

Supporting information for

**Creation of Co(II) single-ion magnets by doping into Zn(II)
diamagnetic metal-organic frameworks**

Masanori Wakizaka,^{1*} Ryuta Ishikawa,² Hisaaki Tanaka,³ Shraddha Gupta,⁴ Shinya Takaishi,⁴ and Masahiro Yamashita^{4,5*}

¹ Frontier Research Institute for Interdisciplinary Sciences, Tohoku University,
6-3 Aramaki-Aza-Aoba, Aoba-Ku, Sendai 980-8578, Japan.

² Department of Chemistry, Faculty of Science, Fukuoka University,
8-19-1 Nanakuma, Jonan-Ku, Fukuoka 814-0180, Japan.

³ Department of Applied Physics, Graduate School of Engineering, Nagoya University, Chikusa,
Nagoya 464-8603, Japan.

⁴ Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba,
Aoba-Ku, Sendai 980-8578, Japan. Fax: +81-22-795-6548; Tel: +81-22-795-6544.

⁵ School of Materials Science and Engineering, Nankai University, Tianjin 300350, P. R. China.

E-mail: masanori.wakizaka.a7@tohoku.ac.jp, yamasita@agnus.chem.tohoku.ac.jp

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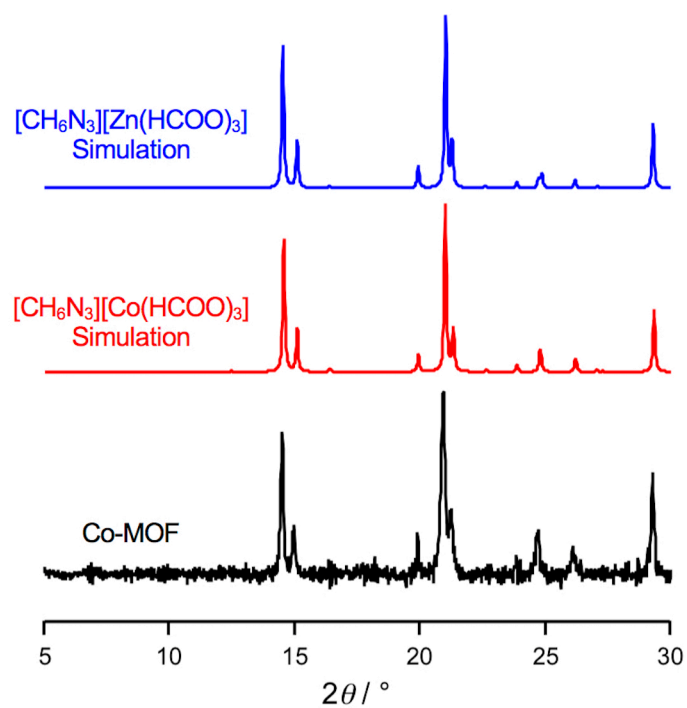
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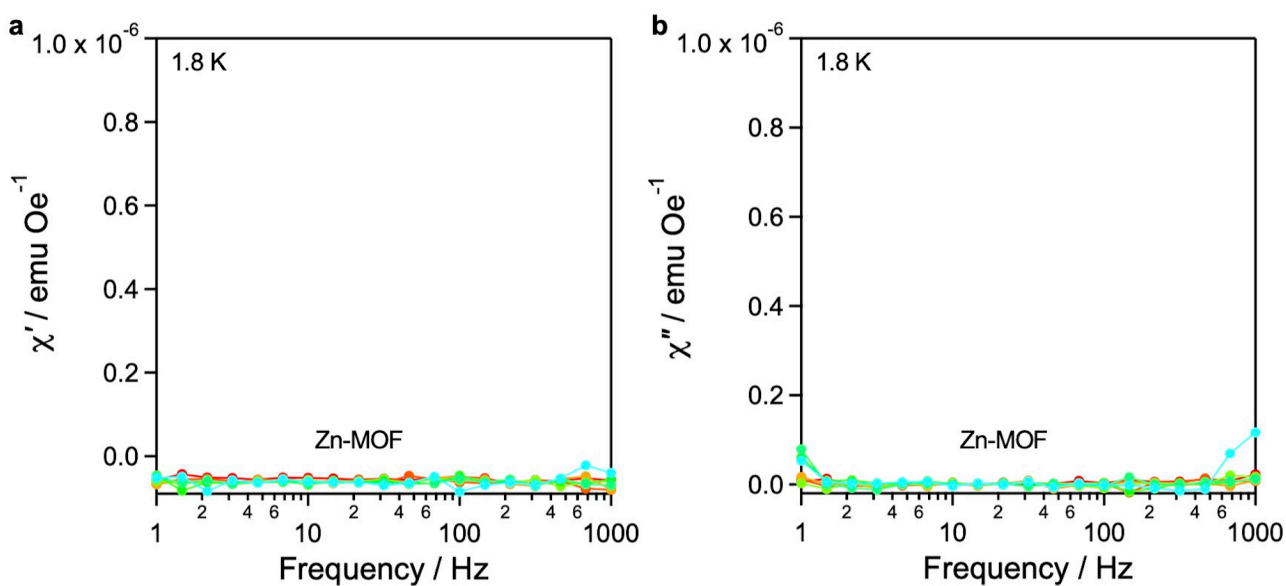
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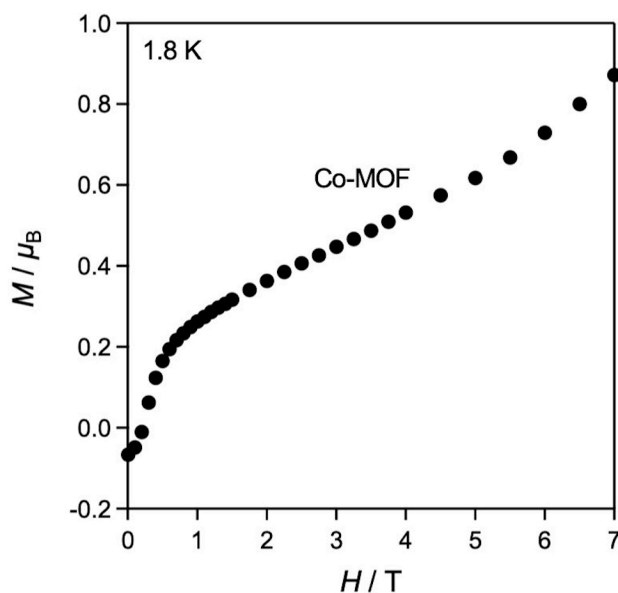
Supplementary Fig. 1. PXRD patterns of Co-MOF (black line) together with simulations of $[\text{CH}_6\text{N}_3][\text{M}(\text{HCOO})_3]$ ($\text{M} = \text{Zn}^{\text{II}}$ (blue line), Co^{II} (red line)).³³

Supplementary Table 1. Summary of ICP-AES data

Sample	[ppm]		[wt%]		[mol _M /mol _{total M}]	
	Co	Zn	Co	Zn	Co	Zn
Zn-MOF	0.000	9.934	0	24.76	0	1
Co/Zn-MOF(0.2%)	0.017	9.916	0.04	24.84	0.19	99.81
Co/Zn-MOF(0.5%)	0.043	9.973	0.11	24.88	0.48	99.52
Co/Zn-MOF(1%)	0.090	10.00	0.225	25	0.99	99.01



Supplementary Fig. 2. (a) The real part (χ') and (b) the imaginary part (χ'') of AC susceptibility of $[\text{CH}_6\text{N}_3][\text{Zn}(\text{HCOO})_3]$ (Zn-MOF) measured at 1.8 K under magnetic field of 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 T. AC drive is 2.5 Oe.



Supplementary Fig. 3. The M - H curve of the first magnetization of $[\text{CH}_6\text{N}_3][\text{Co}^{\text{II}}(\text{HCOO})_3]$ (Co-MOF) at 1.8 K after heating at 100 K under zero-magnetic field.

Supplementary Table 2. Summary of CASSCF calculation data



Spin system	$S = 3/2$	$S = 1/2$
g_x, g_y, g_z	1.72, 2.23, 2.93	2.92, 3.55, 6.48
D [cm^{-1}]	+122	–
E [cm^{-1}]	19.0	–

Structure of $[\text{Co}^{\text{II}}(\text{HCOO})_6]^{4-}$ was obtained from ref. 33.

Supplementary Table 3. Atomic coordinates of $[\text{Co}^{\text{II}}(\text{HCOO})_6]^{4-}$ using the reported single crystal X-ray structure with hydrogen positions optimized by the DFT calculation ^a

	<i>x</i>	<i>y</i>	<i>z</i>
Co	0.02425030	0.00004091	0.00000914
O	-0.06262584	-4.13695130	-0.56969792
O	-2.86647001	0.44950430	-3.06977004
O	-2.86622938	-0.44944726	3.07003852
O	-1.55190371	0.53638901	-1.29880433
O	-1.55180568	-0.53636436	1.29896351
O	0.04919550	-1.93332221	-0.81819738
O	2.61511916	0.31285334	-3.28081291
O	1.30079554	0.62255615	-1.53487255
O	-0.06248354	4.13694327	0.56972660
O	2.61538156	-0.31293600	3.28053261
O	1.30090506	-0.62261641	1.53469152
O	0.04930511	1.93330396	0.81822523
C	-0.00669317	-2.97267719	-0.14005947
C	-1.89534804	0.05800251	-2.39630241
C	-1.89515135	-0.05796721	2.39648403
C	2.27186301	0.09089423	-2.10432109
C	2.27203760	-0.09096625	2.10406322
C	-0.00660622	2.97265905	0.14008772
H	-0.01087399	-2.82751507	0.96299905
H	-1.27871780	-0.78418421	-2.78660026
H	-1.27847656	0.78421164	2.78673207
H	2.86498078	-0.65068309	-1.50592986
H	2.86511580	0.65060122	1.50562553
H	-0.01086761	2.82749422	-0.96296848

^a Ref. 33

Supplementary Table 4. CASSCF computed spin-free and spin-orbit states of $[\text{Co}^{\text{II}}(\text{HCOO})_6]^{4-}$

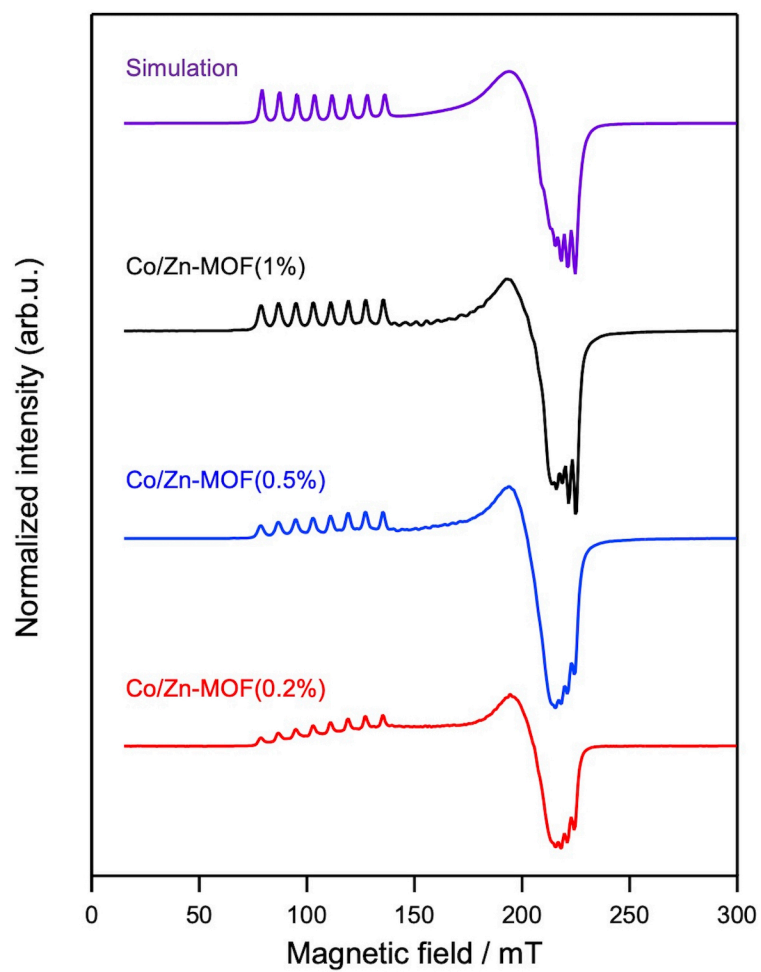
spin-free states (cm^{-1})		spin-orbit states (cm^{-1})	
0.0	34051.2	0.0	26652.1
87.3	34083.5	260.6	27055.9
479.4	34283.7	451.5	28933.7
5940.3	34507.4	865.1	29318.1
6029.5	34598.3	1081.6	29418.3
6437.4	34690.9	1178.4	29482.8
13155.4	34725.5	6398.0	29675.3
15277.4	34776.8	6441.9	29862.2
15606.9	46916.2	6525.8	31696.0
20076.5	47048.3	6608.5	31835.0
20135.0	47153.5	6925.4	34318.7
20193.2	47739.6	7035.9	34465.2
20360.4	47793.2	13707.0	34607.9
20510.9	47980.1	13709.1	35012.5
20630.7	48675.2	15755.2	35103.7
23126.1	72302.8	16085.2	35224.5
23377.7	72487.9	20294.2	35714.6
23457.2	72530.5	20416.7	35970.4
24312.0	72828.9	20839.9	47249.8
25962.4	72852.8	21008.1	47628.6
26060.0		21150.3	47769.7
26104.2		21356.2	48211.5
28463.0		23457.0	48295.7
28707.1		23459.9	48613.7
28765.6		23666.6	49225.6
28965.6		23736.9	72740.0
29164.2		23816.8	72999.4
29362.1		24177.6	73144.1
31126.8		24748.4	73266.6
31266.4		26513.5	73613.2

Supplementary Table 5. NEVPT2 computed spin-free and spin-orbit states of $[\text{Co}^{\text{II}}(\text{HCOO})_6]^{4-}$

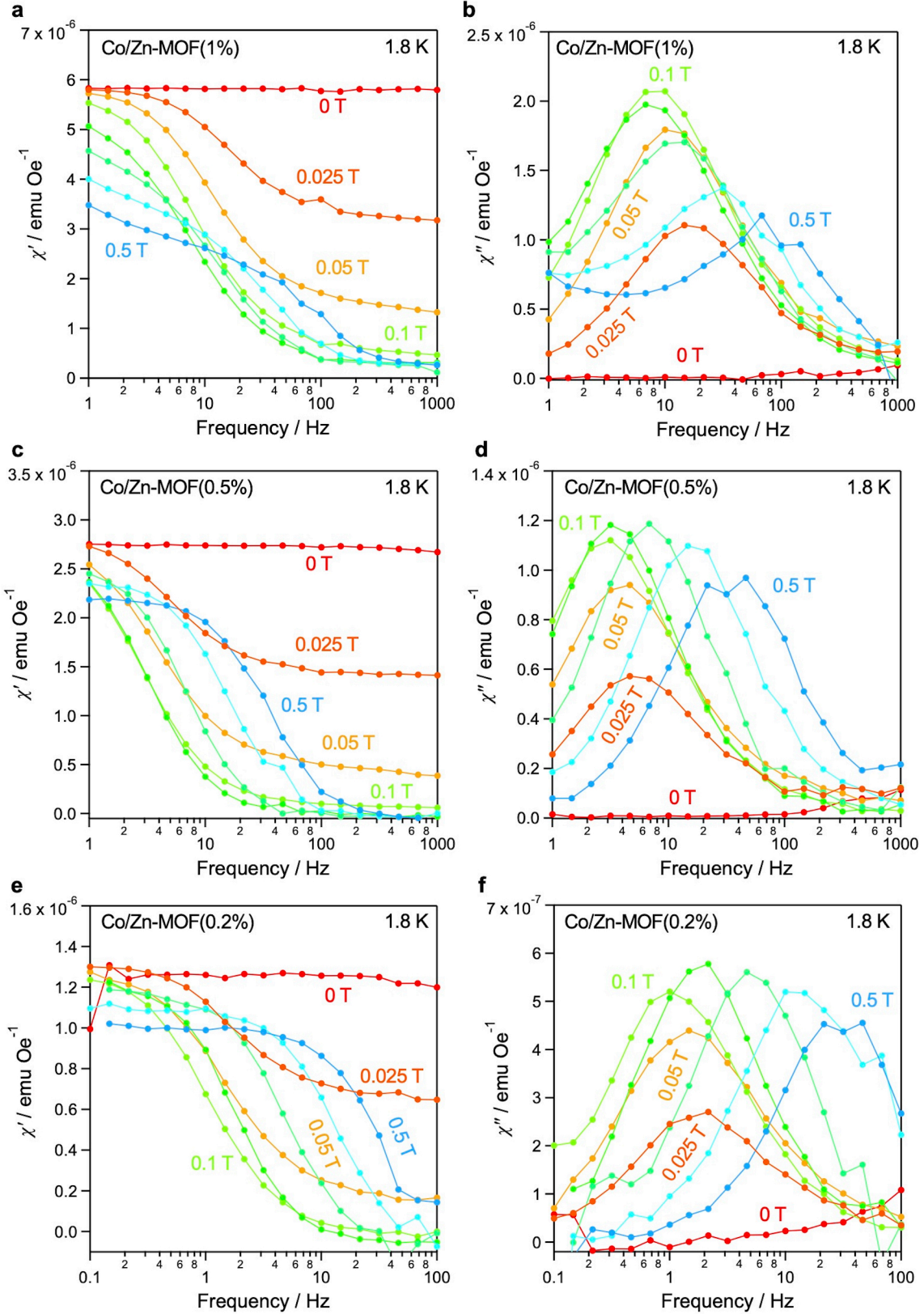
spin-free states (cm^{-1})		spin-orbit states (cm^{-1})	
0.0	33241.2	0	23647.1
130.8	33324.8	252.1	25076.6
568.6	33388.4	474.6	27801.1
7490.5	34408.9	867.7	28295.3
7629.6	34483.8	1130.5	28451.6
8046.5	34526.0	1227.9	29069.4
11652.0	34765.2	7918.1	29174.0
12104.2	34790.1	7945.7	29440.9
16258.0	42263.6	8081.4	31092.7
18602.3	42426.7	8150.3	31308.9
18611.5	42554.7	8495.5	33549.5
18669.8	43893.9	8597.7	33604.1
18968.8	43965.8	12127.6	34021.8
19151.9	44186.7	12577.8	34851.0
19314.1	44738.3	16740.6	34943.0
21538.5	64658.5	16743.3	35162.2
21796.4	64925.1	18797.4	35361.0
21859.3	64957.0	18934.3	35839.2
22599.1	65219.2	19300.6	42589.9
22700.9	65223.5	19545.9	42973.9
22789.4		19757.7	43142.5
24473.5		19983.3	44332.5
27322.7		21686.1	44437.6
27783.4		21791.5	44778.5
27806.6		21896.9	45251.0
28617.6		22002.8	65087.8
28699.2		22050.9	65384.9
28982.7		22412.2	65528.2
30556.6		23493.2	65638.4
30779.1		23615.2	65969.7

Supplementary Table 6. CASSCF and NEVPT2 computed spin-orbit coupling constant (ζ), Racah parameter (B and C), and ligand-field splitting for $[\text{Co}^{\text{II}}(\text{HCOO})_6]^{4-}$

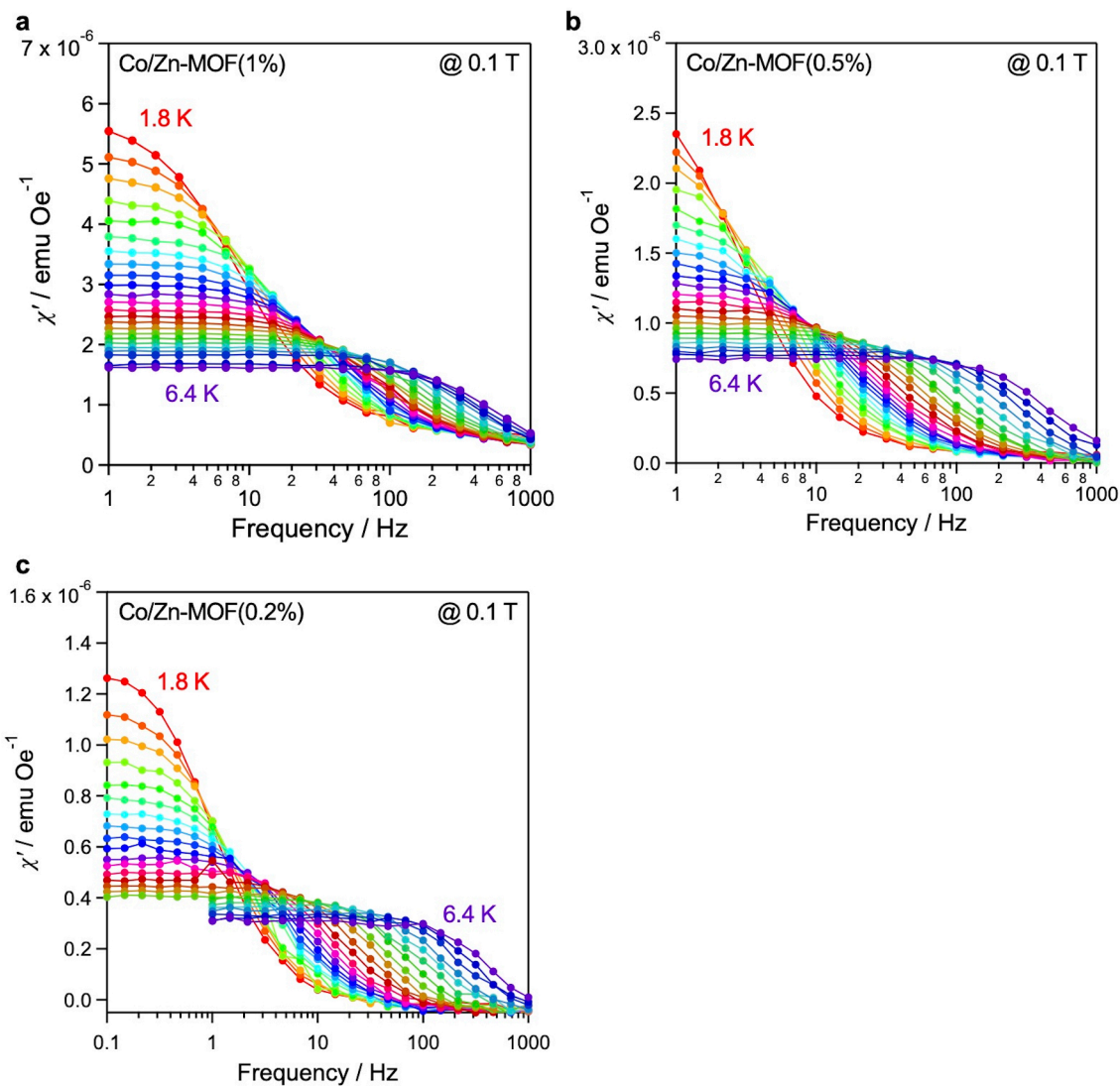
	Co ²⁺ free ion		[Co ^{II} (HCOO) ₆] ⁴⁻	
ζ	527		520	
B	1081	(1252)	1045	(1214)
C	4224	(4621)	4045	(4499)
			0	(0)
			281	(216)
ligand-field splitting			362	(310)
			7221	(6758)
			7647	(7152)



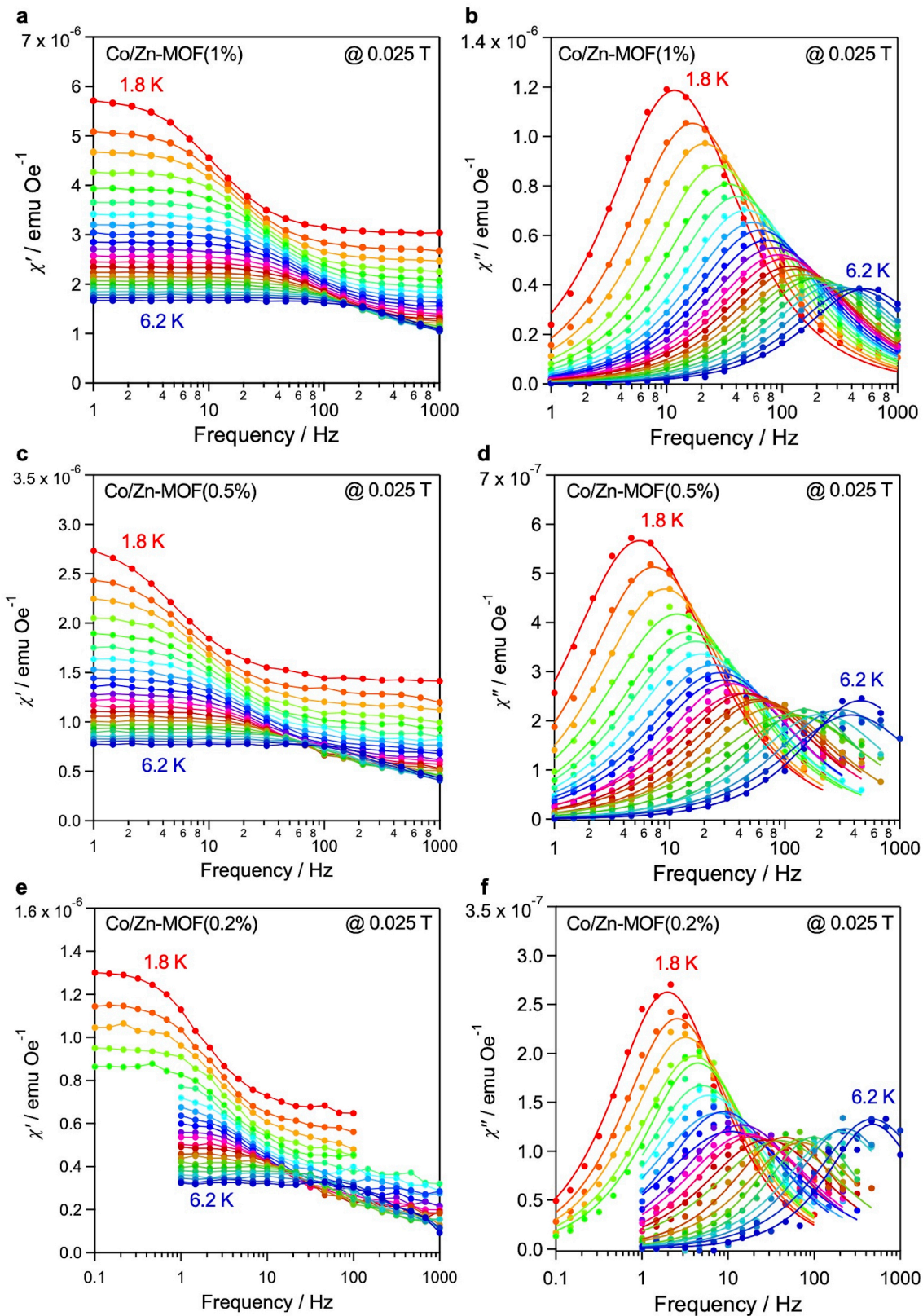
Supplementary Fig. 4. ESR spectra of Co/Zn-MOFs, together with that of a simulation applied $S' = 1/2$, $g_x' = 6.23$ (0.05), $g_y' = 3.31$ (0.34), $g_z' = 3.08$ (0.02), ${}^{\text{Co}}A_x = 710$ MHz, ${}^{\text{Co}}A_y = 0$ MHz, ${}^{\text{Co}}A_z = 85$ MHz, $\text{lwpp} = \text{Gaussian (0.9 mT)} + \text{Lorentzian (0.9 mT)}$ using EasySpin.⁵¹



Supplementary Fig. 5. The real part (χ') and the imaginary part (χ'') of AC susceptibility of (a, b) Co/Zn-MOF(1%), (c, d) (0.5%), and (e, f) (0.2%), measured at 1.8 K under a static magnetic field of 0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 T. AC drive is 2.5 Oe.



Supplementary Fig. 6. The real part of AC susceptibility (χ') of (a) Co/Zn-MOF(1%), (b) (0.5%), and (c) (0.2%), measured at 1.8–6.4 K under a static magnetic field of 0.1 T. AC drive is 2.5 Oe.



Supplementary Fig. 7. The real part (χ') and the imaginary part (χ'') of AC susceptibility of (a, b) Co/Zn-MOF(1%), (c, d) (0.5%), and (e, f) (0.2%), measured at 1.8–6.4 K under a static magnetic field of 0.025 T. AC drive is 2.5 Oe.

Supplementary Table 7. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(1%) at 0.1 T

T [K]	$\chi_T - \chi_S$ [10^{-6} emu/Oe]	t [s]	α
1.8	5.36(4)	0.0182(2)	0.160(7)
2	4.85(4)	0.0140(2)	0.146(7)
2.2	4.47(4)	0.0111(2)	0.142(7)
2.4	4.02(5)	0.0085(2)	0.13(1)
2.6	3.75(4)	0.0071(1)	0.134(8)
2.8	3.49(3)	0.00592(9)	0.137(8)
3	3.25(3)	0.00500(8)	0.131(8)
3.2	3.02(3)	0.00430(5)	0.127(9)
3.4	2.88(2)	0.00374(5)	0.129(6)
3.6	2.68(3)	0.00329(6)	0.13(1)
3.8	2.57(3)	0.00290(5)	0.13(1)
4	2.43(2)	0.00253(4)	0.123(8)
4.2	2.33(2)	0.00215(3)	0.131(8)
4.4	2.23(3)	0.00187(4)	0.13(1)
4.6	2.11(2)	0.00166(3)	0.113(9)
4.8	2.02(2)	0.00137(2)	0.114(7)
5	1.95(2)	0.00118(2)	0.10(1)
5.2	1.89(2)	0.00098(2)	0.09(1)
5.4	1.80(1)	0.000789(1)	0.077(7)
5.6	1.76(2)	0.00065(2)	0.08(1)
5.8	1.71(2)	0.000502(2)	0.07(1)
6	1.60(1)	0.000419(1)	0.054(7)
6.2	1.55(1)	0.000355(1)	0.038(7)
6.4	1.49(2)	0.000284(1)	0.026(9)

Parentheses show standard deviations.

Supplementary Table 8. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(1%) at 0.025 T

T [K]	$\chi_T - \chi_S$ [10^{-6} emu/Oe]	t [s]	α
1.8	2.77(4)	0.0136(3)	0.10(1)
2	2.45(3)	0.0095(2)	0.10(1)
2.2	2.25(3)	0.0075(1)	0.09(1)
2.4	2.05(3)	0.0058(1)	0.10(1)
2.6	1.90(3)	0.0047(1)	0.10(1)
2.8	1.76(3)	0.00389(9)	0.10(1)
3	1.65(2)	0.00327(7)	0.10(1)
3.2	1.53(2)	0.00285(6)	0.10(1)
3.4	1.46(1)	0.00247(4)	0.100(8)
3.6	1.39(2)	0.00217(4)	0.11(1)
3.8	1.33(2)	0.00187(5)	0.12(1)
4	1.24(1)	0.00170(3)	0.11(1)
4.2	1.19(2)	0.00150(3)	0.10(1)
4.4	1.15(2)	0.00135(4)	0.12(1)
4.6	1.08(1)	0.00121(2)	0.09(1)
4.8	1.04(1)	0.00105(2)	0.10(1)
5	0.97(1)	0.00096(1)	0.080(8)
5.2	0.97(1)	0.00081(1)	0.079(9)
5.4	0.93(1)	0.00066(1)	0.08(1)
5.6	0.90(1)	0.00056(1)	0.08(1)
5.8	0.85(1)	0.00047(1)	0.055(8)
6	0.85(1)	0.00037(1)	0.067(9)
6.2	0.83(1)	0.00031(1)	0.05(1)

Parentheses show standard deviations.

Supplementary Table 9. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(0.5%) at 0.1 T

T [K]	$\chi_T - \chi_S$ [10^{-6} emu/Oe]	t [s]	α
1.8	2.73(1)	0.0524(4)	0.123(4)
2	2.49(2)	0.0410(4)	0.133(5)
2.2	2.26(1)	0.0326(3)	0.129(4)
2.4	2.02(3)	0.0242(7)	0.14(1)
2.6	1.89(2)	0.0207(4)	0.14(1)
2.8	1.76(1)	0.0172(4)	0.151(6)
3	1.62(2)	0.0141(4)	0.143(9)
3.2	1.53(1)	0.0122(2)	0.150(6)
3.4	1.44(1)	0.0104(4)	0.146(7)
3.6	1.35(1)	0.0088(1)	0.146(6)
3.8	1.29(1)	0.0075(1)	0.145(8)
4	1.21(1)	0.0065(1)	0.14(1)
4.2	1.17(1)	0.0053(1)	0.14(1)
4.4	1.13(1)	0.0042(1)	0.141(9)
4.6	1.05(1)	0.00340(6)	0.109(9)
4.8	1.01(1)	0.00271(4)	0.106(9)
5	0.96(7)	0.00214(2)	0.087(6)
5.2	0.98(2)	0.00168(5)	0.09(2)
5.4	0.93(2)	0.00130(3)	0.07(1)
5.6	1.00(2)	0.00082(3)	0.13(2)
5.8	0.92(2)	0.00064(2)	0.11(2)
6	0.97(3)	0.00045(2)	0.10(2)
6.2	0.85(2)	0.00040(1)	0.05(2)
6.4	0.93(2)	0.00026(1)	0.08(2)

Parentheses show standard deviations.

Supplementary Table 10. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(0.5%) at 0.025 T

T [K]	$\chi_T - \chi_S$ [10^{-6} emu/Oe]	t [s]	α
1.8	1.43(3)	0.0290(9)	0.15(2)
2	1.25(2)	0.0218(4)	0.13(1)
2.2	1.14(1)	0.0175(3)	0.12(1)
2.4	1.07(3)	0.0137(7)	0.16(2)
2.6	0.97(2)	0.0110(6)	0.15(3)
2.8	0.94(3)	0.0095(5)	0.16(2)
3	0.85(2)	0.0084(3)	0.15(2)
3.2	0.82(3)	0.0066(3)	0.17(3)
3.4	0.77(2)	0.0059(3)	0.16(2)
3.6	0.73(2)	0.0053(2)	0.16(2)
3.8	0.67(1)	0.0046(1)	0.12(1)
4	0.68(2)	0.0038(2)	0.17(2)
4.2	0.63(1)	0.0034(1)	0.13(2)
4.4	0.62(2)	0.0027(1)	0.16(3)
4.6	0.55(1)	0.0026(1)	0.09(1)
4.8	0.55(1)	0.0020(1)	0.12(2)
5	0.58(1)	0.0014(1)	0.20(3)
5.2	0.52(1)	0.0012(1)	0.14(2)
5.4	0.47(1)	0.0011(1)	0.04(2)
5.6	0.51(2)	0.0008(1)	0.11(2)
5.8	0.52(1)	0.0005(1)	0.10(2)
6	0.51(2)	0.0004(1)	0.12(3)
6.2	0.51(2)	0.0003(1)	0.04(2)

Parentheses show standard deviations.

Supplementary Table 11. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(0.2%) at 0.1 T

T [K]	$\chi_r - \chi_s$ [10^{-6} emu/Oe]	t [s]	α
1.8	1.31(2)	0.151(3)	0.13(1)
2	1.18(1)	0.111(2)	0.14(1)
2.2	1.08(1)	0.092(2)	0.14(1)
2.4	0.97(2)	0.077(2)	0.12(1)
2.6	0.91(1)	0.062(2)	0.15(1)
2.8	0.82(1)	0.049(1)	0.17(1)
3	0.78(1)	0.043(1)	0.16(1)
3.2	0.74(1)	0.034(1)	0.18(1)
3.4	0.70(1)	0.029(1)	0.17(1)
3.6	0.65(1)	0.0247(7)	0.14(1)
3.8	0.62(1)	0.0182(5)	0.16(1)
4	0.59(1)	0.0149(5)	0.14(2)
4.2	0.56(1)	0.0109(2)	0.12(1)
4.4	0.53(1)	0.0086(3)	0.19(2)
4.6	0.50(1)	0.0062(2)	0.09(1)
4.8	0.49(1)	0.00453(7)	0.080(8)
5	0.45(1)	0.00336(7)	0.06(1)
5.2	0.53(2)	0.0012(1)	0.17(3)
5.4	0.54(2)	0.0013(1)	0.19(4)
5.6	0.50(2)	0.00096(6)	0.16(3)
5.8	0.49(2)	0.00075(5)	0.14(4)
6	0.51(2)	0.00050(2)	0.13(2)
6.2	0.48(2)	0.00037(2)	0.11(2)
6.4	0.48(2)	0.00029(2)	0.06(3)

Parentheses show standard deviations.

Supplementary Table 12. AC susceptibility fitting data of the imaginary part of Co/Zn-MOF(0.2%) at 0.025 T

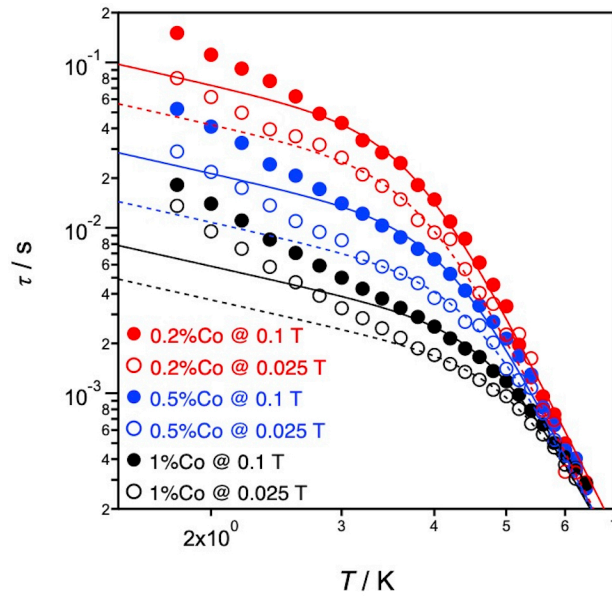
T [K]	$\chi_T - \chi_S$ [10^{-6} emu/Oe]	t [s]	α
1.8	0.68(1)	0.080(3)	0.17(2)
2	0.61(2)	0.062(3)	0.16(2)
2.2	0.57(2)	0.050(2)	0.17(2)
2.4	0.52(2)	0.039(2)	0.18(2)
2.6	0.49(2)	0.036(2)	0.15(3)
2.8	0.45(1)	0.032(2)	0.19(3)
3	0.44(2)	0.027(2)	0.20(4)
3.2	0.43(3)	0.021(2)	0.27(5)
3.4	0.39(1)	0.018(1)	0.21(3)
3.6	0.39(2)	0.015(2)	0.30(5)
3.8	0.37(2)	0.011(1)	0.23(4)
4	0.35(2)	0.0094(7)	0.25(4)
4.2	0.31(1)	0.0086(5)	0.19(3)
4.4	0.33(2)	0.0056(5)	0.24(4)
4.6	0.33(2)	0.0040(4)	0.25(4)
4.8	0.29(1)	0.0035(3)	0.14(4)
5	0.29(2)	0.0023(2)	0.18(5)
5.2	0.25(1)	0.0023(1)	0.07(3)
5.4	0.26(1)	0.0016(1)	0.07(3)
5.6	0.31(2)	0.00079(7)	0.16(4)
5.8	0.29(2)	0.00069(8)	0.11(6)
6	0.35(2)	0.00034(3)	0.17(4)
6.2	0.28(2)	0.00033(3)	0.06(6)

Parentheses show standard deviations.

Supplementary Table 13. Relaxation time fitting data

Sample	Static field [T]	B [$\text{s}^{-1} \text{K}^{-2}$]	C [$10^{-3} \text{s}^{-1} \text{K}^{-9}$]
Co/Zn-MOF(1%)	0.1	0.465(5)	6.1(7)
	0.025	0.252(2)	6.3(8)
Co/Zn-MOF(0.5%)	0.1	0.139(1)	6.0(3)
	0.025	0.0763(8)	5.8(6)
Co/Zn-MOF(0.2%)	0.1	0.0474(4)	5.3(5)
	0.025	0.0313(4)	5.8(10)

Parentheses show standard deviations.



Supplementary Fig. 8. Log-scale plots of magnetic relaxation time (τ) versus temperature (T). For Co/Zn-MOF(1%), Co/Zn-MOF(0.5%), and Co/Zn-MOF(0.2%), measured under a static magnetic field of 0.1 and 0.025 T. Solid and dotted lines show fitting curves using the spin-lattice and Raman processes.