3}.

Structure of $\mathbf{Cr^{V}(O)(TBP_8Cz)}$. Two of the eight tert-butylphenyl (TBP) groups are found to be disordered over two orientations. The occupancy factors of the two major components of the disorder refine to 0.54(2) and 0.760(5). The Cr^{V}≡O fragment is also slightly disordered, with the oxo ligand coordinated on either side of the plane of the corrolazine ligand. The occupancy factor of the major component of the disorder refines to 0.9175(8). The crystal lattice contains some amount of ordered and disordered lattice MeCN solvent molecules. The occupancy factors of the ordered lattice MeCN solvent molecules were refined using free variables, and there are *ca.* 1.94 ordered MeCN molecules per Cr complex. Some electron density in the asymmetric unit – *i.e.*, some amount of very disordered solvent MeCN molecules with partial occupancy – has been taken out in the final refinement using the SQUEEZE procedure (SQUEEZE details are provided in the CIF file, Spek, 2003). The crystal that was mounted on the diffractometer was not single, but rather two crystals stuck together with random orientations (the crystal was not twinned). The diffraction patterns of components 1 and 2 are related by a rotation of *ca.* 2.80° around the reciprocal vector 0.7123**a*** + 0.6150**b*** + 0.3382**c***. Data integration of both components was performed using CrysAlisPro (Version 1.171.37.31 Agilent Technologies, 2014), and a HKLF 5 file was made. In order to perform the

SQUEEZE procedure , the detwinning option was set in SHELXL-2013 via a LIST 8 style FCF. The BASF scale factor refines to 0.2615(14).

$Cr^{V}(O)(TBP_8Cz)$: Fw = 1503.50, brown plate, 0.20 × 0.10 × 0.03 mm^3, triclinic, *P*-1 (no. 2), $a = 13.2521(4)$, $b = 16.7844(5)$, $c = 22.5120(8)$ Å, $\alpha = 75.947(3)$, $\beta = 75.899(3)$, $\gamma = 78.856(3)°$, $V = 4663.0(3)$ Å^3, $Z = 2$, $D_x = 1.071$ g cm^{-3}, $\mu = 1.381$ mm^{-1}, abs. corr. range: 0.803–0.967. 49216 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max} = 0.60$ Å^{-1}. 21055 Reflections were unique ($R_{int} = 0.0413$), of which 11606 were observed [$I > 2\sigma(I)$]. 1206 Parameters were refined using 675 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0491/0.1091. $R1/wR2$ [all refl.]: 0.0860/0.1174. S = 0.787. Residual electron density found between −0.42 and 0.40 e Å^{-3}.

Structure of $Cr^{III}(TBP_8Cz)(CH_3CN)_2$. The crystal lattice was found to contain a small impurity of $Cr^{V}(O)(TBP_8Cz)$ (starting material), and the occupancy factor of the minor impurity refines to 0.053(2). The crystal lattice also contains some amount of uncoordinated acetonitrile solvent molecules. The asymmetric unit contains one ordered (occupancy factor: 0.799(7)) and one disordered (the occupancy factors of the two components of the disorder refine to 0.588(8) and 0.341(8)) MeCN lattice molecules.

$Cr^{III}(TBP_8Cz)(CH_3CN)_2$: Fw = 1557.35, dark brown irregular block, 0.37 × 0.14 × 0.10 mm^3, triclinic, *P*-1 (no. 2), $a = 12.2628(3)$, $b = 18.0788(4)$, $c = 20.8997(5)$ Å, $\alpha = 75.7972(18)$, $\beta = 81.3662(19)$, $\gamma = 75.8437(19)°$, $V = 4335.30(18)$ Å^3, $Z = 2$, $D_x = 1.193$ g cm^{-3}, $\mu = 1.500$ mm^{-1}, T_{min}–T_{max}: 0.710–0.895. 56707 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max} = 0.62$ Å^{-1}. 17015 Reflections were unique ($R_{int} = 0.0267$), of which 14721 were observed [$I > 2\sigma(I)$]. 1117 Parameters were refined using 118 restraints. *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0637/0.1812. *R*1/*wR*2 [all refl.]: 0.0717/0.1908. S = 1.022. Residual electron density found between -0.50 and 0.90 e Å^{-3}.

References:

Sheldrick, G. M. Acta Cryst. **2008**, A*64*, 112

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Synthesis of Cr^{V}(O)(TBP$_8$Cz) (3). An amount of Cr(CO)$_6$ (0.14 mmol, 30 mg) was added to the metal-free corrolazine, TBP$_8$CzH$_3$ (44 mg, 0.032 mmol), in refluxing toluene under air. After 2 h, the toluene was removed under vacuum. The crude material was then purified by flash column chromatography on silica gel using CH$_2$Cl$_2$/hexanes (60:40) as eluent. The purified material was collected and dried under vacuum. Purity checked by UV-vis (Figure S2) and TLC. Crystals were obtained by slow vapor diffusion of acetonitrile into a toluene solution of **3** over the course of two weeks. Yield, (19 mg, 42%). R$_f$ = 0.77 (CH$_2$Cl$_2$:Hex, 60:40 on silica gel). UV-vis (CH$_2$Cl$_2$): λ_{max} (nm) ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1}) 448 (7.08) (soret), 653 (2.71) (Q band). *Anal. Calcd* for C$_{96}$H$_{104}$N$_7$CrO: C, 80.98; H, 7.36; N, 6.89. Found: C, 81.01; H, 7.62; N, 6.47.

Synthesis of Cr^{III}(TBP$_8$Cz)(CH$_3$CN)$_2$ (4). To an amount of **3** (0.9 mmol) in toluene was added PPh$_3$ (1 equiv) in a drybox, followed by vapor diffusion of acetonitrile into the reaction mixture. After two weeks, X-ray quality crystals of **4** were obtained. UV-vis: 465 nm (soret), 711 nm (Q band).

Evans method measurement. An amount of **3** (0.84 mM) in CDCl$_3$ containing 0.03 % TMS was placed in an NMR tube with a coaxial inner tube containing blank solvent (CDCl$_3$ with 0.03 % v/v TMS). ^{1}H NMR spectra were recorded at 298 K, and the chemical shift of the TMS peak in the presence of the paramagnetic **3** was compared to that of the TMS peak in the inner tube containing only the TMS standard (Figure S4). The effective spin-only magnetic moment was calculated by a simplified Evans method analysis[4] according to Eq. 1:

$$\mu_{eff} = 0.0618\sqrt{\frac{\Delta\nu \mathrm{T}}{2\mathrm{fM}}} \qquad (1)$$

where f is the oscillator frequency (MHz) of the superconducting spectrometer, T is the temperature (K), M is the molar concentration of the paramagnetic metal complex, and $\Delta\nu$ is the difference in frequency (Hz) between the two reference (TMS) signals.

EPR Spectroscopy of Cr^{III}(TBP$_8$Cz). To an amount of **3** (1.3 mmol) dissolved in toluene was added a toluene solution of PPh$_3$ (1.3 mmol, 1 equiv) in a drybox and allowed to react for 16 h. A subtle color change from a lustrous green to a deep, dull forest green was observed. This solution was loaded into an EPR tube, and an EPR spectrum (9.44 GHz, 294 K) was obtained. The same sample was annealed at 77 K and an EPR spectrum was recorded at 12 K (Figure S7).

Kinetics of the Reaction of 3 with TEMPOH(D). To an amount of **3** (2.4×10^{-8} mol) dissolved in degassed CH$_2$Cl$_2$ (2 mL) was added TEMPOH(D) (25 – 100 equiv) and the reaction was followed by UV-vis. The spectrum for **3** (448, 653 nm) isosbestically converted to a new spectrum for Cr^{III}(TBP$_8$Cz) (λ_{max} = 465, 711 nm). Plots of the decay in absorbance due to **3** at 653 nm versus time appeared to be pseudo-first-order up to 5 half-lives, and were well-fit by the first-order expression shown in Eq 2:

$$Abs_t = Abs_f + (Abs_0 - Abs_f)e^{-k_{obs}t} \qquad (2)$$

where Abs$_t$ = absorbance at time t, Abs$_f$ = final absorbance, Abs$_0$ = initial absorbance, and k_{obs} is the pseudo-first-order rate constant (Figure S8). A plot of k_{obs} versus concentration of TEMPOH was found to be linear, and the slope of the best-fit line gave k_2, the second-order rate constant (Figures S8, S9).

Quantitation of TEMPO• by X-band EPR Spectroscopy. An amount of **3** dissolved in toluene (1 mM) was mixed with TEMPOH (5 equivalents) under an Ar atmostphere. The reaction mixture was loaded into an EPR tube, and an EPR spectrum (294 K) (Figure S11, blue) was obtained. The 3-line signal centered at g = 2.00 is assigned to the TEMPO radical product and gives an 82% yield according to the stoichiometry given in Scheme 1. Quantification of the TEMPO• product was determined by double integration against a calibration curve of an external TEMPO radical standard. The 9-line signal centered at g = 1.987 is attributed to unreacted $Cr^{V}(O)$ complex (5% of starting **3** by quantitation). The starting TEMPOH substrate contained a small TEMPO• impurity (~7% by quantitation, Figure S11, red spectrum).

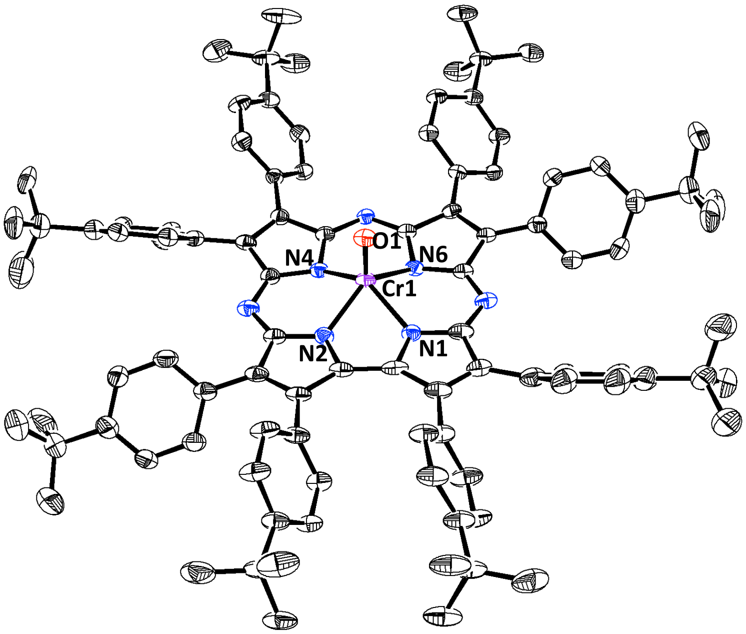

Figure S1. Displacement ellipsoid plot (50% probability level) of $Cr^{V}(O)(TBP_8Cz)$ (**3**) at 110(2) K. H-atoms and disorder are omitted for clarity.

Table S1. Comparison of atomic distances from X-ray diffraction for the first coordination sphere of $Cr^{V}(O)(TBP_8Cz)$ (**3**) and $Mn^{V}(O)(TBP_8Cz)$ (**2**).

M-X	M = Cr (Å)	M = Mn (Å)
M-O1	1.553(2)	1.5455(18)
M-N1	1.913(2)	1.8808(19)
M-N2	1.901(2)	1.873(2)
M-N4	1.900(2)	1.8855(18)
M-N6	1.916(2)	1.8974(19)
M-N_4 plane	0.613	0.588

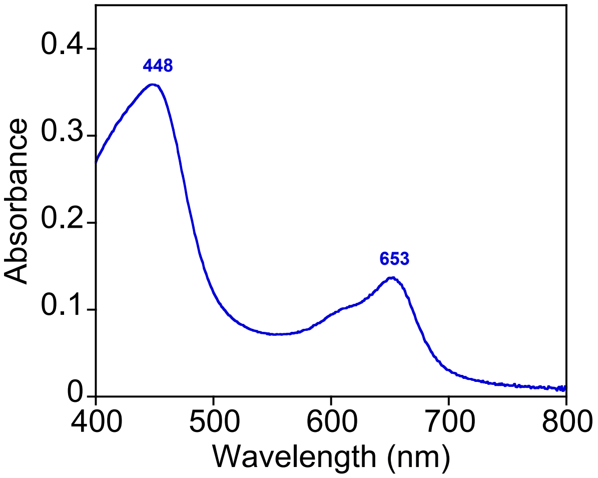

Figure S2. UV-visible spectrum of complex **3** (5 μM) in CH_2Cl_2.

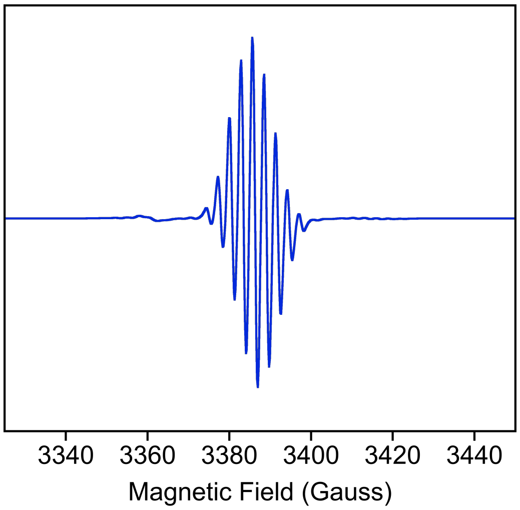

Figure S3. The EPR spectrum (9.44 GHz) of **3** (2.0 mM in CH_2Cl_2) was obtained at 294 K under non-saturating microwave power conditions. Hyperfine coupling to four equivalent nitrogen atoms gives a 9-line signal centered at g = 1.987 with a hyperfine coupling constant of $A_{iso}(^{14}N)$ = 2.9 G. Satellite signals at 3360 and 3414 G are attributed to coupling to the ^{53}Cr nucleus. Experimental conditions: Microwave frequency = 9.4400 GHz; Microwave power = 0.06 mW; Modulation amplitude = 1 G, Receiver gain = 5 × 10^3.

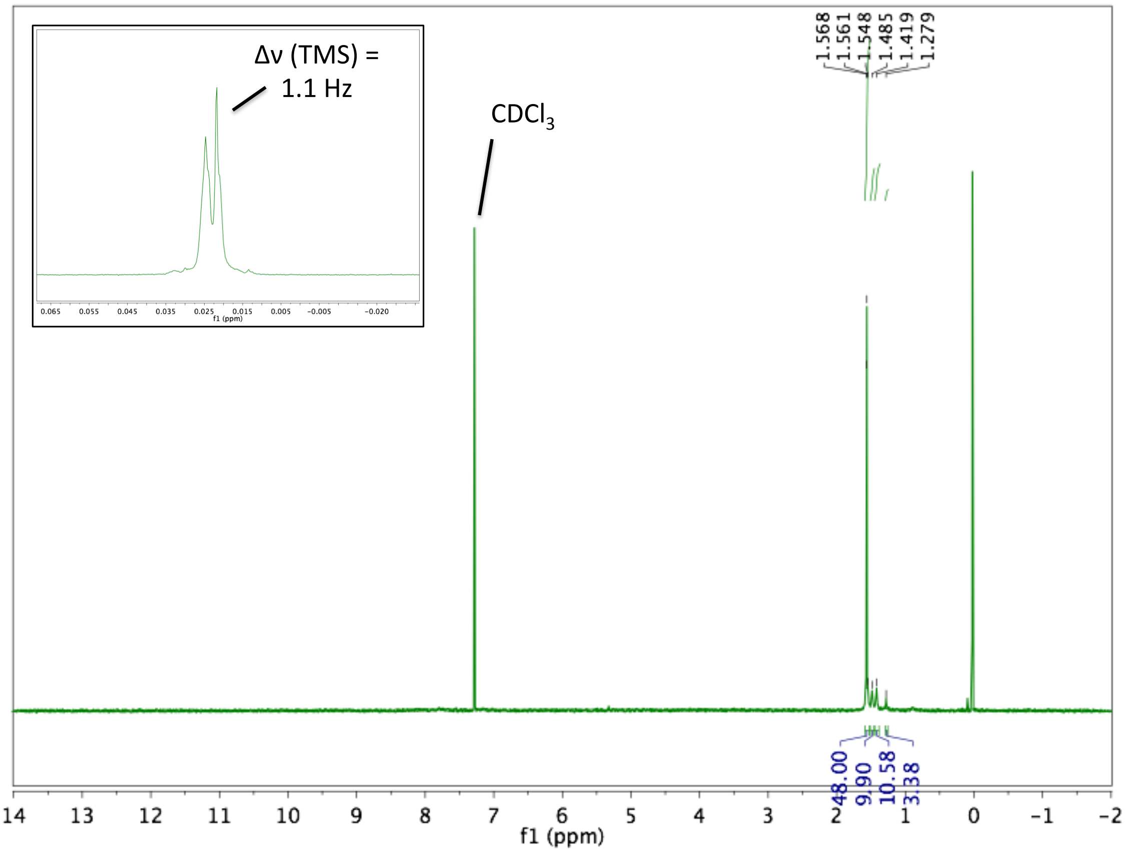

Figure S4. Evans method 1H-NMR spectrum of **3** (0.84 mM) in $CDCl_3$ (0.03 % TMS v/v).

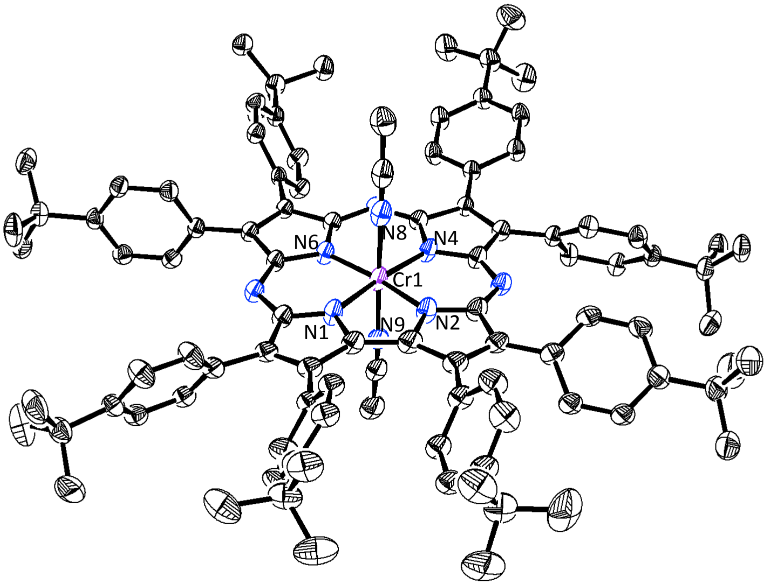

Figure S5. Displacement ellipsoid plot (50% probability) of $Cr^{III}(TBP_8Cz)(CH_3CN)_2$ (**4**) at 110(2) K. H-atoms and disorder are omitted for clarity.

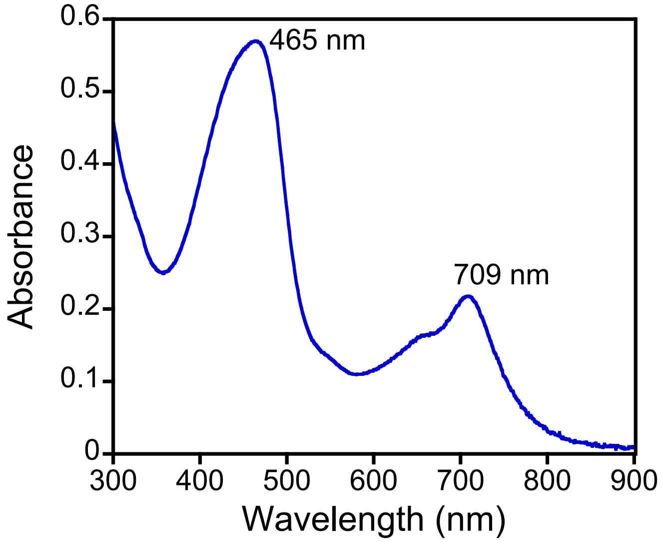

Figure S6. UV-visible spectrum of crystals of **4** redissolved in CH_2Cl_2.

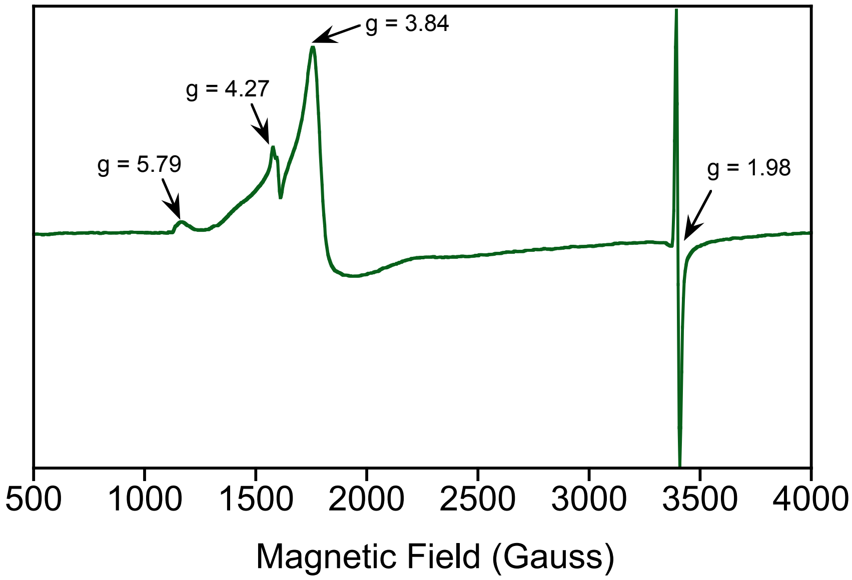

Figure S7. Low temperature (12 K) X-band EPR spectrum of $Cr^{III}(TBP_8Cz)$, synthesized by addition of PPh_3 (1 equiv) in toluene to **3** (2.6 mM). The sharp signal at g~2 is likely due to a small amount of unreacted $Cr^V(O)(TBP_8Cz)$, which has an S = ½ ground state (d^1 ion). Experimental conditions: Microwave frequency = 9.43 GHz; Microwave power = 0.2 mW; Modulation amplitude = 10 G, Receiver gain = 5×10^3.

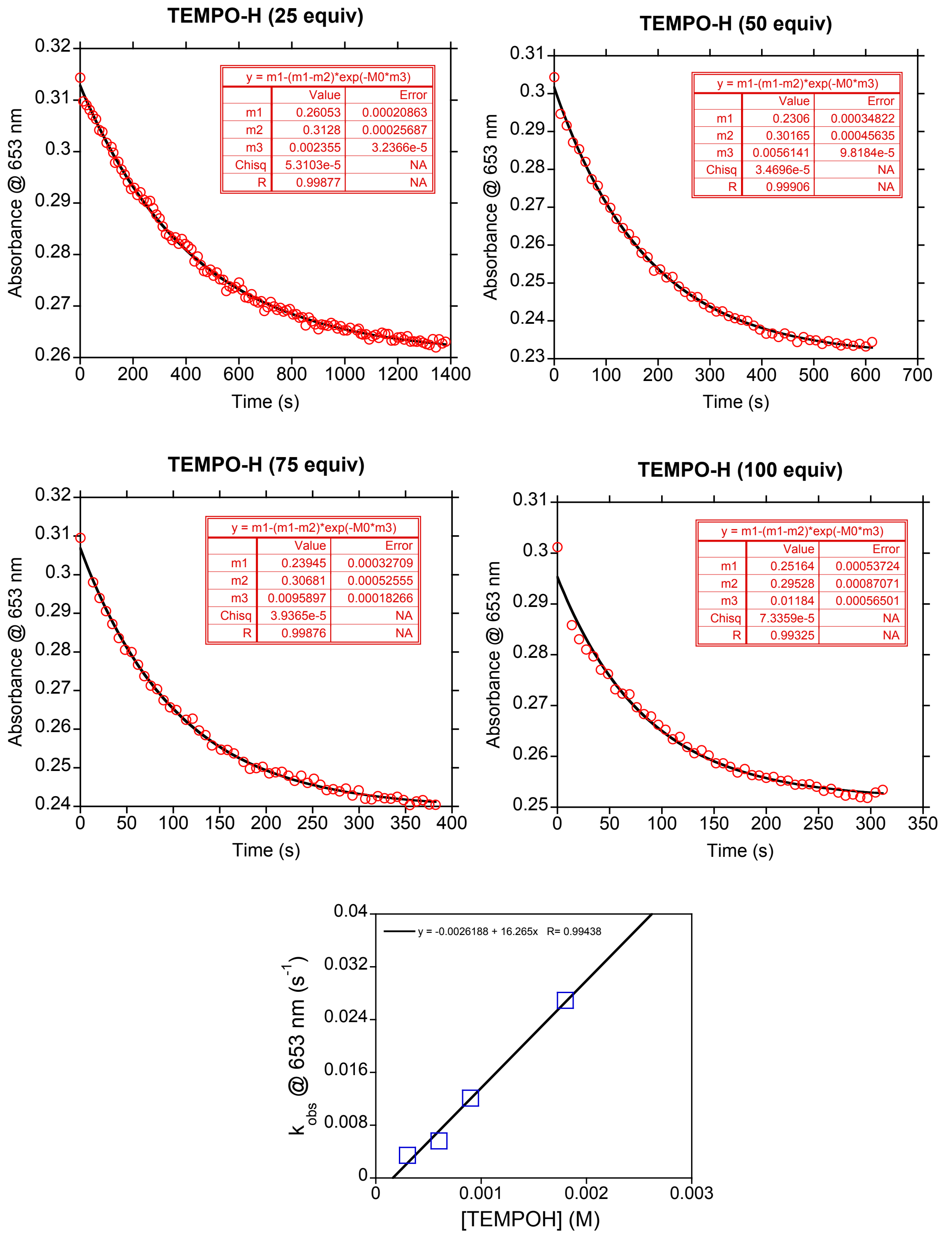

Figure S8. Kinetic plots at 653 nm versus time for the reaction between **3** and TEMPOH (25 – 100 equiv), and corresponding second order plot of k_{obs} versus [TEMPOH], where the slope of the best fit line gives $k_2 = 16 \pm 1\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

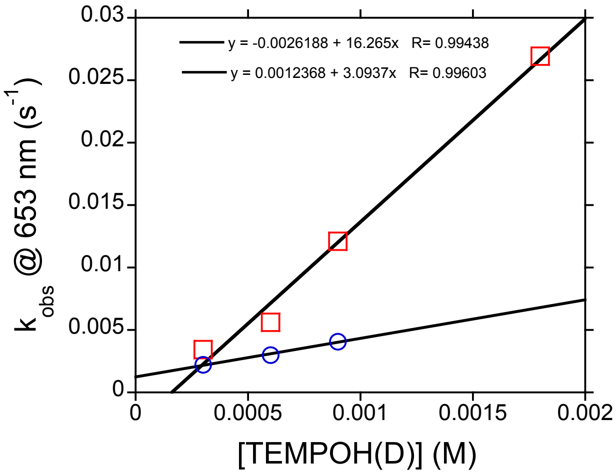

Figure S9. Second-order plots for the reaction of **3** with either TEMPOH (red squares) or TEMPOD (blue circles). The ratio of the second-order rate constants from the slopes of the best fit lines gives a KIE (k_H/k_D) of 5.2 ± 0.6.

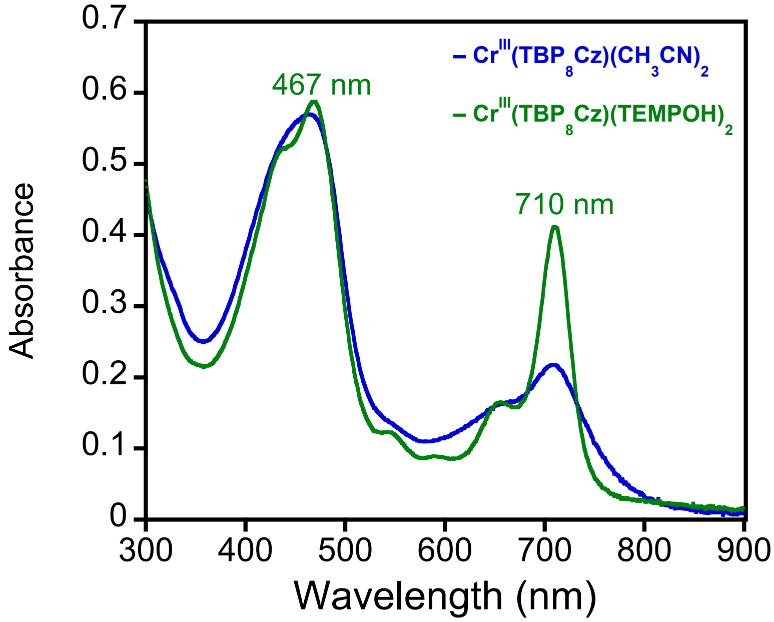

Figure S10. UV-visible spectra of crystals of **4** dissolved in CH_2Cl_2 (blue line) and after addition of excess TEMPOH to **4** (green line), which matches the final spectrum obtained from the reaction of **3** with TEMPOH.

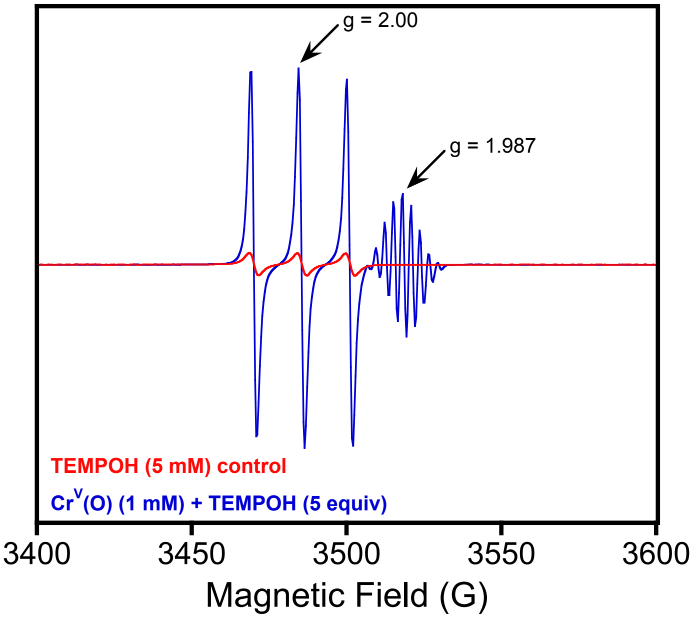

Figure S11. Room temperature EPR spectrum (9.77 GHz) for the reaction of **3** with TEMPOH (blue spectrum) in toluene to give an 82% yield of TEMPO• (3-line signal at g=2.00). The red spectrum is the starting TEMPOH substrate, with a TEMPO• impurity (~7 % by quantitation). Experimental conditions: Microwave power = 0.2 mW; Modulation amplitude = 1 G, Receiver gain = 5 × 10^3.

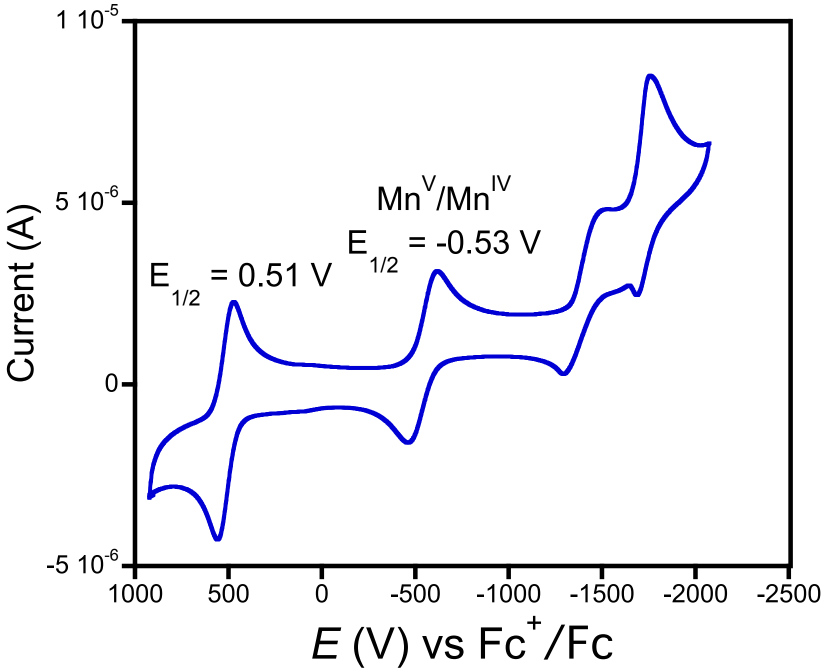

Figure S12. Cyclic voltammogram of a 0.33 mM solution of **2** in CH_2Cl_2 with 0.1 M $TBAPF_6$ as supporting electrolyte, scan rate 25 mV/s.

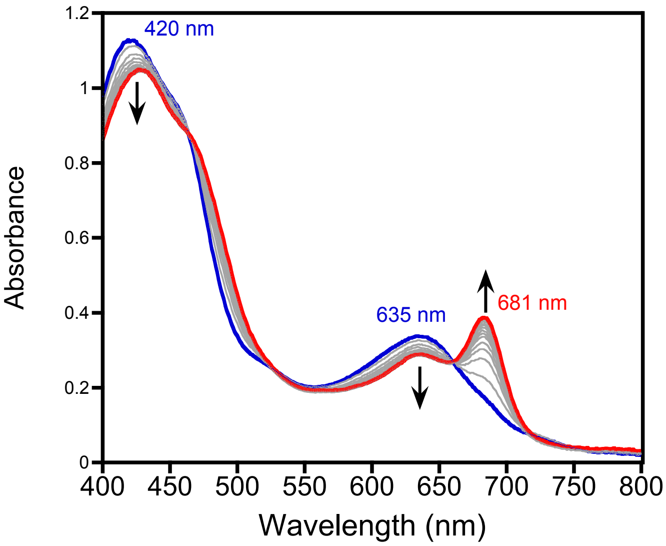

Figure S13. Time resolved UV-vis spectra for the reaction of **2** (0 – 3 h) with Me_2Fc ($E_{1/2}$ = -0.24 V versus Fc^+/Fc) and acetic acid (pK_a = 23.51). Effective BDFE for the reductant/acid pair is 81.6 kcal/mol.

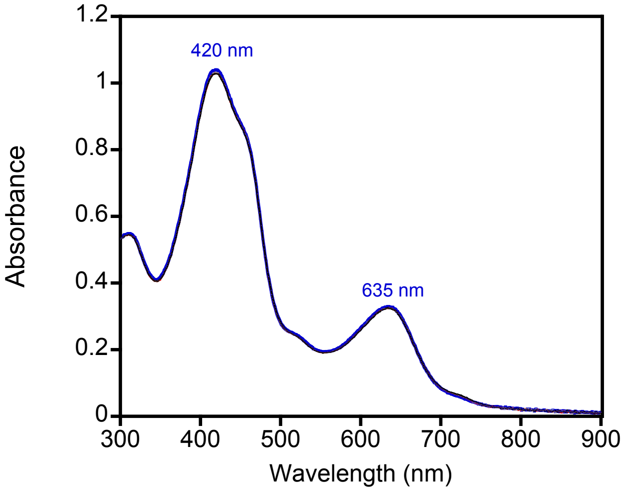

Figure S14. UV-vis spectrum for the mixture of **2** (0 – 3 h) with Fc ($E_{1/2}$ = 0.0 V versus Fc^+/Fc) and acetic acid (pK_a = 23.5), showing no change in the spectrum for **2**. Effective BDFE for the reductant/acid pair is 87.1 kcal/mol.

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