SUPPORTING INFORMATION

Supramolecular chains and coordination nano-wires constructed of high-spin $Co^{II}_9W^V_6$ clusters and 4,4'-bpdo linkers

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1. Crystal data and structure refinement of **1**, $\mathbf{2^{MeOH}}$ and $\mathbf{2^{Ap}}$ (Table S1) S2

2. Detailed structure parameters of **1** (Table S2) S3

3. Detailed structure parameters of $\mathbf{2^{MeOH}}$ and $\mathbf{2^{Ap}}$ (Table S3) S4

4. Results of Continuous Shape Measure Analysis for $[W^V(CN)_8]^{3-}$ units (Table S4) S5

5. Ideal and observed dihedral δ and φ angles in $[W^V(CN)_8]^{3-}$ units (Table S5) S6

6. PXRD patterns of **1** and **2** (Figure S1) S7

7. Field-cooled and zero-field-cooled magnetization curves for **1** and **2** (Figure S2) S8

8. χ_M'' versus *T* curves for **2** under various applied *dc* magnetic fields (Figure S3) S9

9. References to Supporting Information S10

Table S1. Crystal data and structure refinement of **1**, $\mathbf{2^{MSol}}$ and $\mathbf{2^{Ap}}$

compound		**1**	$\mathbf{2^{MSol}}$	$\mathbf{2^{Ap}}$
method		single-crystal XRD	single-crystal XRD	single-crystal XRD
formula		$Co_9W_6C_{83}N_{50}O_{29}H_{83}$	$Co_{2.25}W_{1.5}C_{44}N_{18}O_8H_{24}$	$Co_{2.25}W_{1.5}C_{50}N_{18}O_{15.5}H_{28}$
formula weight [g·mol^{-1}]		3878.46	1341.18	1537.27
T [K]		293(2)	293(2)	90(2)
λ [Å]		0.71069	0.71073	0.71075
crystal system		monoclinic	tetragonal	tetragonal
space group		*C* 2/c	*I* 4/m	*I* 4/m
unit cell	a [Å]	28.725(5)	26.5160(3)	26.0758(16)
	b [Å]	19.529(5)	26.5160(3)	26.0758(16)
	c [Å]	32.405(5)	19.4450(3)	19.3540(11)
	β [deg]	113.411(5)	90.000	90.000
V [Å^3]		16682(6)	13671.7(3)	13159.7(14)
Z		4	8	8
calculated density [g·cm^{-3}]		1.544	1.303	1.552
absorption coeff. [cm^{-1}]		5.050	3.105	3.245
F(000)		7400	5198	6138
crystal size [mm × mm × mm]		0.25 × 0.08 × 0.06	0.52 × 0.06 × 0.06	0.40 × 0.08 ×0.05
Θ range [deg]		2.09 – 26.37	3.21 – 25.34	3.01 – 27.49
limiting indices		-35 < h < 32 -24 < k < 24 -40 < l < 35	-31 < h < 31 -31 < k < 31 -23 < l < 23	-33 < h < 33 -33 < k < 33 -25 < l < 24
collected reflections		43909	43365	63558
unique reflections		16941	6381	7758
R_{int}		0.0964	0.0957	0.0815
completeness [%]		99.2	98.6	99.8
max and min transmission		0.752 and 0.365	0.836 and 0.295	0.855 and 0.357
refinement method		full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters		16941/37/870	6381/20/375	7758/42/519
GOF on F^2		1.021	1.146	1.037
final R indices		R_1 = 0.0638 [$I > 2\sigma(I)$] wR_2 = 0.1508 (all data)	R_1 = 0.0511 [$I > 2\sigma(I)$] wR_2 = 0.1379 (all data)	R_1 = 0.0402 [$I > 2\sigma(I)$] wR_2 = 0.1047 (all data)
largest diff peak and hole		2.910 and -1.205 e·A^{-3}	1.569 and -1.947 e·A^{-3}	1.440 and -1.362 e·A^{-3}

Table S2. Detailed structure parameters of **1**

Parameter	**1**
W1-C	2.141(10) – 2.190(12) Å
W2-C	2.131(14) – 2.174(12) Å
W3-C	2.132(11) – 2.181(10) Å
C-N (W1)	1.115(13) – 1.164(13) Å
C-N (W2)	1.125(17) – 1.169(17) Å
C-N (W3)	1.131(13) – 1.158(13) Å
W1-C-N	175.8(9) – 179.0(9)°
W2-C-N	175.0(10) – 179.5(12)°
W3-C-N	174.4(9) – 179.5(13)°
Co4-N-C	175.2(8)° (N21-C21) 176.2(9)° (N11-C11) 179.4(9)° (N31-C31)
Co5-N-C	172.6(9)° (N14-C14) 175.9(10)° (N28-C28) 176.8(10)° (N25-C25)
Co6-N-C	172.9(9)° (N12-C12) 173.8(9)° (N22-C22) 178.3(10)° (N35-C35)
Co7-N-C	173.5(9)° (N34-C34) 173.9(9)° (N24-C24) 176.5(9)° (N18-C18)
Co8-N-C	169.5(9)° (N32-C32) 172.6(9)° (N15-C15) 177.3(9)° (N36-C36)
Co5-O(MeOH)	2.088(8) Å 2.102(9) Å 2.116(9) Å
Co6-O(MeOH)	2.099(9) Å 2.101(7) Å 2.118(8) Å
Co7-O(MeOH)	2.090(7) Å 2.103(8) Å 2.120(8) Å
Co8-O(MeOH)	2.097(8) Å 2.110(7) Å 2.127(7) Å
N1-O7	1.327(12) Å
N1-C6	1.316(16) Å
N1-C2	1.305(15) Å

Parameter	**1**
Co4-N(CN)	2.085(9) Å 2.090(8) Å 2.092(9) Å
Co5-N(CN)	2.082(10) Å 2.095(10) Å 2.099(9) Å
Co6-N(CN)	2.101(9) Å 2.106(10) Å 2.110(10) Å
Co7-N(CN)	2.081(10) Å 2.101(9) Å 2.104(10) Å
Co8-N(CN)	2.086(9) Å 2.110(9) Å 2.128(9) Å
N-Co4-N	86.8(3) 88.1(4) 89.2(3)° 89.6(5) 90.5(3) 93.6(3)° 94.5(5) 175.2(3) 176.0(5)°
N-Co5-O	89.3(4) 92.1(4) 175.9(4)° 88.2(4) 89.9(4) 174.9(4)° 90.5(4) 90.6(4) 174.8(4)°
N-Co5-N	92.3(4) 92.6(4) 94.5(4)°
O-Co5-O	84.9(4) 86.7(4) 87.8(4)°
N-Co6-O	86.3(4) 89.4(4) 173.2(3)° 89.6(3) 90.2(4) 173.7(4)° 91.5(4) 93.4(4) 179.1(4)°
N-Co6-N	90.3(4) 92.8(4) 95.6(4)°
O-Co6-O	85.2(3) 86.3(4) 89.3(3)°
N-Co7-O	90.0(3) 90.8(4) 175.1(3)° 89.1(4) 92.2(4) 175.9(3)° 90.5(3) 91.6(3) 175.5(4)°
N-Co7-N	90.9(4) 92.4(4) 93.8(4)°
O-Co7-O	85.1(4) 86.2(4) 87.0(3)°
N-Co8-O	86.6(3) 90.0(3) 173.4(3)° 89.8(3) 91.9(3) 177.4(3)° 87.9(3) 88.6(3) 171.7(3)°
N-Co8-N	90.8(4) 92.2(3) 98.0(3)°
O-Co8-O	84.0(3) 89.7(3) 89.8(3)°
C-C (4,4'-bpdo)	1.346(19) – 1.404(17) Å

Table S3. Detailed structure parameters of $\mathbf{2}^{\mathbf{MSol}}$ and $\mathbf{2}^{\mathbf{Ap}}$

Parameter	$\mathbf{2}^{\mathbf{MSol}}$	$\mathbf{2}^{\mathbf{Ap}}$
W1-C	2.143(9) – 2.161(13) Å	2.153(6) – 2.169(6) Å
W2-C	2.152(15) – 2.2030(2) Å	2.149(8) – 2.183(9) Å
C-N (W1)	1.146(12) – 1.172(10) Å	1.138(6) – 1.150(8) Å
C-N (W2)	1.099(10) – 1.22(3) Å	1.121(11) – 1.196(14) Å
W1-C-N	176.4(8) – 179.1(8)°	175.6(4) – 179.1(5)°
W2-C-N	175.1(5) – 180.00(2)°	176.9(13) – 180.000(1)°
Co3-N-C	176.7(8)° (N13-C13) 180.00(2)° (N23-C23)	173.9(5)° (N23-C24) 180.000(1)° (N22-C20)
Co4-N-C	175.0(6)° (N15-C15) 175.3(8)° (N24-C24) 179.3(9)° (N14-C14)	174.5(4)° (N27-C28) 175.9(4)° (N21-C19) 178.8(4)° (N26-C25)
Co3-N(CN)	2.080(11) Å 2.096(9) Å	2.080(7) Å 2.080(5) Å
Co4-N(CN)	2.098(7) Å 2.100(7) Å 2.113(10) Å	2.088(4) Å 2.095(4) Å 2.144(5) Å
Co4-O(MeOH)	2.119(7) Å	2.128(4) Å
Co4-O(4,4’-bpdo)	2.064(6) Å 2.104(6) Å	2.051(3) Å 2.089(3) Å
N-Co3-N	89.998(1) – 90.002(1)° 179.995(1) – 180.00(1)°	90.000(1)° 180.000(1)°
N-Co4-N	90.9(3)° 91.9(4)° 93.4(3)°	90.36(17)° 90.99(16)° 93.39(14)°
N-Co4-O(MeOH)	87.6(3)° 87.8(3)° 178.4(3)°	86.29(15)° 87.38(14)° 176.18(15)°
N-Co4-O(4,4’-bpdo)	92.1(3)°, 94.3(3)°, 171.3(3)° 90.3(3)°, 95.0(3)°, 172.9(3)°	90.51(13) 95.33(15) 172.56(15)° 92.22(16) 93.71(13) 172.41(16)°
O(MeOH)-Co4-O(4,4’-bpdo)	86.6(3)° 88.4(3)°	86.54(13)° 91.33(13)°
O(4,4’-bpdo)-Co4-O(4,4’-bpdo)	81.6(2)°	82.15(12)°
O-N(4,4’-bpdo)	1.320(9) Å 1.335(9) Å 1.339(11) Å	1.320(5) Å 1.324(5) Å 1.335(5) Å
C-N(4,4’-bpdo)	1.310(14), 1.319(12) Å 1.345(11), 1.357(11) Å 1.339(11), 1.344(14) Å	1.318(7), 1.336(6) Å 1.347(6), 1.359(6) Å 1.344(7), 1.352(6) Å
C-C(4,4’-bpdo)	1.363(14) – 1.458(17) Å 1.367(14) – 1.486(12) Å 1.361(13) – 1.388(14) Å	1.378(7) – 1.404(7) Å 1.374(7) – 1.405(6) Å 1.372(7) – 1.395(7) Å

Table S4. Results of Continuous Shape Measure Analysis for $[W^{V}(CN)_8]^{3-}$ units in **1**, $\mathbf{2^{MSol}}$ and $\mathbf{2^{Ap}}$ in the comparison to results for purely solvated $\{Co^{II}_9(MeOH)_{24}[W^{V}(CN)_8]_6\}\cdot 19H_2O$[S1] phase.

$[W^{V}(CN)_8]^{3-}$ unit	Purely solvated Co_9W_6 phase[S1]	**1**	$\mathbf{2^{MSol}}$	$\mathbf{2^{Ap}}$
W1				
CSM BTP-8[§]	1.097	1.133	0.808	0.778
CSM SAPR-8	1.255	1.196	1.687	1.719
CSM DD-8	0.909	0.863	1.752	1.781
W2				
CSM BTP-8	1.642	1.300	1.319	1.404
CSM SAPR-8	2.241	1.808	3.797	3.872
CSM DD-8	0.427	0.620	2.969	2.967
W3				
CSM BTP-8	1.165	1.050	-	-
CSM SAPR-8	1.669	1.360	-	-
CSM DD-8	1.121	0.926	-	-

[§]CSM BTP-8 – the parameter corresponding to the bicapped trigonal prism;
CSM SAPR-8 – the parameter corresponding to the square antiprism;
CSM DD-8 – the parameter corresponding to the dodecahedron;
CSM = 0 for the ideal geometry and increases with the increase of the degree of distortion.[S2-S4]

Table S5. Ideal and observed dihedral δ and φ angles[S5] in $[W^{V}(CN)_8]^{3-}$ units in **1**, $\mathbf{2}^{\mathbf{MSol}}$ and $\mathbf{2}^{\mathbf{Ap}}$ in the comparison to results for purely solvated Co_9W_6 phase.[S1]

Complex	δ [deg]	φ [deg]
Ideal BTP-8	0; 21.8; 48.2; 48.2	14.1
Ideal SAPR-8	0; 0; 52.4; 52.4	24.5
Ideal DD-8	29.5; 29.5; 29.5; 29.5	0
$[W1(CN)_8]^{3-}$ in purely solvated Co_9W_6 phase[S1]	12.8; 26.5; 40.5; 43.5	11.0
$[W2(CN)_8]^{3-}$ in purely solvated Co_9W_6 phase[S1]	20.9; 31.9; 32.6; 39.2	5.1
$[W3(CN)_8]^{3-}$ in purely solvated Co_9W_6 phase[S1]	11.3; 32.5; 39.7; 46.9	10.9
$[W1(CN)_8]^{3-}$ in **1**	13.9; 24.8; 40.5; 43.4	11.4
$[W2(CN)_8]^{3-}$ in **1**	15.8; 31.8; 38.5; 40.2	8.3
$[W3(CN)_8]^{3-}$ in **1**	13.8; 28.8; 42.5; 44.1	11.4
$[W1(CN)_8]^{3-}$ in $\mathbf{2}^{\mathbf{MSol}}$	0; 33.4; 44.4; 46.5	14.2
$[W2(CN)_8]^{3-}$ in $\mathbf{2}^{\mathbf{MSol}}$	11.2; 42.0; 42.0; 43.9	13.7
$[W1(CN)_8]^{3-}$ in $\mathbf{2}^{\mathbf{Ap}}$	0; 33.9; 43.8; 47.2	14.1
$[W2(CN)_8]^{3-}$ in $\mathbf{2}^{\mathbf{Ap}}$	12.5; 40.4; 40.4; 43.2	11.9

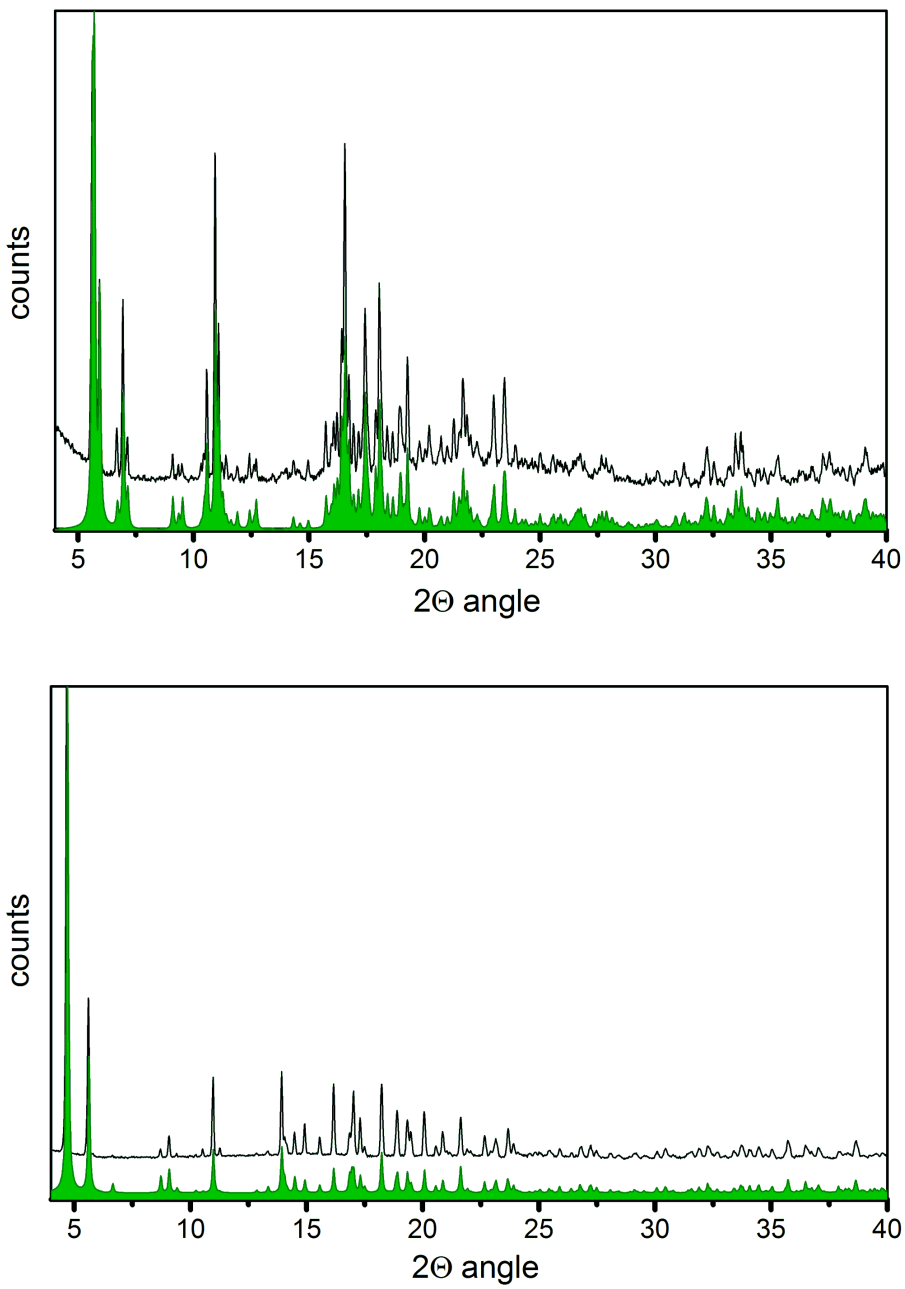
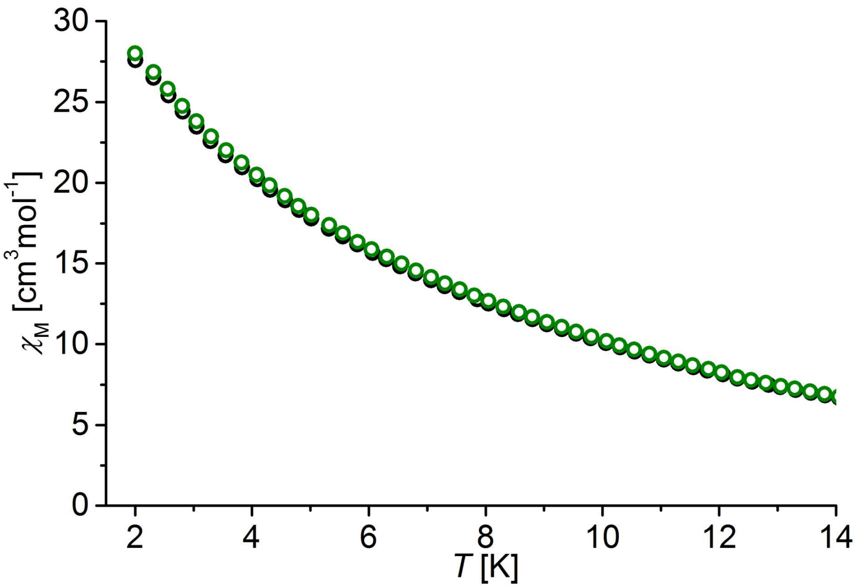


Figure S1 PXRD patterns of compounds **1** (top) and **2** (bottom). Black solid lines are the experimental patterns and color lines are the respective calculated patterns from single-crystal XRD models.



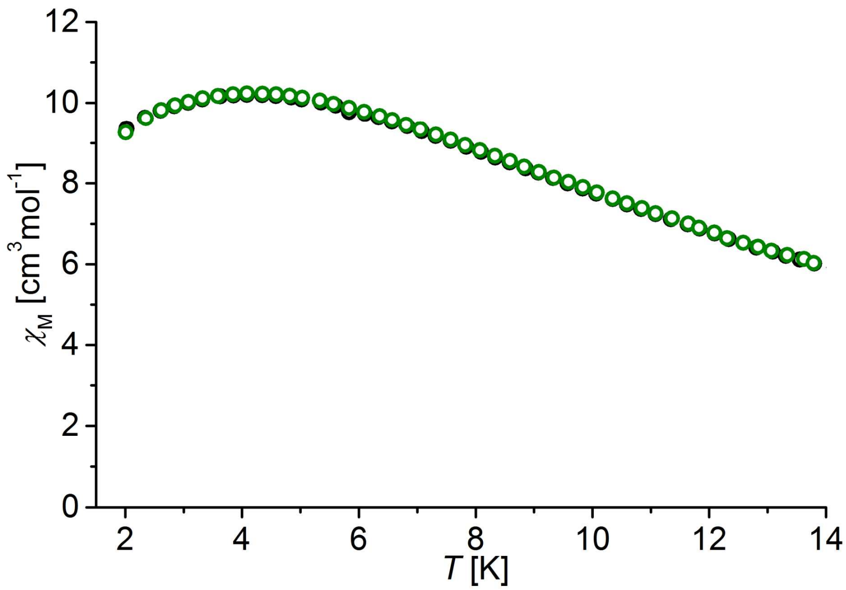


Figure S2 Magnetic properties of **1** (top) and **2** (bottom): field-cooled (FC, green) and zero-field cooled (ZFC, black) magnetization curves under H = 10 Oe in the 2 – 15 K range.

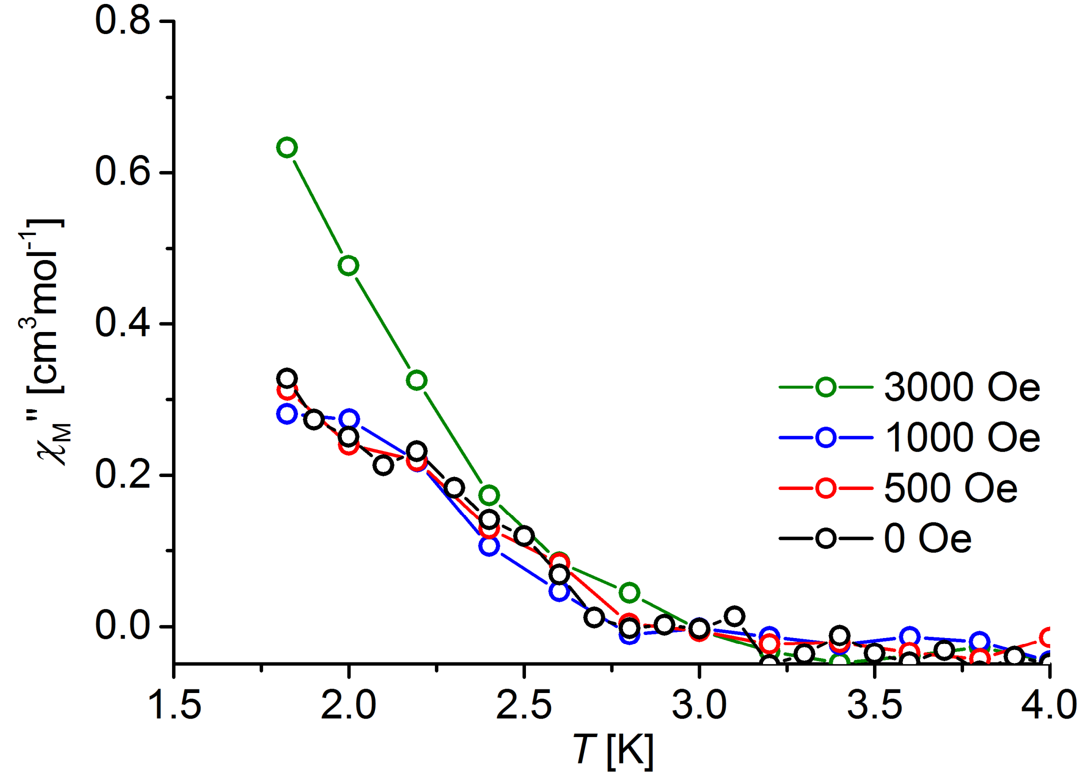


Figure S3 Magnetic properties of **2**: *ac* magnetic susceptibility χ_M" versus T curves under various applied *dc* magnetic fields (H_{dc} = 0, 500, 1000, 3000 Oe, H_{ac} = 3 Oe, ν = 100 Hz)

References to Supporting Information

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