Supporting Information

Two-dimensional Assembly of $[Mn^{III}_2Mn^{II}_2]$ Single-Molecule Magnets and $[Cu(pic)_2]$ linking units (Hpic = Picolinic acid)

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Experimental Section

Synthesis. All chemicals and solvent were obtained from commercial sources and used without further purification. Compound **1** was prepared under aerobic conditions. ***Caution!*** Although we have experienced no problems while working with them, perchlorate salts are potentially explosive and should be handled with extreme care and only in small quantities.

$[Cu(pic)_2]•2H_2O$. To an aqueous solution (20 mL) of $CuCl_2•2H_2O$ (0.585 g, 3.40 mmol) was added picolinic acid (1.04 g, 8.45 mmol) and NaOH (0.135 g, 3.37 mmol). The dark blue powder was filtered and dried in air. (yield: 82 %) Anal. Calc. for $[Cu(pic)_2]•2H_2O$ ($CuC_{12}H_{12}N_2O_6$): C, 41.92; H, 3.52; N, 8.15 %; Found: C, 41.90; H, 3. 28 ; N, 8.00 %; Selected IR data (KBr, cm^{-1}): 3107 (w), 3034 (w), 3001 (w), 1643 (s), 1603 (m), 1474 (w), 1449 (w), 1348 (s), 1258 (m), 1268 (w), 1168 (w), 1048 (m), 849 (m), 825 (w), 776 (m), 694 (m), 545 (br), 458 (m).

$[Mn_4(hmp)_6\{Cu(pic)_2(ClO_4)_2\}_2]•2CH_3CN$, 1. $Mn(ClO_4)_2•6H_2O$ (0.500 g, 1.38 mmol) and hmpH (0.378 g, 3.45 mmol) were dissolved by stirring in 20 mL of CH_3CN. To this solution, 510 μL (0.72 mmol) of a 20wt % water solution of $(Et_4N)OH$ was added dropwise. After stirring 1 min, **$[Cu(pic)_2]•2H_2O$** (0.237 g, 0.69 mmol) was added to solution. The purple-brown solution was stirred for 1 h at 50 ^{o}C. After filtration, the resulting solution was transferred to a small beaker, itself placed inside the larger vial of diethyether. The whole crystallization set-up was closed hermetically and then kept undisturbed for slow diffusion. Purple-brown parallelepiped crystals were isolated in 2 days. (Yield: 53 %). Anal. Calc. for $[Mn_4(hmp)_6\{Cu(pic)_2(ClO_4)_2\}_2]$

($C_{60}H_{52}N_{10}O_{30}Cl_4Cu_2Mn_4$): C, 38.30; H, 2.79; N, 7.44 %; Found: C, 38.07; H, 2.98; N, 8.39 %. Selected IR data (KBr, cm^{-1}): 3438 (br), 1635 (s), 1620 (s), 1598 (s), 1482 (m), 1443 (m), 1400 (m), 1384 (m), 1295 (w), 1269 (w), 1093 (br), 1047 (br), 860 (w), 763 (m), 622 (m), 565 (w), 413 (w).

X-ray Crystallography and Solution of Structure. X-ray crystallographic data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. A suitable crystal was picked out from the mother liquid, affixed to the end of a glass fiber using silicone grease and quickly transferred to the goniostat where it was cooled for data collection. DENZO-SMN[1] was used for data integration and SCALEPACK[1] corrected data for Lorentz-polarisation effects. All structures were solved by the direct method and refined by a full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package.[2] All of the non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms on the parent carbon atoms were included in fixed calculated positions. Crystal data for **1**: $C_{64}H_{58}N_{12}O_{30}Cl_4Cu_2Mn_4$, Mr = 1963.86, triclinic space group $P\text{-}1$, a = 11.968(2), b = 12.369(3), c = 14.349(3) Å, α = 97.20(3), β = 112.67(3), γ = 101.36(3)°, V = 1873.5(7) Å^3, Z = 1, T = 150(2) K, ρ = 1.741 g cm^{-3}, μ(Mo-Kα) = 1.448 mm^{-1}, 12527 reflections measured, 6493 unique (R_{int} = 0.037) which were used in all calculations. $R_1(wR_2)$ = 0.0479(0.1388) for 6493 reflections with $I > 2\sigma(I)$. CCDC reference number: 760082. Data collection and structure solution details of these complexes are listed in Tables S1-S3. The final difference Fourier map has a large residual electron-density peak (1.664 eÅ^{-3}) located 1.07 Å from the nearest atom (Cl(2)). However, the electron density could not be refined as an O atom.

Other Measurements.

Elemental analysis for C, H and N were performed following the classical Pregl-Dumas technique on a ThermoFischer Flash EA1112.

IR spectra were recorded in the range 400-4000 cm^{-1} on a Nicolet 750 Magna-IR spectrometer using a KBr pellet.

Magnetic data were collected using a Quantum Design MPMS-XL SQUID magnetometer in the 1.8 - 300 K temperature range and between -7 and +7 T. Magnetic measurements were obtained reproducibly on 25.00 and 12.07 mg of microcrystalline powders restrained in frozen CH_3CN/Et_2O mother liquor. ac magnetic susceptibility data were collected under an ac field of 3 Oe, oscillating at frequencies in the range 1-1500 Hz. All data were corrected for diamagnetic contributions from the sample holder, as well as for the intrinsic core diamagnetism of the compound. The coherence of the collected data was checked between the different techniques of measurements (dc and ac).

Magnetization measurements on oriented single crystals were carried out with an array of micro-SQUIDs.[3] This magnetometer works in the temperature range of 0.04 to ca. 7 K and in fields of up to 1.4 T with sweeping rates as high as 0.28 Ts^{-1}, and exhibits field stability of better than μT. The time resolution is approximately 1 ms. The field can be applied in any direction of the micro-SQUID plane with precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure good thermalization, a single crystal was fixed with apiezon grease.

References :

1. Otwinowski, Z.; Minor, W. *Methods Enzymol.*, **1996**, *276*, 307.
2. (a) Sheldrick, G. M. *SHELXL97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, **1997**; (b) Sheldrick, G. M. *SHELXS97*, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, **1997**.
3. Wernsdorfer, W. *Adv. Chem. Phys.*, **2001**, *118*, 99.

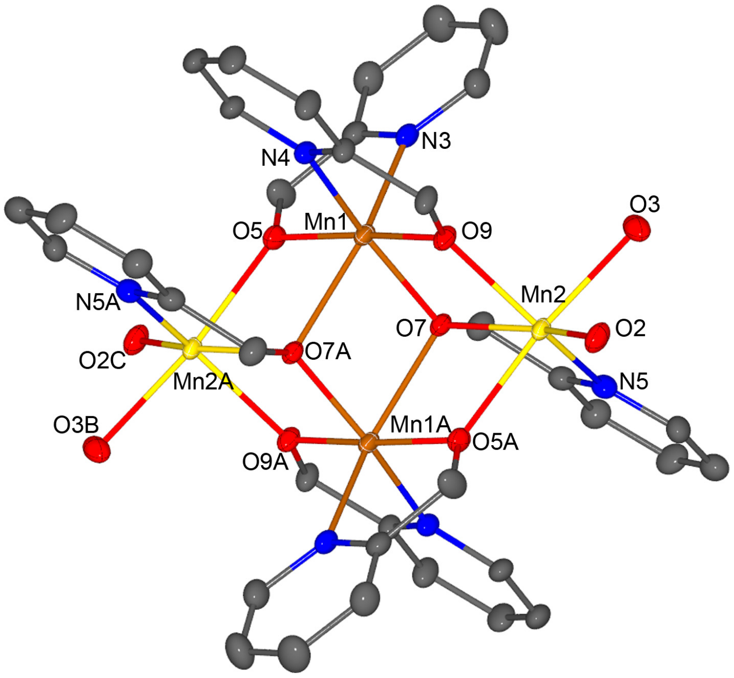

Figure S1: Close view of [Mn_4] core structure in the network of **1**. The hydrogen atoms, $Cu(pic)_2$ units, ClO_4^- anions and CH_3CN are omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: -x+1,-y+1,-z; B: -x+1,-y+1,-z+1; C: -x,-y,-z

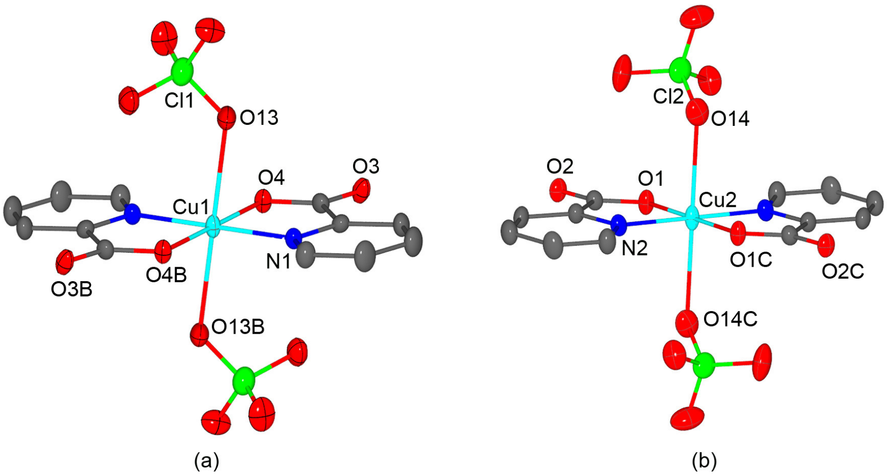

Figure S2: Coordination environments of Cu sites. Symmetry transformations used to generate equivalent atoms: B: -x+1,-y+1,-z+1; C: -x,-y,-z.

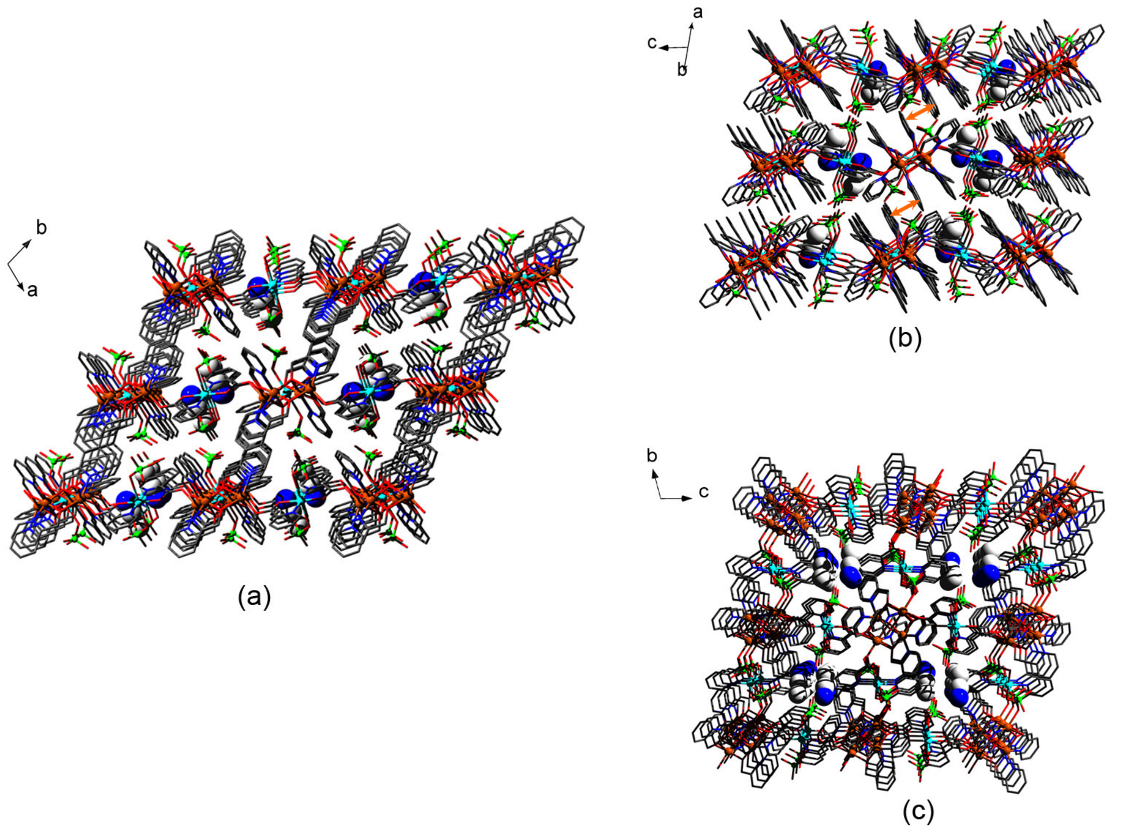

Figure S3: **(a)** Packing arrangement of **1** viewed along the *c* axis showing the π…π interactions between the pyridine rings in two adjacent layers; **(b)** View of the distance between two adjacent pyridine ring planes in two adjacent layers. The closest distance is ca. 3.46 Å; **(c)** View of the CH_3CN solvent molecules located in the interspaces of the adjacent layers. All the CH_3CN molecules are shown by space-filling style for clarity.

Table S1: Crystal Data and Structure Refinement for **1**

	1
Empirical formula	$C_{64}H_{58}N_{12}O_{30}Cl_4Cu_2Mn_4$
M	1963.86
λ /Å	0.71073Å
T /K	150(2)
Crystal dimensions /mm	0.16 × 0.12 × 0.10
Crystal system	Triclinic
Space group	*P-1*
a /Å	11.968(2)
b /Å	12.369(3)
c /Å	14.349(3)
α /°	97.20(3)
β /°	112.67(3)
γ /°	101.36(3)
V /Å^3	1873.5(7)
Z	1
D_c /Mg m^{-3}	1.741
μ /mm^{-1}	1.448
F(000)	992
θ Range /°	3.29–25.00
Measured reflections	12527
Independent reflections	6493
Data/restraints/parameters	6493 / 0 / 526
R_{int}	0.0370
R_1 ($I > 2\sigma(I)$)[a]	0.0479
wR_2 (all data)[a]	0.1388
Goodness-of-fit on F^2	0.941
$\Delta\rho_{\mathrm{max,\ min}}$/ e Å^{-3}	1.664, -1.012

[a] $R_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2-F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$

Table S2: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2$ $\times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mn(1)	5758(1)	5798(1)	1152(1)	26(1)
Mn(2)	3368(1)	3737(1)	746(1)	27(1)
Cu(1)	5000	5000	5000	30(1)
Cu(2)	0	0	0	38(1)
O(1)	1403(3)	1251(3)	169(2)	39(1)
O(2)	3332(3)	2225(3)	1298(2)	40(1)
O(3)	2867(3)	4275(3)	2004(2)	43(1)
O(4)	4507(3)	4968(3)	3537(2)	33(1)
O(5)	6345(3)	6954(3)	582(2)	31(1)
O(7)	3977(3)	5249(2)	118(2)	26(1)
O(9)	5299(3)	4547(3)	1676(2)	30(1)
N(1)	3276(3)	4032(3)	4515(3)	31(1)
N(2)	1079(4)	46(3)	1465(3)	35(1)
N(3)	5447(3)	7288(3)	1954(3)	31(1)
N(4)	7491(3)	5848(3)	2296(2)	30(1)
N(5)	1617(3)	4112(3)	-223(3)	32(1)
C(5)	2650(4)	3820(4)	3484(3)	30(1)
C(26)	3389(4)	4389(4)	2959(3)	33(1)
C(20)	7487(4)	4946(4)	2731(3)	32(1)
C(6)	2206(4)	814(4)	1820(3)	32(1)
C(7)	3099(4)	1019(4)	2823(3)	37(1)
C(16)	8586(4)	6642(4)	2579(3)	35(1)
C(29)	6220(4)	4139(4)	2392(3)	34(1)
C(18)	9710(4)	5603(5)	3712(4)	42(1)
C(22)	704(5)	5399(4)	-1175(4)	40(1)
C(4)	1450(4)	3103(4)	2961(4)	39(1)
C(23)	-477(5)	4685(5)	-1490(4)	44(1)
C(27)	2337(4)	1479(4)	1034(3)	32(1)
C(10)	821(5)	-535(4)	2114(4)	44(1)
C(24)	-603(5)	3686(5)	-1164(4)	43(1)
C(8)	2846(5)	395(5)	3485(4)	45(1)
C(25)	466(4)	3447(4)	-527(3)	37(1)
C(3)	894(5)	2588(5)	3536(4)	54(2)
C(19)	8593(4)	4789(5)	3441(4)	41(1)

C(2)	1547(5)	2797(5)	4591(4)	54(2)
C(21)	1752(4)	5095(4)	-543(3)	33(1)
C(30)	3063(4)	5856(4)	-148(4)	35(1)
C(9)	1685(5)	-376(5)	3125(4)	51(1)
C(17)	9689(5)	6540(5)	3280(4)	42(1)
C(1)	2733(5)	3531(5)	5060(4)	42(1)
Cl(1)	6585(1)	2773(1)	-4916(1)	35(1)
Cl(2)	-1957(1)	1185(1)	938(1)	58(1)
O(10)	6244(4)	1568(3)	-5033(3)	55(1)
O(11)	7257(4)	3322(4)	-3838(3)	59(1)
O(12)	7357(4)	3071(4)	-5442(3)	65(1)
O(14)	-946(4)	1525(4)	647(3)	64(1)
O(13)	5456(4)	3119(3)	-5351(3)	63(1)
O(15)	-2143(5)	2129(4)	1456(4)	80(1)
O(16)	-1577(4)	483(3)	1682(3)	62(1)
O(17)	-3067(4)	535(4)	72(4)	84(2)
C(31)	-1686(6)	908(5)	4034(5)	59(2)
C(32)	-1303(6)	-99(6)	3872(5)	60(2)
N(6)	-972(7)	-882(6)	3756(5)	86(2)
C(15)	5699(4)	8198(4)	1575(3)	34(1)
C(11)	5007(5)	7381(5)	2693(4)	41(1)
C(28)	6137(5)	8036(4)	747(4)	43(1)
C(14)	5548(5)	9228(4)	1924(4)	44(1)
C(13)	5123(6)	9318(5)	2702(5)	55(1)
C(12)	4857(6)	8382(5)	3085(4)	53(1)

Table S3: Selected bond lengths (Å) and bond angles (º) of **1**

Mn(1)-O(9)	1.880(3)	Mn(2)-O(2)	2.120(3)
Mn(1)-O(5)	1.883(3)	Mn(2)-O(9)	2.121(3)
Mn(1)-O(7)	1.987(3)	Mn(2)-O(5A)	2.167(3)
Mn(1)-N(4)	2.073(4)	Mn(2)-O(3)	2.179(3)
Mn(1)-N(3)	2.220(4)	Mn(2)-N(5)	2.200(4)
Mn(1)-O(7A)	2.261(3)	Mn(2)-O(7)	2.288(3)
Mn(1)-Mn(1A)	3.232(2)	Mn(1)-Mn(2)	3.2390(15)
Cu(1)-O(4)	1.942(3)	Cu(2)-O(1C)	1.960(3)
Cu(1)-O(4B)	1.942(3)	Cu(2)-O(1)	1.960(3)
Cu(1)-N(1)	1.971(4)	Cu(2)-N(2C)	1.985(4)
Cu(1)-N(1B)	1.971(4)	Cu(2)-N(2)	1.985(4)
Cu(1)-O(13)	2.526(4)	Cu(2)-O(14)	2.630(4)
Cu(1)-O(13B)	2.526(4)	Cu(2)-O(14C)	2.630(4)
O(9)-Mn(1)-O(7A)	93.97(12)	O(2)-Mn(2)-O(7)	161.29(12)
O(5)-Mn(1)-O(7A)	80.04(12)	O(9)-Mn(2)-O(7)	70.88(11)
O(7)-Mn(1)-O(7A)	81.12(13)	O(5A)-Mn(2)-O(7)	73.92(11)
N(4)-Mn(1)-O(7A)	94.35(13)	O(3)-Mn(2)-O(7)	110.64(13)
N(3)-Mn(1)-O(7A)	156.57(12)	N(5)-Mn(2)-O(7)	74.55(12)
Mn(1)-O(5)-Mn(2A)	111.23(15)	Mn(1)-O(7)-Mn(1A)	98.88(13)
Mn(1)-O(7)-Mn(2)	98.27(12)	Mn(1A)-O(7)-Mn(2)	94.71(11)
Mn(1)-O(9)-Mn(2)	107.95(13)		
O(4)-Cu(1)-O(4B)	180.000(1)	O(1)-Cu(2)-N(2C)	96.85(14)
O(4)-Cu(1)-N(1)	83.64(14)	O(1C)-Cu(2)-O(1)	180.0(2)
O(4)-Cu(1)-N(1B)	96.36(14)	O(1)-Cu(2)-N(2)	83.15(14)
O(4)-Cu(1)-O(13)	86.81(14)	O(1)-Cu(2)-O(14C)	87.40(14)
O(4)-Cu(1)-O(13B)	93.21(14)	O(1)-Cu(2)-O(14C)	92.62(14)

Symmetry transformations used to generate equivalent atoms: A: -x+1,-y+1,-z; B: -x+1,-y+1,-z+1; C: -x,-y,-z

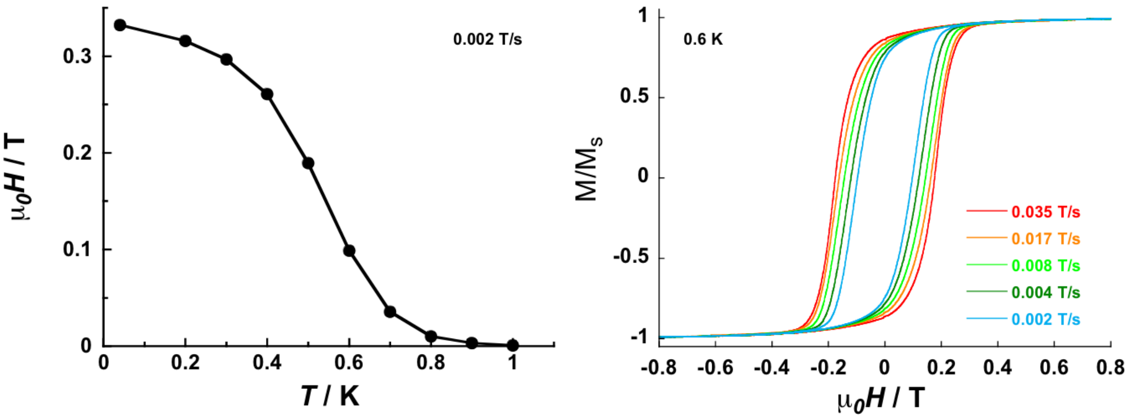

Figure S4: Coercive field *vs.* T at a dc field sweeping rate of about 0.002 T/s for **1** (right) and normalized magnetization (M/M_S; M_S being the magnetization at saturation) *vs.* field for **1** with the sweeping rate of the dc field in the range of 0.002 - 0.035 T/s.

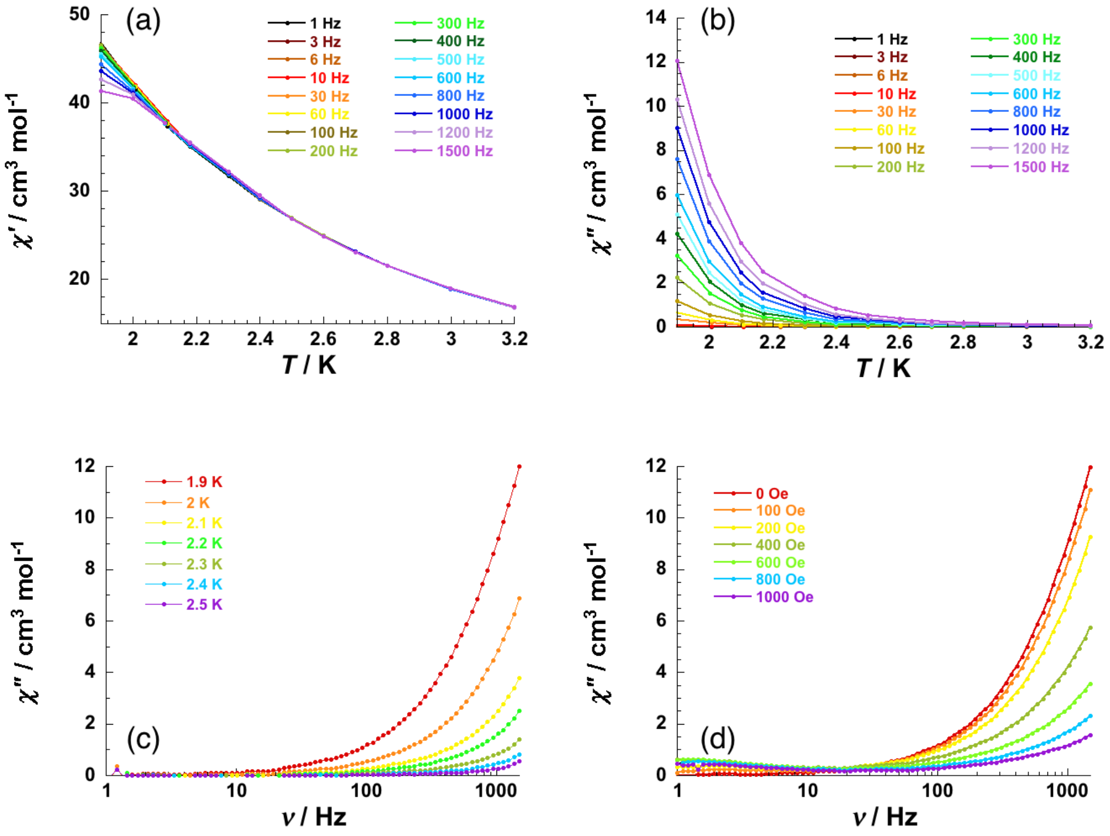

Figure S5: Temperature dependence of (a) the in-phase, χ', and (b) out-of-phase, χ'', components of the ac magnetic susceptibility for **1**, collected in a 3 Oe ac field oscillating at frequencies between 1 and 1500 Hz in zero-dc field. Frequency dependence of the out-of-phase, χ'', components of the ac magnetic susceptibility for **1**, collected in a 3 Oe ac field (c) between 1.9 and 2.5 K in zero-dc field and (d) between 0 and 1000 Oe dc field at 1.9 K.