

Supporting Information for:

A Redox-Switchable Single-Molecule Magnet Incorporating $[\text{Re}(\text{CN})_7]^{3-}$

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Experimental Details

All reagents were obtained from commercial vendors. Diethyl ether and acetonitrile were passed over alumina and degassed by three freeze-pump-thaw cycles prior to use. THF was purchased in a Sure/Seal™ bottle, dried over sodium/benzophenone, and distilled under nitrogen. All other reagents were used without further purification. The compound $(\text{NBu}_4)_3[\text{Re}(\text{CN})_7]$ was prepared as described previously.¹ The pentadentate ligand PY5Me₂ was synthesized in a manner analogous to that previously reported for PY5H₂.² An alternative preparation for PY5Me₂ has also been reported.³

[(PY5Me₂)MnI]I. Solid PY5Me₂ (2.16 g, 4.86 mmol) was added to a stirred suspension of MnI₂ (1.50, 4.86 mmol) in THF (150 mL), and the mixture was stirred for 48 h. The resulting white powder was collected by filtration, washed with THF (30 mL) and diethyl ether (30 mL), and dried under reduced pressure to yield 3.33 g (91%) of product. IR (neat): 1592, 1476, 1463, 1447, 1433, 1404, 1293, 1057, 1016, 863, 791, 749 cm⁻¹. ESI/MS⁺ (m/z): [M]⁺ 625.1. Anal. Calcd. for C₂₉H₂₅I₂MnN₅: C, 46.30; H, 3.35; N, 9.31. Found: C, 46.68; H, 3.72; N, 8.98.

[(PY5Me₂)Mn(MeCN)](PF₆)₂. A solution of TlPF₆ (1.10 g, 3.15 mmol) in acetonitrile (3 mL) was added to a stirred solution of [(PY5Me₂)MnI]I (1.18 g, 1.57 mmol) in acetonitrile (14 mL). A yellow precipitate (presumably TII) formed immediately, and the mixture was stirred for an additional 48 h. The solution was filtered through Celite, and diethyl ether vapor was diffused into the yellow filtrate to afford 1.08 g (83%) of product as yellow parallelepiped-shaped crystals. IR (neat): 2301, 2275, 1595, 1585, 1483, 1470, 1452, 1438, 1059, 1018, 829, 794, 774, 754 cm⁻¹. ESI/MS⁺ (m/z): [M]²⁺ 269.5. Anal. Calcd for C₃₁H₂₈F₁₂MnN₆P₂: C, 44.89; H, 3.40; N, 10.13. Found: C, 44.78; H, 3.33; N, 10.15.

[(PY5Me₂)₄Mn₄Re(CN)₇](PF₆)₅·6H₂O (1). A yellow solution of (Bu₄N)₃[Re(CN)₇] (17 mg, 0.015 mmol) in acetonitrile (3 mL) was chilled to -35 °C and added to a similarly-chilled yellow solution of [(PY5Me₂)Mn(MeCN)](PF₆)₂ (50 mg, 0.060 mmol) in acetonitrile (3 mL), immediately producing a blue solution. Diffusion of diethylether vapor into the solution at -35 °C afforded blue parallelepiped-shaped crystals of [(PY5Me₂)₄Mn₄Re(CN)₇](PF₆)₅·H₂O·3MeCN

¹Bennett, M. V.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 2394.

²Dyker, G.; Muth, O. *Eur. J. Org. Chem.* **2004**, *21*, 4319.

³Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, *10*, 2205.

(**1'**), together with a small amount of Bu₄N(PF₆) precipitate. Due to the extreme thermal sensitivity of the product, analyses were performed on this impure mixture. The sample was dried in air at room temperature for ca. 2 min prior to elemental analysis. IR (neat): $\nu_{\text{CN}} = 2098, 2031 \text{ cm}^{-1}$. Anal. Calcd. for C₁₇₁H₂₂₀F₄₈Mn₄N₃₀O₆P₈Re (**1**·3Bu₄N(PF₆)): C, 47.13 H, 5.09; N, 9.64. Found: C, 47.60; H, 5.12; N, 9.43.

[(PY5Me₂)₄Mn₄Re(CN)₇](PF₆)₄·10H₂O (2**).** A yellow solution of (NBu₄)₃[Re(CN)₇] (17 mg, 0.015 mmol) in acetonitrile (3 mL) was added to a yellow solution of [(PY5Me₂)Mn(MeCN)](PF₆)₂ (50 mg, 0.060 mmol) in acetonitrile (3 mL). The resulting solution changed colors from blue to green to yellow within the course of 1 min. Diffusion of diethyl ether vapor into the yellow solution afforded yellow parallelepiped-shaped crystals of [(PY5Me₂)₄Mn₄Re(CN)₇](PF₆)₄·3H₂O·4MeCN·Et₂O (**2'**) suitable for X-ray analysis. The crystals were dried in air to yield 17 mg (36%) of product. IR (neat): $\nu_{\text{CN}} = 2097, 2031 \text{ cm}^{-1}$. Anal. Calcd. for C₁₂₃H₁₂₀F₂₄Mn₄N₂₇O₁₀P₄Re: C, 47.31; H, 3.87; N, 12.11. Found: C, 47.64; H, 3.73; N, 12.01.

X-ray Structure Determinations. X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on Kapton loops. Each crystal was frozen under a stream of N₂ while data were collected on a Bruker APEX diffractometer. A matrix scan using at least 20 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by Patterson maps with the aid of successive difference Fourier maps, and were refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically, except for counteranions and the uncoordinated solvent molecules in both **1'** and **2'**. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). The structure of **1'** was solved in the space group *C2/m*. Due to the poor quality of the data and the large amount of anion and solvent molecule disorder, it was not possible to establish reliably the number of counterions in the structure. The structure **2'** was

also solved in the space group $C2/m$. A floating variable was used to determine the occupancy of the PF_6^- anions. While the total number of anions refined to a value close to four, it varied significantly by cycle. The cause of this problem was two anions occupying nearly but not precisely the same crystallographic site. Due to this difficulty, a restraint was put in place to maintain the total number of PF_6^- anions at four.

Mass Spectrometry. Mass spectra were acquired using a quadrupole time-of-flight (Q-Tof) mass spectrometer equipped with a Z-spray electrospray ionization (ESI) source (Q-Tof Premier™, Waters, Beverly, MA). Ions were formed by syringe infusion ESI or by nanoelectrospray ionization (nanoESI). For syringe infusion ESI, sample solutions were pumped from a 250 μL Gastight® syringe (Hamilton, Reno, NV) into the ESI probe at flow rates of 6 to 10 $\mu\text{L}/\text{min}$ using a syringe pump. Charged droplets of the sample solution were emitted from a stainless steel capillary (inner diameter 127 μm) held at a potential of 0.2 to 3.5 kV, with a nitrogen nebulizing gas flow of 800 L/hr. For nanoESI, ions were formed from emitters made from borosilicate capillary tubes (1.0 mm o.d./0.78 mm i.d, Sutter Instruments, Novato, CA). These capillaries were pulled to a tip with an inner diameter of roughly 5 to 10 μm using a Flaming/Brown micropipette puller (Model P-87, Sutter). The spray was initiated by applying a potential of 0.5 to 1 kV to a Pt wire (0.127 mm diameter, Aldrich, Milwaukee, WI) inserted into the nanoESI emitter to within approximately 2 mm of the tip. The flow rates were roughly 50 to 200 nL/min. No back pressure was used for nanoESI. The typical instrument parameters were as follows: sample cone 10 to 180 V, extraction cone 3.0 V, ion guide 1.0 V, source block temperature 80 °C, desolvation (nebulizing) gas temperature 150 °C, accelerating voltage into the argon-filled cell 4 V, first pumping stage pressure 1.5 mbar, ion transfer stage pressure 6×10^{-4} mbar, quadrupole analyzer pressure 2×10^{-5} mbar, argon-filled cell 8×10^{-3} mbar, Tof analyzer pressure 9×10^{-7} mbar. No cone gas flow was used. The Tof analyzer was operated in “V” mode. For each mass spectrum, the sample cone and extraction cone voltages were adjusted to optimize signal for the ions of interest and the ESI capillary voltage was adjusted to maintain ion counts below the dead-time threshold (<0.1 ions per push) to prevent spectral distortion effects due to detector saturation. External mass calibration was performed using solutions of sodium formate or sodium iodide immediately prior to measuring samples. Mass spectra were processed using MassLynx software (version 4.1, Waters).

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Magnetic Measurements. Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer. DC magnetic susceptibility data were collected at temperatures ranging from 5 to 300 K, and at fields of 1000, 5000, and 10000 Oe. Magnetization data were collected at applied fields of 1, 2, 3, 4, 5, 6, and 7 T at temperatures ranging from 1.8 to 10 K. AC magnetic susceptibility measurements were performed in zero applied field using a switching field of 4 G at temperatures from 1.8 to 10 K.

In order to measure thermally-sensitive compound **1**, a chilled sample of the reaction mixture of was sealed under diethyl ether in a borosilicate tube. Due to the instability of **1** it could not readily be separated from the diamagnetic side product, $\text{Bu}_4\text{N}(\text{PF}_6)$. Consequently magnetic measurements were performed on a mixture of the two solids. In addition, the instability of the sample at room temperature precluded determination of an accurate mass. The sample mass was therefore estimated by extrapolating the susceptibility data to 300 K and assuming a match to the moment expected for an uncoupled cluster containing for four Mn^{II} centers and one $[\text{Re}(\text{CN})_7]^{3-}$ complex. We note that modest changes in the estimated mass had little effect on the J values obtained when fitting the data. Measurements on compound **2** were straightforward, and were performed using pulverized crystals loaded into a polycarbonate capsule.

Other Physical Measurements. Cyclic voltammetry was performed in a 0.1 M solution of $(\text{Bu}_4\text{N})\text{PF}_6$ in acetonitrile at $-35\text{ }^\circ\text{C}$ using a Bioanalytical systems CV-50W voltammograph, a glassy carbon working electrode, a platinum wire supporting electrode, and a silver wire reference electrode. Reported potentials are all referenced to the $[\text{FeCp}_2]^{0/+}$ couple and were determined using ferrocene. At $-35\text{ }^\circ\text{C}$, the peak separation for the the $[\text{FeCp}_2]^{0/+}$ couple is 104 mV, indicating an increase at low temperature. Infrared spectra were collected on a Nicolet Avatar 360 FTIR spectrometer with an attenuated total reflectance accessory. Carbon, hydrogen, and nitrogen analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley.

Table S1. Crystallographic data^a for compounds **1'**, and **2'**

identification	1'	2'
Formula	C ₁₂₉ H ₁₀₀ F ₃₀ Mn ₄ N ₃₀ OP ₅ Re	C ₁₃₅ H ₁₀₀ F ₂₄ Mn ₄ N ₃₁ O ₄ P ₄ Re
FW	3217.21	3206.31
T, K	173(2)	138(2)
cryst. syst., space group	Monoclinic, C2/m	Monoclinic, C2/m
Z	1	1
a, Å	38.414(13)	38.945(4)
b, Å	24.631(8)	24.649(2)
c, Å	17.267(6)	17.3178(15)
β , °	113.491(6)	113.609(2)
V, Å ³	14984(9)	15233(2)
d_{calc} , g/cm ³	1.363	1.380
abs. coeff. mm ⁻¹	1.259	1.243
data / restr. / param.	6131 / 0 / 798	15811 / 6 / 929
GOF on F^2	1.359	1.084
R_1 (wR_2), %, [$I > 2\sigma(I)$] ^b	0.1161 (0.3038)	0.0806 (0.2244)
R_1 (wR_2), %, all data	0.1643 (0.3551)	0.1411 (0.2585)

^aObtained with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

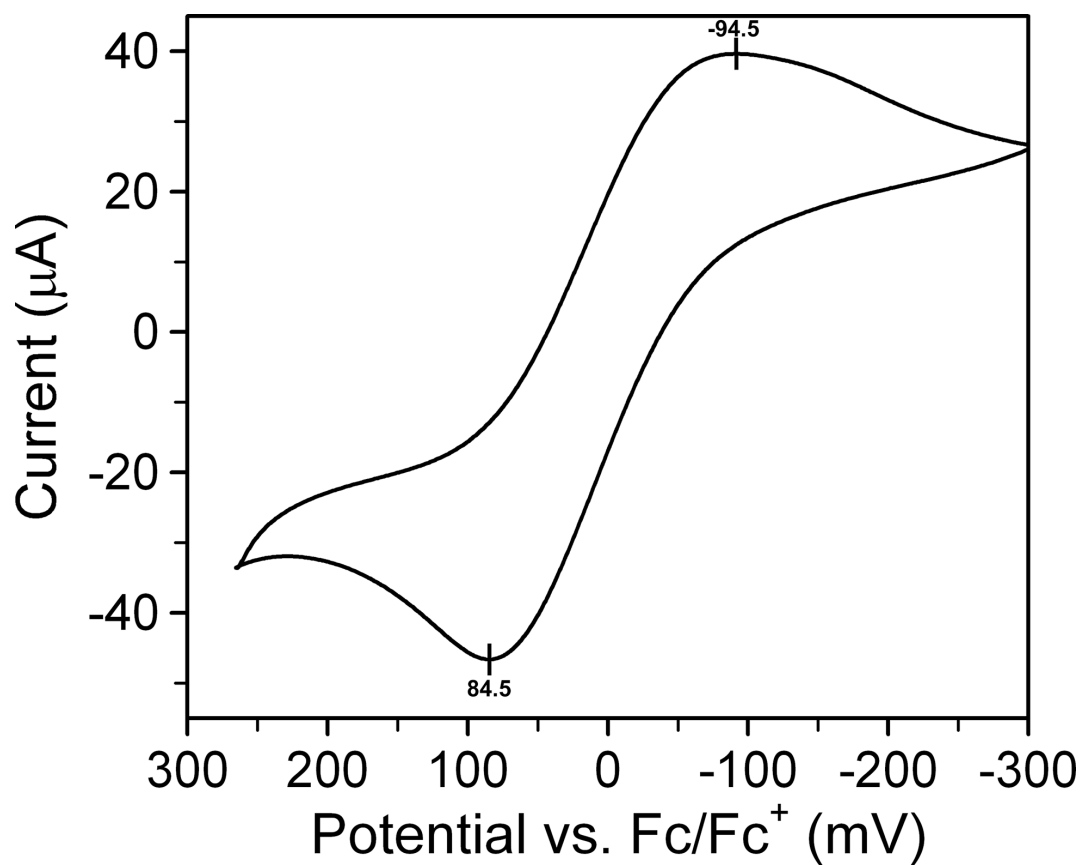


Figure S1. Cyclic voltammogram of **1** scanned at 50 mV/s at -35 °C in 0.1 M acetonitrile solution of (Bu₄N)PF₆. Note that under the conditions, the peak separation for the [FeCp₂]^{0/+} couple was measured to be 104 mV.

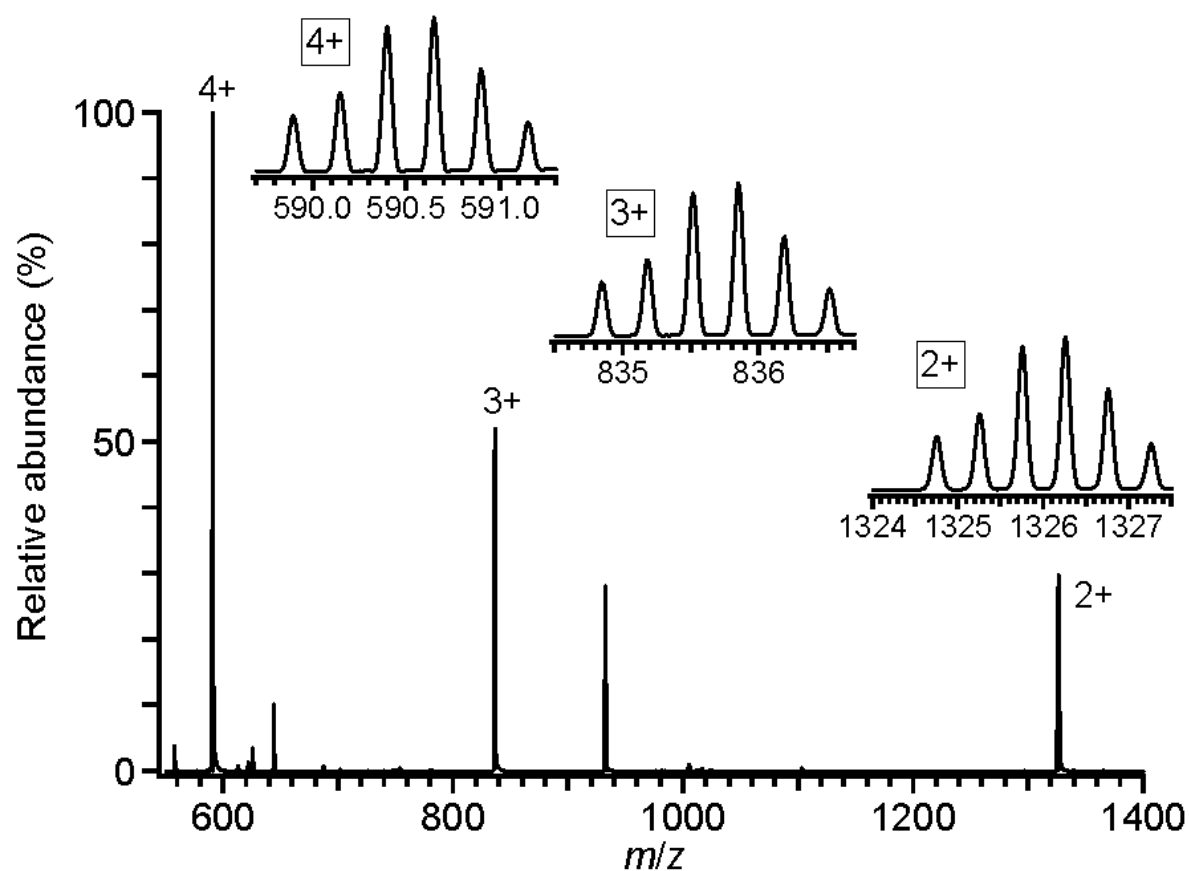


Figure S2. An example electrospray ionization mass spectrum measured for an acetonitrile solution of **2**. The insets show detail for the $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$, $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)\}^{3+}$, and $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_2\}^{2+}$ ions, which are denoted as “4+”, “3+”, and “2+”, respectively.

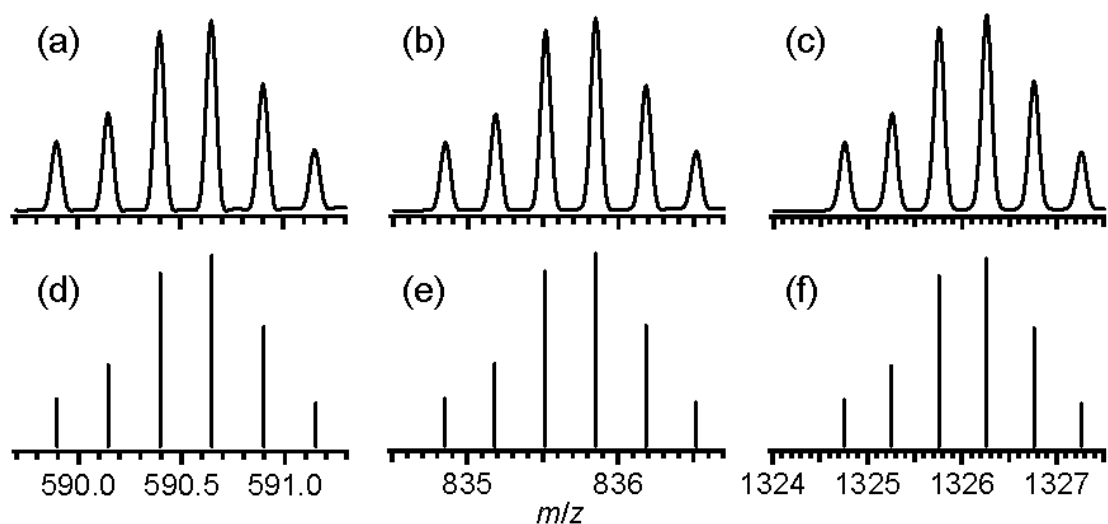


Figure S3. Comparison of measured (a, b, c) and calculated (d, e, f) isotopic distributions of ions formed from an acetonitrile solution of **2**, namely, $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$ (a, d), $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)\}^{3+}$ (b, e), and $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_2\}^{2+}$ (c, f). The distributions of (d), (e), and (f) are calculated based on the natural abundances of the isotopes.

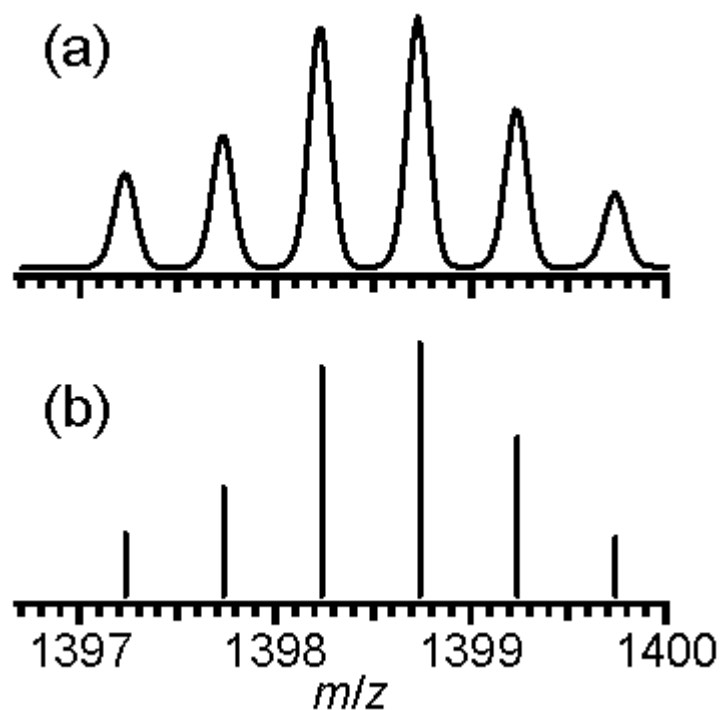


Figure S4. Comparison of measured (a) and calculated (b) isotopic distributions of the $\{[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7](\text{PF}_6)_3\}^{2+}$ ion formed from an acetonitrile solution of **1**. The distribution of (b) is calculated based on the natural abundances of the isotopes. In this experiment, the chilled reactants were mixed immediately before injection in an effort to maintain the metastable blue form of the compound. During the measurement, however, the electrospray droplets passed through an 80 °C heating block used for ion desolvation. Thus, the reduced $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{4+}$ cluster was expected to be the major species observed, with only a small amount of the oxidized $[(\text{PY5Me}_2)_4\text{Mn}_4\text{Re}(\text{CN})_7]^{5+}$ cluster remaining. Indeed, other than the set of peaks shown here, the majority of the peaks observed in the high- m/z portion of the spectrum corresponded to ions containing the reduced cluster (as in Figure S1).

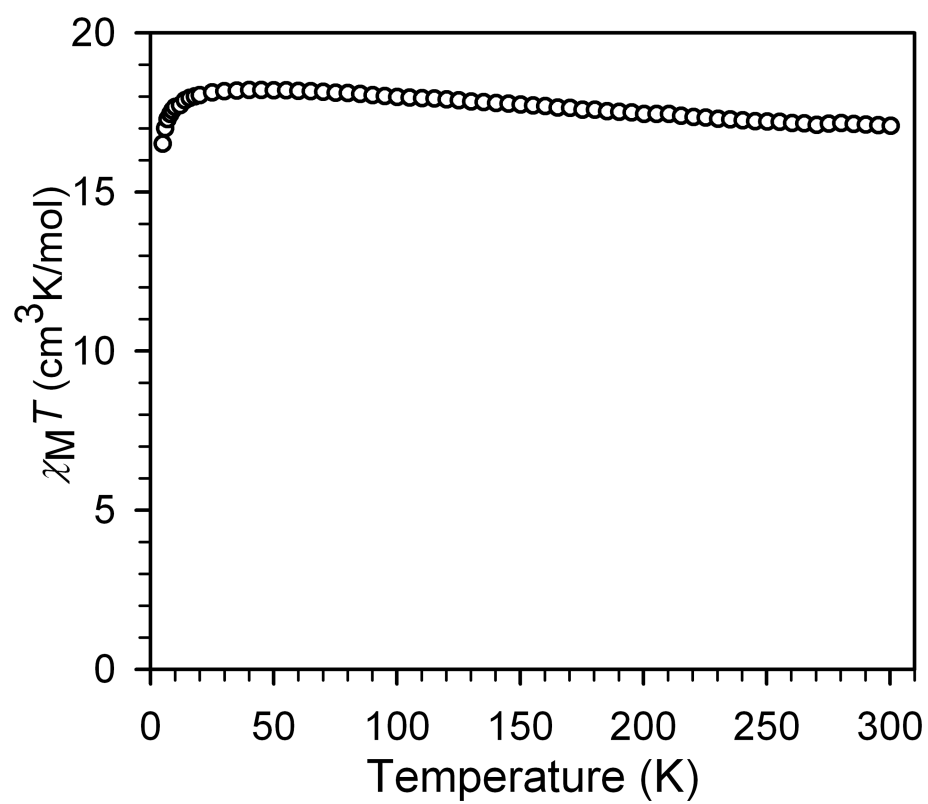


Figure S5. Variable-temperature dc magnetic susceptibility data for compound **2**.

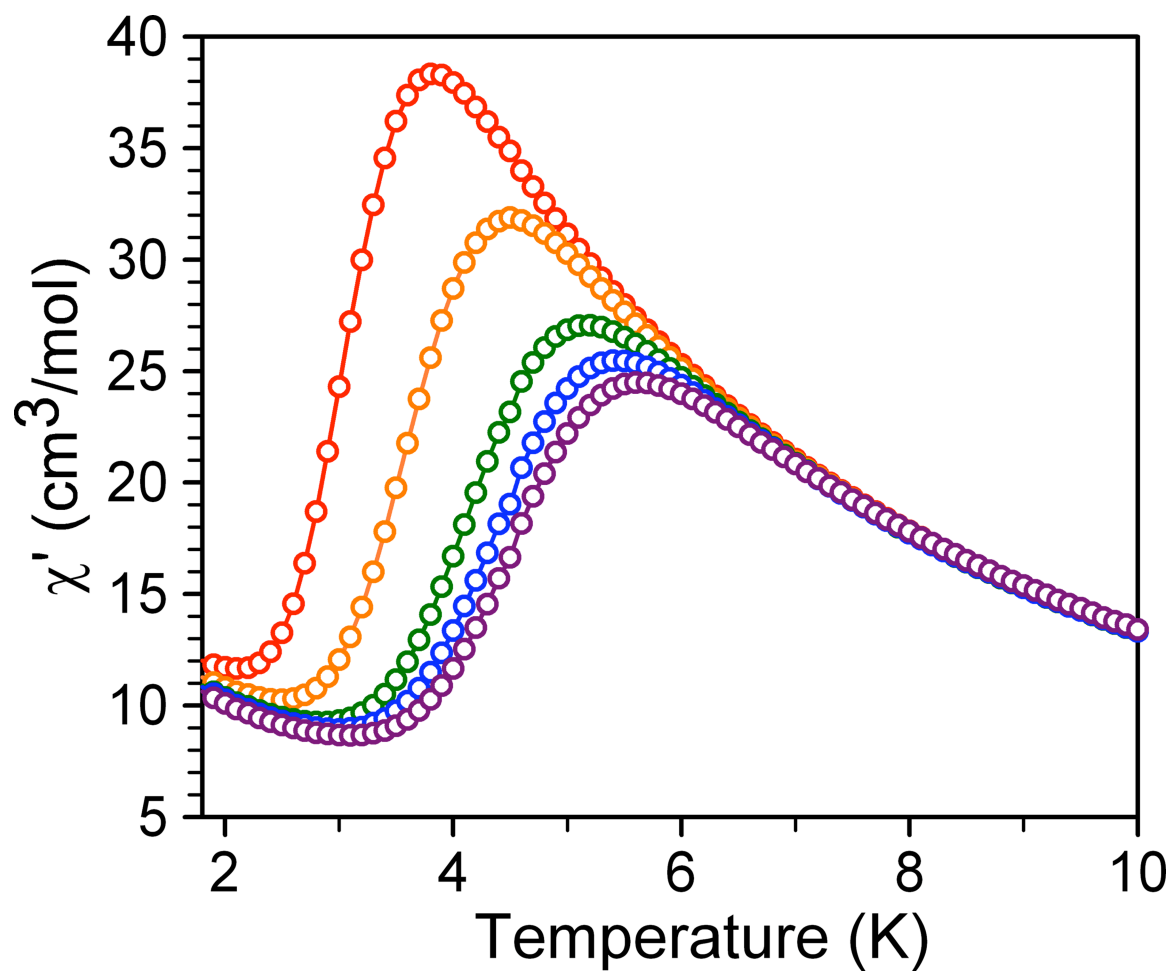


Figure S6. In-phase ac magnetic susceptibility data for **1**, collected at switching frequencies of 1 (red), 10 (orange), 500 (green), 1030 (blue), 1488 (purple) Hz.