

Supporting Information for:

**Diiron and Dimanganese Complexes of a Binucleating Cyclam Ligand: Four-Electron
Reversible Oxidation Chemistry at High Potentials**

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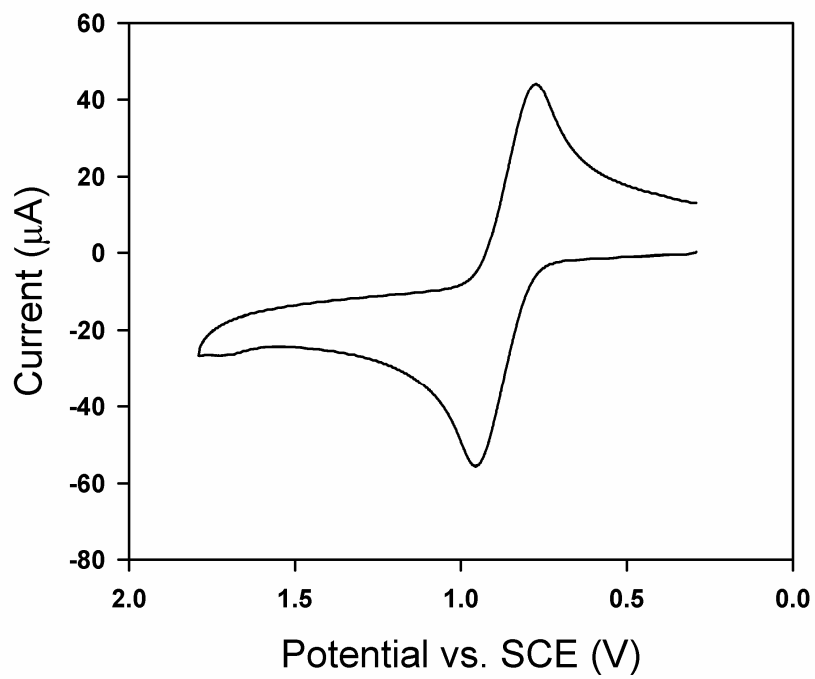


Figure S1. Cyclic voltammogram of **7** in acetonitrile (0.1 M Bu₄NClO₄).

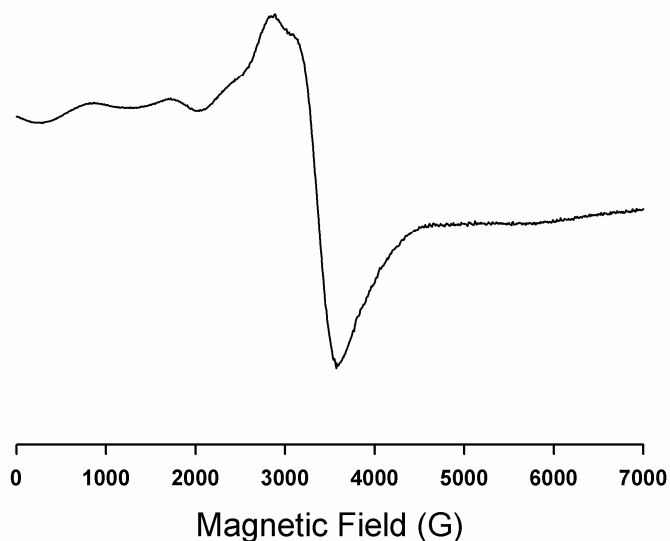


Figure S2. X-band EPR of $[(\text{cyclam}_2^i\text{PrO})\text{Mn}_2(\mu\text{-CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ (**4**) in MeCN. The spectrum was recorded on a 1 mM solution of **4** at 77 K. Microwave power, 2.0 mW; microwave frequency, 9.68 GHz; modulation amplitude, 10 G; gain, 2000.

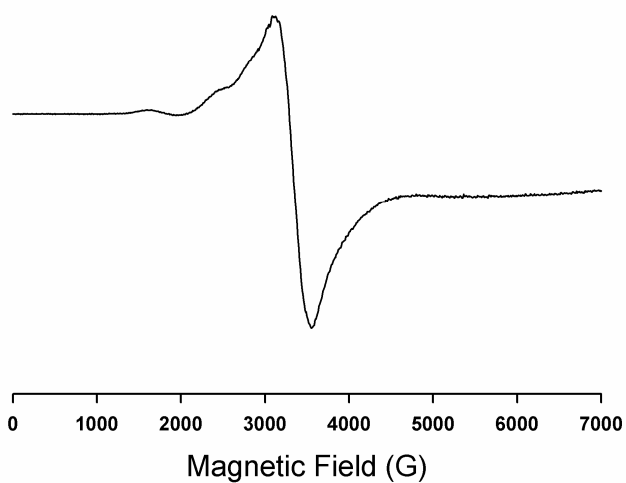


Figure S3. X-band EPR of $[(\text{cyclam}_2^i\text{PrO})\text{Mn}_2(\mu\text{-CF}_3\text{SO}_3)](\text{CF}_3\text{SO}_3)_2$ (**4**) in MeCN with 10% water. The spectrum was recorded on a 1 mM solution of **4** at 77 K. Microwave power, 2.0 mW; microwave frequency, 9.68 GHz; modulation amplitude, 10 G; gain, 2000.

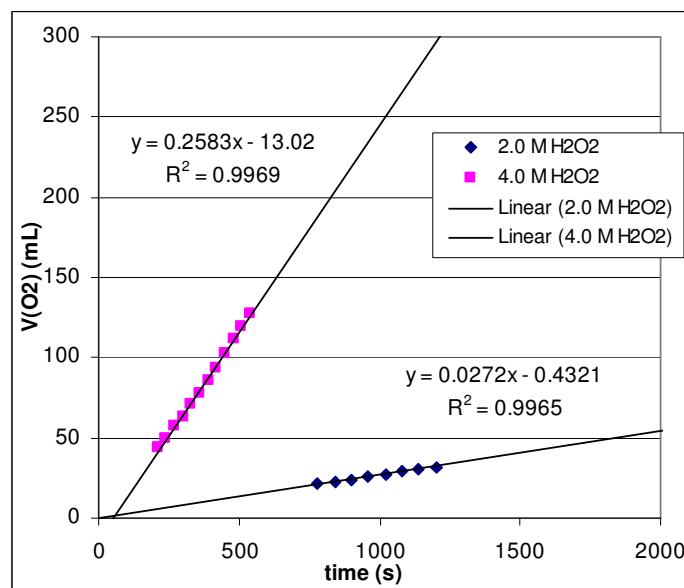
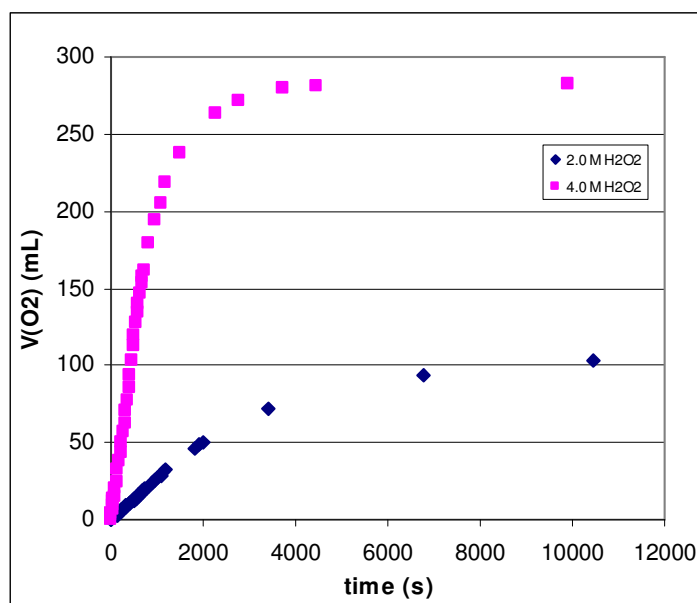


Figure S4. Top: Volume of O₂ produced vs. time for the disproportionation reaction of H₂O₂ catalyzed by compound **4**. Bottom: The same data expanded to display the first 10 minutes of the reaction. The symbols represent experimental data, and lines represent a fit to the data.

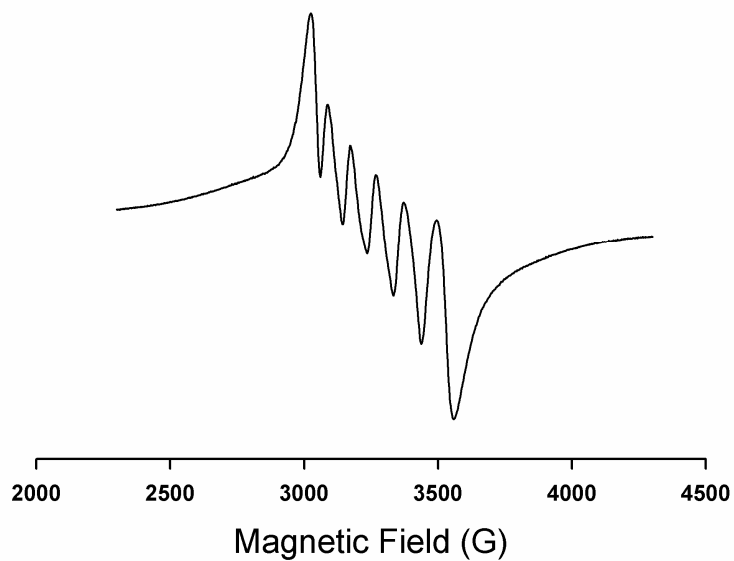


Figure S5. X-band EPR spectrum of the product from the reaction of [(cyclam₂ⁱPrO)Mn₂(μ-CF₃SO₃)](CF₃SO₃)₂ (**4**) with 15 equivalents of PhIO in MeCN. The spectrum was recorded on a reaction solution which was 1 mM in **4** at 77 K. Microwave power, 2.0 mW; microwave frequency, 9.68 GHz; modulation amplitude, 10 G; gain, 2000.

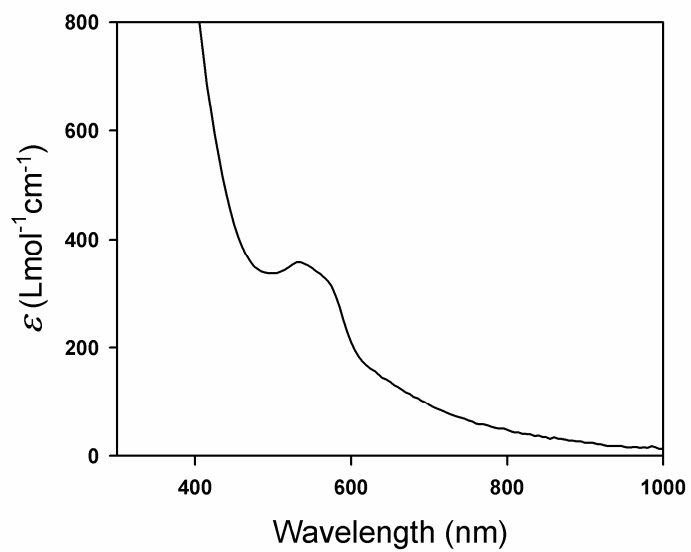


Figure S6. UV-visible spectrum of the product from the reaction of [(cyclam₂^{*i*}PrO)Fe₂(μ -CF₃SO₃)](CF₃SO₃)₂ (**7**) with 15 equivalents of PhIO in MeCN.

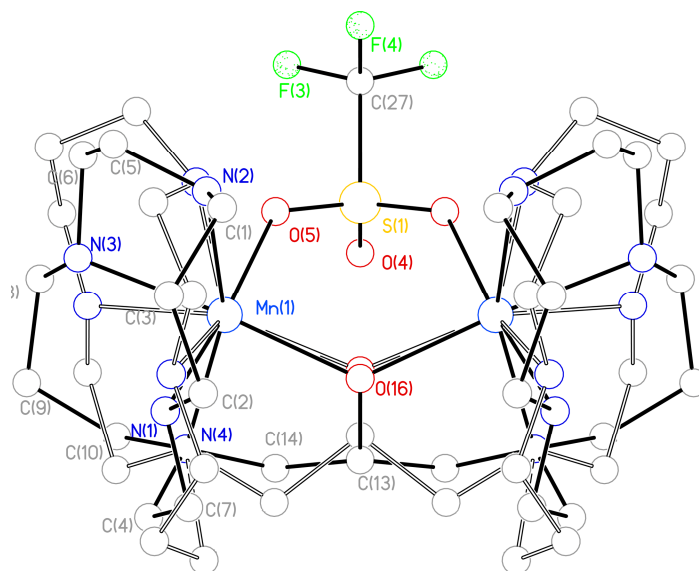


Figure S7. Structure of $[(\text{cyclam}_2\text{PrO})\text{Mn}_2(\mu\text{-CF}_3\text{SO}_3)]^{2+}$ in **4** showing both conformations of the disordered ligand. For clarity, H atoms and triflate counteranions have been omitted, and only atom labels for one conformation of the structure are shown.

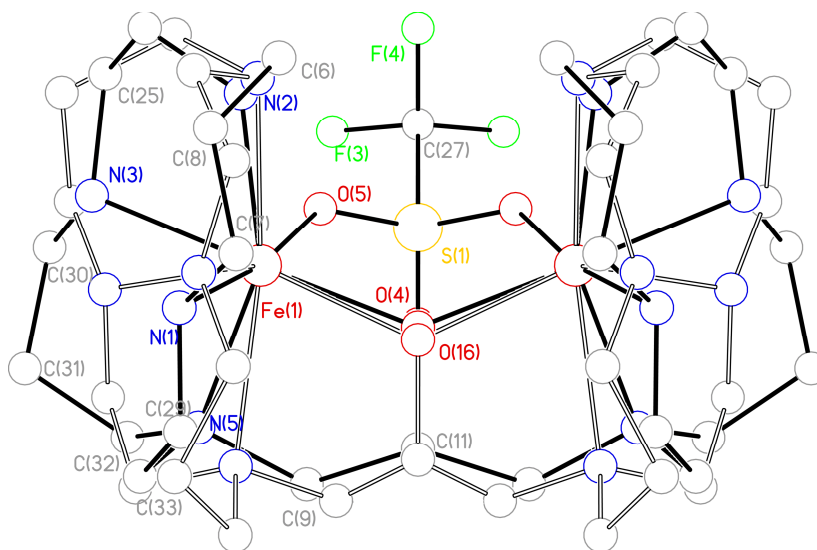


Figure S8. Structure of $[(\text{cyclam}_2\text{PrO})\text{Fe}_2(\mu\text{-CF}_3\text{SO}_3)]^{2+}$ in **4** showing both conformations of the disordered ligand. For clarity, H atoms and triflate counteranions have been omitted, and only atom labels for one conformation of the structure are shown.

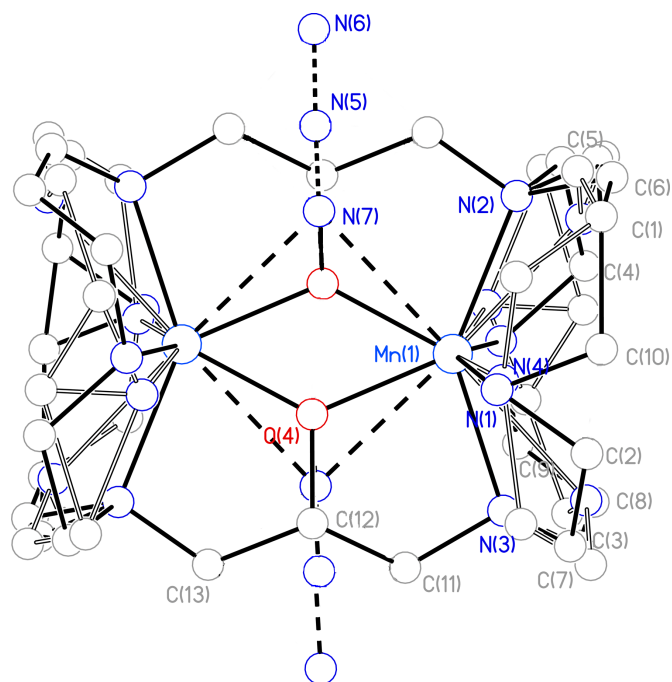


Figure S9. Structure of $[(\text{cyclam}_2'\text{PrO})\text{Mn}_2(\mu\text{-N}_3)]^{2+}$ in **5** showing both orientations of the molecules in the disordered structure. For clarity, H atoms and triflate counteranions have been omitted, and only atom labels for one conformation of the structure are shown.