

Electronic Supplementary Information

Incorporation of guanidinium ions between **Cu^{II}-[M^V(CN)₈]³⁻ double-layers magnetic system**

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Table S1. Results of continuous shape measures analysis for tungsten centres.

Geometry	S _{BTP}	S _{SAPR}	S _{DD}
BTP-8	0.000	2.262	2.709
SAPR-8	2.262	0.000	2.848
DD-8	2.709	2.848	0.000
[W ^{1A} (CN) ₈] [*]	0.721	1.870	1.939
[W ^{1B} (CN) ₈] [*]	1.039	2.142	1.893

S_{BTP} – the shape measure relative to the bicapped trigonal prism; S_{SAPR} – the shape measure relative to the square antiprism; S_{DD} – the shape measure relative to the dodecahedron, * moieties with ½ occupancy

Table S2. Results of continuous shape measures analysis for copper centres.

Geometry	S _{TBPY}	S _{SPY}
TBPY-5	0.000	5.384
SPY-5	5.384	0.000
[Cu ₂ (NC) ₅]	5.292	0.162

S_{TBPY} – the shape measure relative to the trigonal bipyramide; S_{SPY} – the shape measure relative to the square pyramid

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	1430(1)	5003(1)	5454(1)	14(1)
Cu(2)	3165(1)	4998(2)	6745(1)	14(1)
C(11)	2124(3)	5038(18)	5973(7)	24(2)
N(11)	2489(3)	4923(15)	6250(7)	28(2)
C(12)	1628(6)	2920(30)	4617(13)	66(5)
N(12)	1731(5)	2060(20)	4083(11)	66(4)
C(13)	1622(3)	6993(13)	4578(6)	12(2)
N(13)	1719(3)	8113(14)	4126(7)	28(2)
C(14)	1628(6)	7100(30)	6609(13)	58(4)
N(14)	1722(6)	7980(30)	7304(12)	76(5)
C(15)	1616(3)	3049(14)	6627(7)	15(2)
N(15)	1721(3)	1928(14)	7225(6)	23(2)
C(16A)	1012(6)	7660(30)	5221(13)	12(4)
N(16A)	806(7)	8920(30)	5041(15)	35(5)
C(17A)	904(9)	4480(40)	4207(19)	35(6)
N(17A)	637(9)	4270(40)	3442(19)	48(6)
C(18A)	897(9)	4500(40)	5980(18)	31(5)
N(18A)	602(13)	4040(60)	6190(30)	86(10)
C(16B)	1063(8)	2510(30)	5099(16)	26(5)
N(16B)	852(8)	1170(40)	4939(17)	46(6)
C(17B)	923(8)	5510(40)	4101(16)	25(5)
N(17B)	648(11)	5790(50)	3370(20)	66(8)
C(18B)	904(7)	5850(30)	5880(16)	23(5)
N(18B)	623(7)	6150(30)	6096(15)	36(5)
C(1)	220(6)	9450(30)	6676(13)	60(4)
N(2)	14(6)	10740(30)	6167(12)	77(5)
N(3)	609(6)	10000(30)	7283(12)	71(4)
N(4)	51(7)	7750(30)	6679(14)	87(5)

Table S4. Bond lengths [\AA] and angles [$^\circ$] for **1**.

Bond lengths [\AA]			
W(1)-C(16B)	2.09(3)	C(12)-N(12)	1.13(2)
W(1)-C(17A)	2.11(3)	N(12)-Cu(2)#4	1.993(16)
W(1)-C(18B)	2.12(2)	C(13)-N(13)	1.144(13)
W(1)-C(15)	2.135(10)	N(13)-Cu(2)#2	1.970(10)
W(1)-C(13)	2.140(9)	C(14)-N(14)	1.15(2)
W(1)-C(12)	2.15(2)	N(14)-Cu(2)#3	1.943(18)
W(1)-C(11)	2.172(11)	C(15)-N(15)	1.148(13)
W(1)-C(17B)	2.18(2)	N(15)-Cu(2)#1	1.979(9)
W(1)-C(18A)	2.18(3)	C(16A)-N(16A)	1.09(3)
W(1)-C(14)	2.184(19)	C(17A)-N(17A)	1.19(4)
W(1)-C(16A)	2.277(19)	C(18A)-N(18A)	1.16(4)
Cu(2)-N(14)#1	1.943(18)	C(16B)-N(16B)	1.15(3)
Cu(2)-N(13)#2	1.970(10)	C(17B)-N(17B)	1.18(4)
Cu(2)-N(15)#3	1.979(9)	C(18B)-N(18B)	1.10(3)
Cu(2)-N(12)#4	1.993(16)	C(1)-N(2)	1.23(2)
Cu(2)-N(11)	2.115(10)	C(1)-N(4)	1.32(3)
C(11)-N(11)	1.143(15)	C(1)-N(3)	1.36(3)
Bond angles [$^\circ$]			
C(16B)-W(1)-C(17A)	52.6(11)	C(11)-W(1)-C(14)	72.9(6)
C(16B)-W(1)-C(18B)	81.0(9)	C(17B)-W(1)-C(14)	123.6(8)
C(17A)-W(1)-C(18B)	77.7(10)	C(18A)-W(1)-C(14)	84.2(8)
C(16B)-W(1)-C(15)	70.0(7)	C(16B)-W(1)-C(16A)	111.8(8)
C(17A)-W(1)-C(15)	122.2(9)	C(17A)-W(1)-C(16A)	74.1(10)
C(18B)-W(1)-C(15)	89.0(7)	C(18B)-W(1)-C(16A)	45.6(8)
C(16B)-W(1)-C(13)	130.9(7)	C(15)-W(1)-C(16A)	130.2(5)
C(17A)-W(1)-C(13)	84.7(8)	C(13)-W(1)-C(16A)	70.3(5)
C(18B)-W(1)-C(13)	115.9(7)	C(12)-W(1)-C(16A)	138.8(7)
C(15)-W(1)-C(13)	147.8(4)	C(11)-W(1)-C(16A)	124.3(6)
C(16B)-W(1)-C(12)	63.3(8)	C(17B)-W(1)-C(16A)	58.8(8)
C(17A)-W(1)-C(12)	72.5(9)	C(18A)-W(1)-C(16A)	70.5(8)
C(18B)-W(1)-C(12)	142.8(8)	C(14)-W(1)-C(16A)	65.1(7)

C(15)-W(1)-C(12)	88.4(6)	N(14)#1-Cu(2)-N(13)#2	158.5(6)
C(13)-W(1)-C(12)	83.3(5)	N(14)#1-Cu(2)-N(15)#3	89.8(6)
C(16B)-W(1)-C(11)	123.9(8)	N(13)#2-Cu(2)-N(15)#3	91.0(4)
C(17A)-W(1)-C(11)	141.5(8)	N(14)#1-Cu(2)-N(12)#4	83.7(7)
C(18B)-W(1)-C(11)	140.3(7)	N(13)#2-Cu(2)-N(12)#4	88.4(5)
C(15)-W(1)-C(11)	74.5(4)	N(15)#3-Cu(2)-N(12)#4	160.1(6)
C(13)-W(1)-C(11)	73.3(4)	N(14)#1-Cu(2)-N(11)	99.2(6)
C(12)-W(1)-C(11)	73.9(6)	N(13)#2-Cu(2)-N(11)	101.6(4)
C(16B)-W(1)-C(17B)	72.4(10)	N(15)#3-Cu(2)-N(11)	101.2(4)
C(17A)-W(1)-C(17B)	19.9(8)	N(12)#4-Cu(2)-N(11)	98.4(6)
C(18B)-W(1)-C(17B)	76.7(9)	N(11)-C(11)-W(1)	175.3(11)
C(15)-W(1)-C(17B)	141.3(7)	C(11)-N(11)-Cu(2)	174.5(10)
C(13)-W(1)-C(17B)	68.3(7)	N(12)-C(12)-W(1)	169.1(18)
C(12)-W(1)-C(17B)	82.5(8)	C(12)-N(12)-Cu(2)#4	165.1(17)
C(11)-W(1)-C(17B)	136.8(7)	N(13)-C(13)-W(1)	177.3(9)
C(16B)-W(1)-C(18A)	58.9(9)	C(13)-N(13)-Cu(2)#2	174.7(10)
C(17A)-W(1)-C(18A)	75.7(10)	N(14)-C(14)-W(1)	169.4(17)
C(18B)-W(1)-C(18A)	25.8(9)	C(14)-N(14)-Cu(2)#3	165.6(17)
C(15)-W(1)-C(18A)	69.9(7)	N(15)-C(15)-W(1)	176.3(9)
C(13)-W(1)-C(18A)	139.6(7)	C(15)-N(15)-Cu(2)#1	173.6(9)
C(12)-W(1)-C(18A)	122.1(9)	N(16A)-C(16A)-W(1)	174.8(18)
C(11)-W(1)-C(18A)	139.8(7)	N(17A)-C(17A)-W(1)	172(2)
C(17B)-W(1)-C(18A)	83.5(9)	N(18A)-C(18A)-W(1)	172(3)
C(16B)-W(1)-C(14)	139.3(8)	N(16B)-C(16B)-W(1)	176(2)
C(17A)-W(1)-C(14)	138.6(9)	N(17B)-C(17B)-W(1)	180(3)
C(18B)-W(1)-C(14)	69.1(8)	N(18B)-C(18B)-W(1)	175(2)
C(15)-W(1)-C(14)	82.1(5)	N(2)-C(1)-N(4)	121(2)
C(13)-W(1)-C(14)	88.0(5)	N(2)-C(1)-N(3)	114.4(19)
C(12)-W(1)-C(14)	146.7(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+3/2 #2 -x+1/2,-y+3/2,-z+1

#3 -x+1/2,y+1/2,-z+3/2 #4 -x+1/2,-y+1/2,-z+1

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^* U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
W(1)	18(1)	13(1)	11(1)	4(1)	5(1)	-1(1)
Cu(2)	22(1)	11(1)	11(1)	-1(1)	7(1)	-1(1)

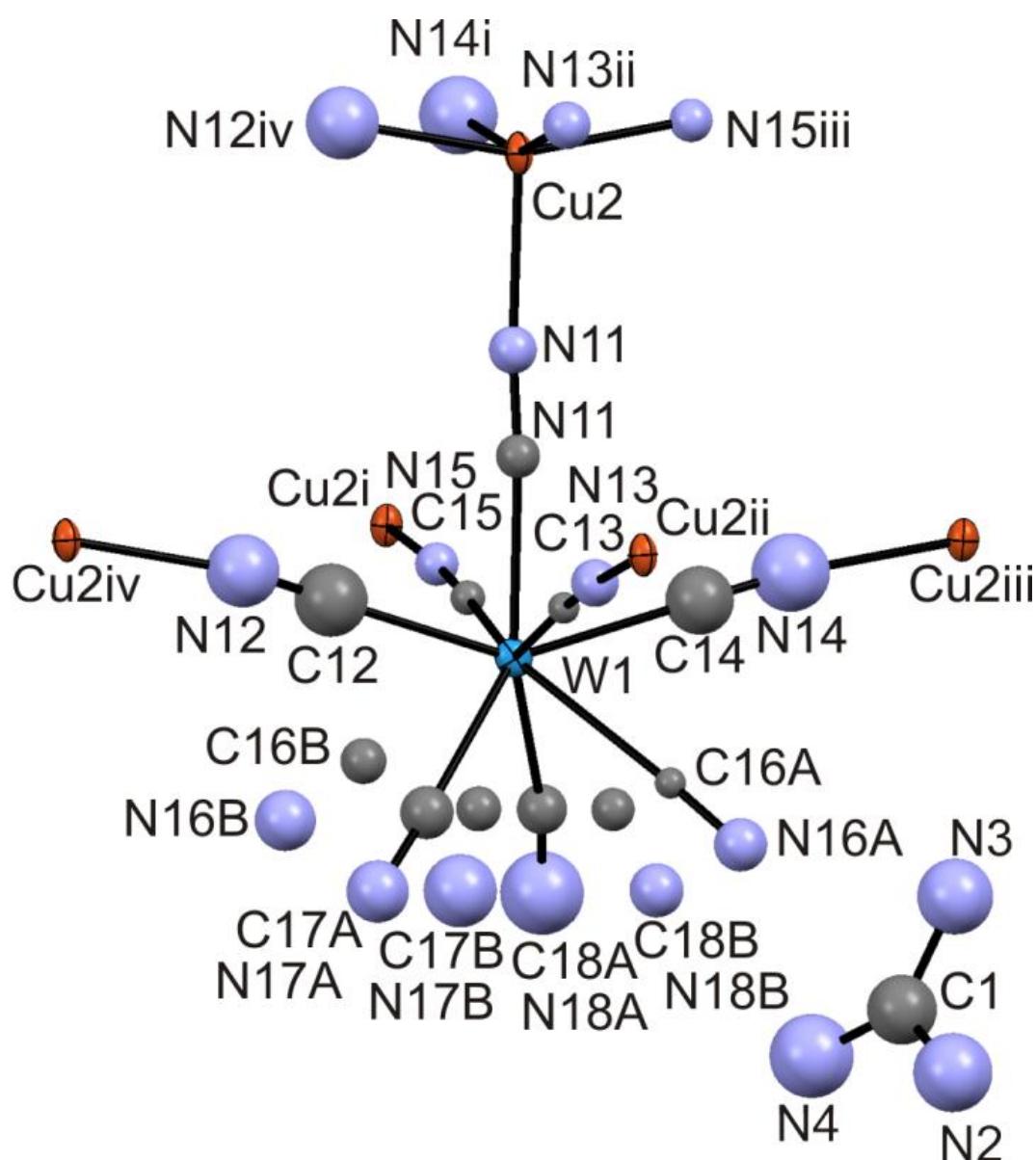


Figure S1. ORTEP diagram of structure unit of **1** with atoms labelling. Colours used: Cu, orange; N, blue; C, gray; W, cyan. Symmetry codes: i = -x+1/2, y-1/2, -z+3/2; ii = -x+1/2, -y+3/2, -z+1; iii = -x+1/2, y+1/2, -z+3/2; iv = -x+1/2, -y+1/2, -z+1. Thermal ellipsoids of 50% probability are shown.

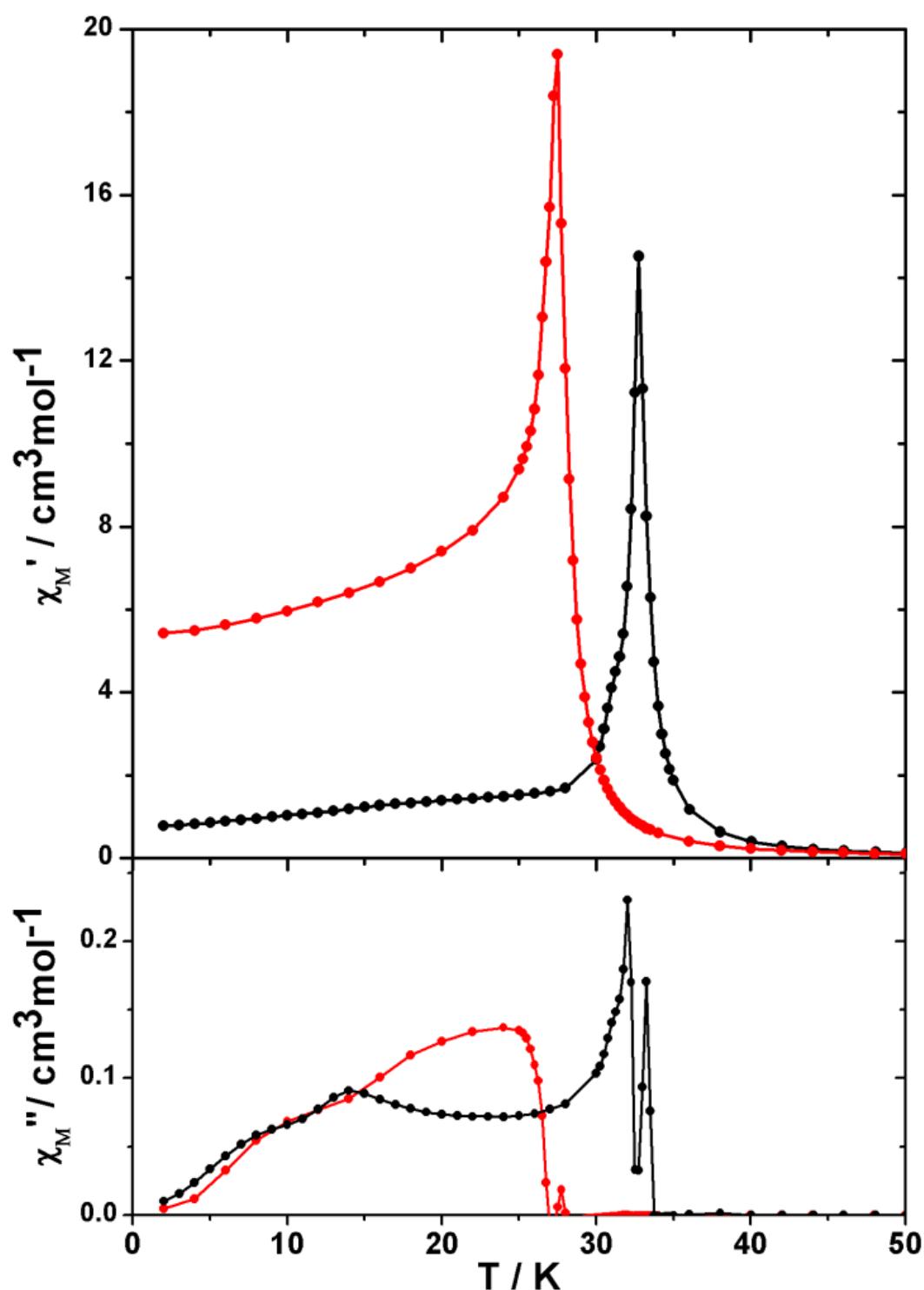


Figure S2. The $\chi_M'(T)$ and $\chi_M''(T)$ curves for **1** (black) and **2** (red) ($H_{\text{AC}} = 3 \text{ Oe}$).

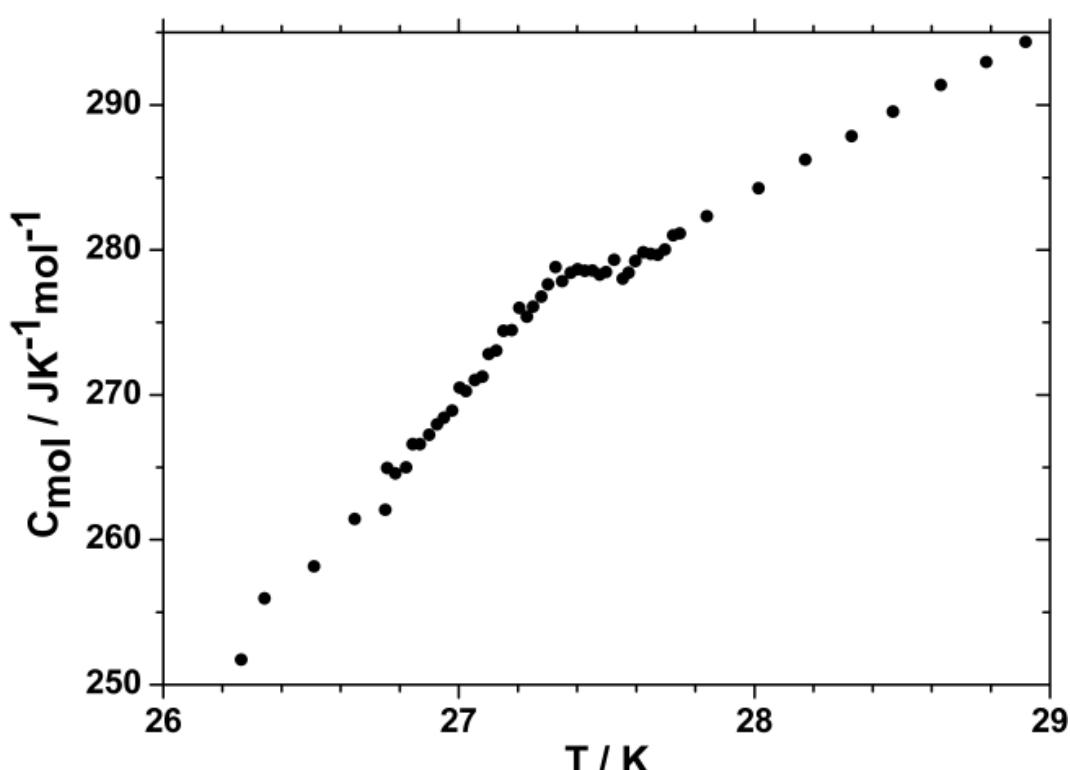


Figure S3. The specific heat capacity of **2** versus temperature ($H = 0$ Oe).

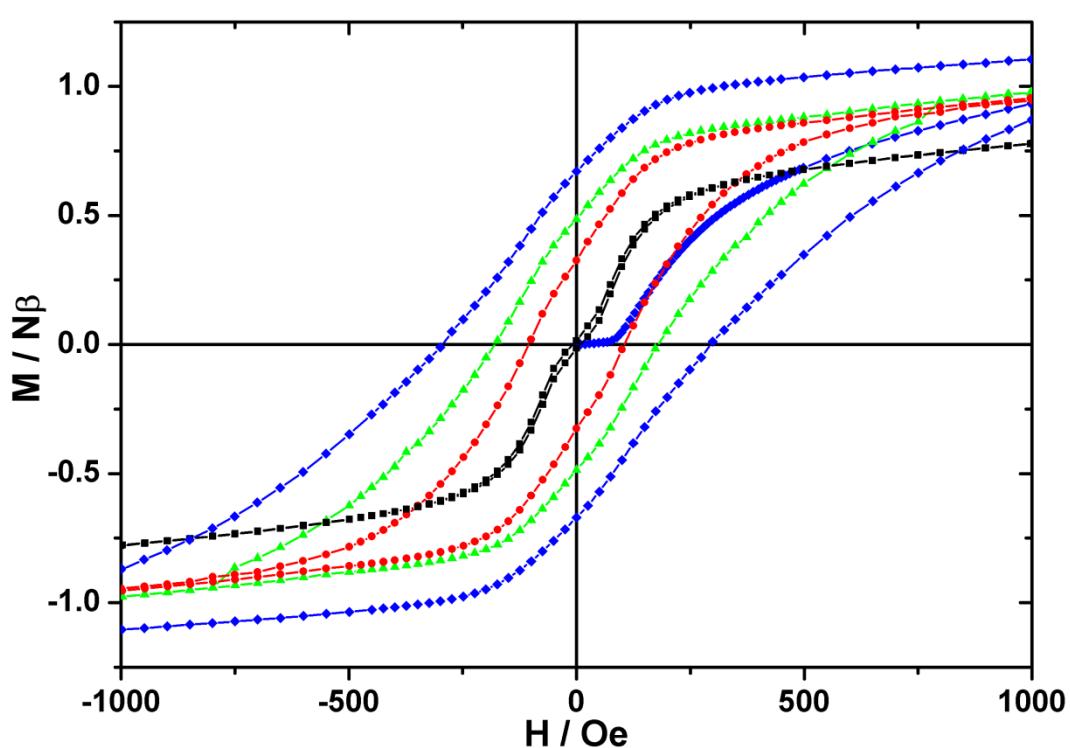


Figure S4. The $M(H)$ curves of **1** measured at 2 (blue diamonds), 10 (green triangles), 20 (red circles), and 30 K (black squares).

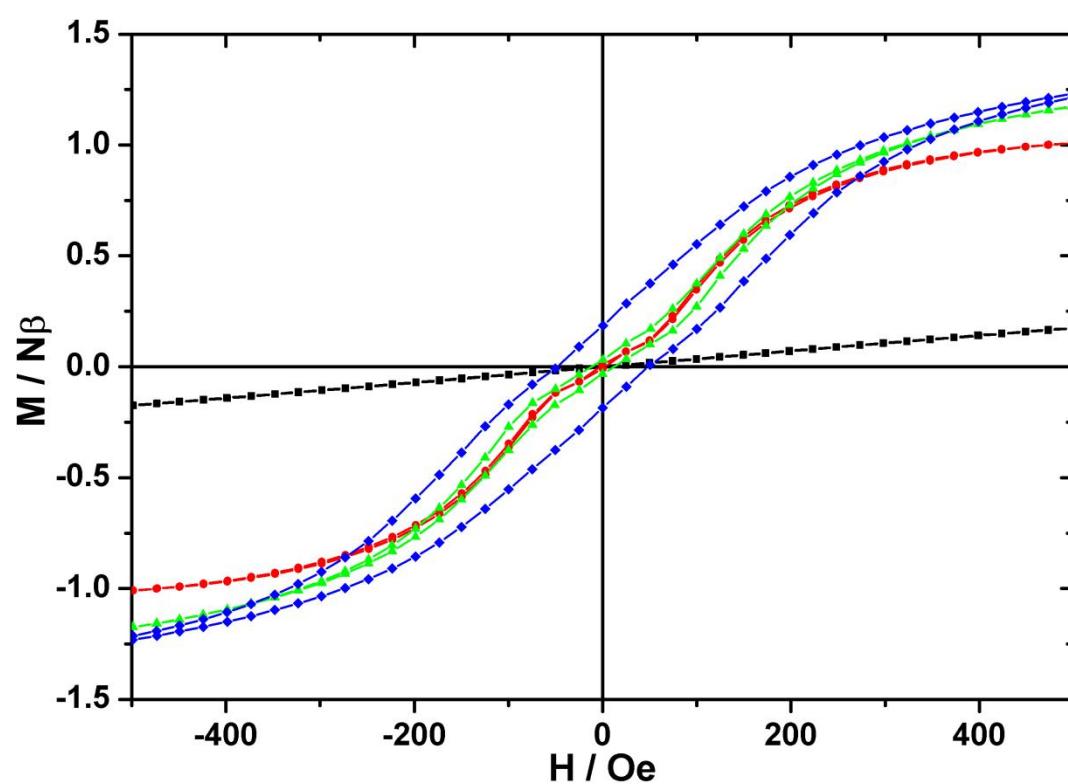


Figure S5. The $M(H)$ curves of **2** measured at 2 (♦), 10 (▲), 20 (●) and 30 K (■).