Linear 3d-4f compounds: Synthesis, structure, and determination of the d-f magnetic interaction

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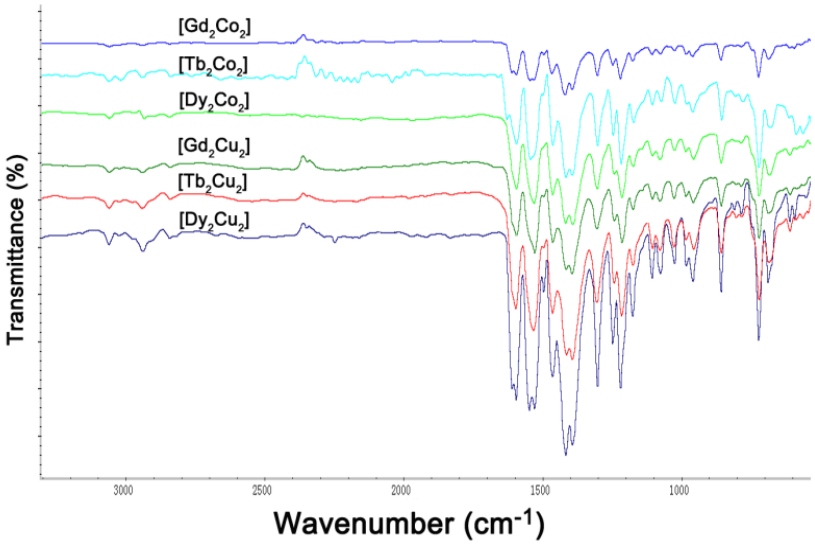

Fig. S1 IR spectra of compounds **1**-**3**, **7**-**9**.

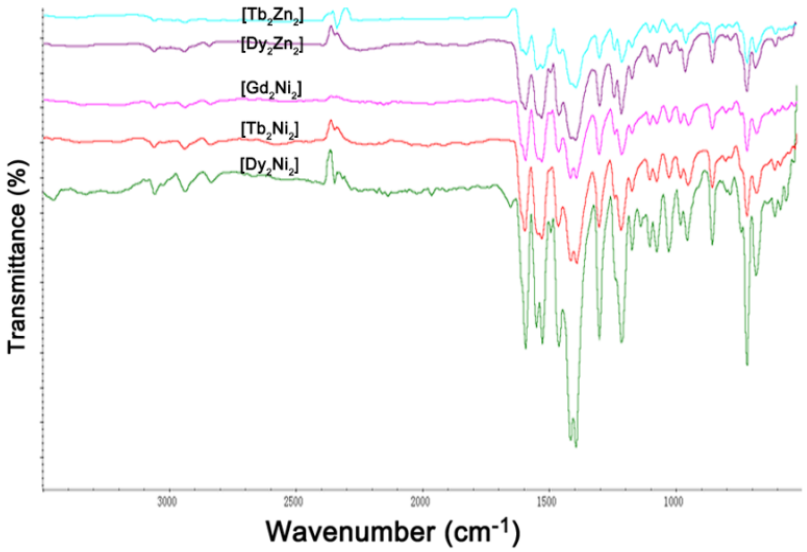

Fig. S2 IR spectra of compounds **4**-**6**, **11** and **12**.

Table S1 Elemental analysis and yield (%) for compounds **1-15**.

	Formula	Yielda %	Elemental analysis: Found (calculated)		
			C	H	N
1	$C_{78}H_{74}Co_2Gd_2N_4O_{25}$	74	49.12 (49.27)	4.21 (3.90)	2.90 (2.95)
2	$C_{78}H_{74}Co_2N_4O_{24}Tb_2$	67	49.43 (49.60)	4.02 (3.92)	2.85 (2.97)
3	$C_{78}H_{74}Co_2Dy_2N_4O_{24}$	71	49.28 (49.41)	3.79 (3.91)	2.94 (2.96)
4	$C_{78}H_{78}Gd_2N_4Ni_2O_{26}$	65	48.92 (48.77)	3.76 (4.06)	2.93 (2.92)
5	$C_{78}H_{72}N_4Ni_2O_{25}Tb_2$	78	49.14 (49.25)	3.89 (3.79)	2.94 (2.95)
6	$C_{78}H_{76}Dy_2N_4Ni_2O_{25}$	69	48.91 (48.96)	3.87 (3.96)	2.93 (2.93)
7	$C_{74}H_{66}Cu_2Gd_2N_4O_{24}$	74	48.34 (47.31)	3.59 (3.52)	3.05 (2.98)
8	$C_{74}H_{62}Cu_2N_4O_{22}Tb_2$	72	48.81 (49.55)	3.75 (3.69)	3.00 (2.96)
9	$C_{76}H_{70}Cu_2Dy_2N_4O_{26}$	80	47.19 (47.61)	3.76 (3.65)	2.90 (2.92)
10	$C_{76}H_{70}Gd_2N_4O_{24}Zn_2$	84	48.75 (48.80)	3.68 (3.75)	3.25 (3.00)
11	$C_{76}H_{70}N_4O_{24}Tb_2Zn_2$	75	48.61 (47.62)	3.68 (3.66)	2.98 (2.92)
12	$C_{76}H_{70}Dy_2N_4O_{24}Zn_2$	83	47.78 (48.53)	3.85 (3.73)	2.98 (2.98)
13	$C_{78}H_{74}Co_2N_4O_{26}Y_2$	54	52.33 (52.61)	4.32 (4.16)	3.02 (3.15)
14	$C_{78}H_{74}N_4Ni_2O_{24}Y_2$	62	53.58 (53.59)	4.02 (4.24)	3.28 (3.21)
15	$C_{74}H_{66}Cu_2N_4O_{24}Y2$	53	53.65 (52.22)	4.13 (3.88)	3.21 (3.29)

Table S2 Crystallographic data for complexes **1-2, 4-5, 7-8, 10-11, 13-15**.

compounds	**1**	**2**	**4**	**5**
chemical formula	$C_{78}H_{74}Co_2Gd_2N_4O_{25}$	$C_{78}H_{74}Co_2N_4O_{24}Tb_2$	$C_{78}H_{78}Gd_2N_4Ni_2O_{26}$	$C_{78}H_{72}N_4Ni_2O_{25}Tb_2$
FW, ($g\cdot mol^{-1}$)	1899.77	1887.11	1919.36	1900.65
temperature (K)	293(2)	296(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
Z	4	4	4	4
a, Å	24.175(4)	24.168(3)	24.011(8)	24.177(7)
b, Å	16.937(3)	16.9669(16)	16.677(6)	16.899(5)
c, Å	22.730(5)	22.816(3)	22.589(10)	22.727(10)
β, °	121.179(3)	121.013(2)	121.27(2)	121.326(18)
V, $Å^3$	7963(3)	8018.3(16)	7731(5)	7932(5)
μ, mm^{-1}	0.71073	0.71073	0.71073	0.71073
F(000)	3808	3784	3840	3816
ρ_{calcd}, $g\cdot cm^{-3}$	1.585	1.563	1.644	1.592
R_1[a], wR_2 ($I \geq 2\sigma(I)$)[b]	0.0546, 0.1306	0.0541, 0.1493	0.0791 0.1785	0.0724, 0.1641
R_1, wR_2 (all data)	0.1092, 0.1597	0.1131, 0.1829	0.1964, 0.2344	0.1902, 0.2210
GOF [c]	1.01	1.019	0.988	0.963

compounds	**7**	**8**	**10**	**11**
chemical formula	$C_{74}H_{66}Cu_2Gd_2N_4O_{24}$	$C_{74}H_{62}Cu_2N_4O_{22}Tb_2$	$C_{76}H_{70}Gd_2N_4O_{24}Zn_2$	$C_{76}H_{70}N_4O_{24}Tb_2Zn_2$

FW, (g·mol^{-1})	1836.88	1804.19	1868.60	1915.13
temperature (K)	296(2)	296(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
Z	4	4	4	4
a, Å	23.668(18)	23.8031(14)	23.749(3)	23.874(3)
b, Å	16.575(13)	16.5092(10)	16.590(2)	16.890(3)
c, Å	23.13(2)	23.023(2)	22.922(3)	22.915(4)
β, °	119.671(14)	119.9340(10)	120.225(12)	120.515(12)
V, Å^3	7885(12)	7840.4(9)	7803.4(17)	7960(2)
μ, mm^{-1}	0.71073	0.71073	0.71073	0.71073
F(000)	3632	3720	3736	3832
ρ_{calcd}, g·cm^{-3}	1.541	1.579	1.591	1.598
R_1[a], wR_2 ($I \geq 2\,\sigma\,(I)$)[b]	0.0861, 0.2397	0.0524, 0.1422	0.0739, 0.1938	0.0761, 0.2067
R_1, wR_2 (all data)	0.1720, 0.3070	0.0847, 0.1648	0.1497, 0.2481	0.1241, 0.2494
GOF [c]	1.029	1.05	1.006	1.059

compounds	**13**	**14**	**15**
chemical formula	$C_{78}H_{74}Co_2N_4O_{26}Y_2$	$C_{78}H_{74}N_4Ni_2O_{24}Y_2$	$C_{74}H_{66}Cu_2N_4O_{24}Y2$
FW, (g·mol^{-1})	1779.09	1746.65	1700.20
temperature (K)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
Z	4	4	4
a, Å	24.133(2)	24.185(3)	23.530(12)
b, Å	17.0815(15)	17.062(2)	16.641(8)
c, Å	22.658(3)	22.656(4)	23.044(16)
β, °	121.2330(10)	121.363(2)	119.75(3)
V, Å^3	7986.5(14)	7983(2)	7834(8)
μ, mm^{-1}	0.71073	0.71073	0.71073
F(000)	3640	3576	3432
ρ_{calcd}, g·cm^{-3}	1.480	1.452	1.435
R_1[a], wR_2 ($I \geq 2\,\sigma\,(I)$)[b]	0.0604, 0.1212	0.0640, 0.1792	0.0927, 0.2581
R_1, wR_2 (all data)	0.1653, 0.1553	0.1423, 0.2176	0.2230, 0.3314
GOF [c]	0.978	0.997	0.995

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, [c] goodness of fit on F^2

Table S3 Selected bond distances (Å), angles (º) for complexes **3**, **6**, **9** and **12**.

	3	**6**	**9**	**12**
M(1) [d]-Dy(1)	3.428(2)	3.4073(13)	3.3988(16)	3.420(16)
M(1)-M(1´)	3.8164(29)	3.8249(19)	3.8268(22)	3.8228(20)
Dy(1)-O(2)	2.307(9)	2.372(6)	2.383(8)	2.326(7)
Dy(1)-O(9)	2.339(9)	2.316(6)	2.341(7)	2.370(7)
Dy(1)-O(4)	2.363(9)	2.663(7)	2.322(7)	2.350(8)
Dy(1)-O(5)	2.393(10)	2.440(6)	2.451(9)	2.364(9
Dy(1)-O(8)	2.428(10)	2.376(7)	2.437(11)	2.449(8)
Dy(1)-O(6)	2.432(11)	2.434(7)	2.413(8)	2.434(11)
Dy(1)-O(7)	2.433(10)	2.426(8)	2.376(9)	2.405(9)
Dy(1)-O(3)	2.491(11)	2.283(5)	2.690(8)	2.503(11)
Dy(1)-O(1)	2.698(11)	2.493(7)	2.491(10)	2.676(9)
M(1)-O(4)	2.008(9)	2.013(6)	1.971(7)	2.014(7)
M(1)-O(2)	2.016(9)	1.992(6)	1.908(7)	2.047(7)
M(1)-N(2)	2.029(12)	2.031(7)	1.937(8)	2.023(9)
M(1)-N(1)	2.069(11)	2.007(6)	1.993(9)	2.078(9)
M(1)-O(10)	2.095(9)	2.058(5)	2.235(7)	2.037(8)
M(1)-O(11)	2.177(11)	2.148(6)	--	--
M(1)-O(2)-Dy(1)	104.7(4)	102.3(3)	104.2(4)	102.7(3)
M(1)-O(4)-Dy(1)	103.0(4)	104.8(2)	104.4(3)	102.9(3)

[d] M represents Co, Ni, Cu and Zn for **3**, **6**, **9** and **12**, respectively.

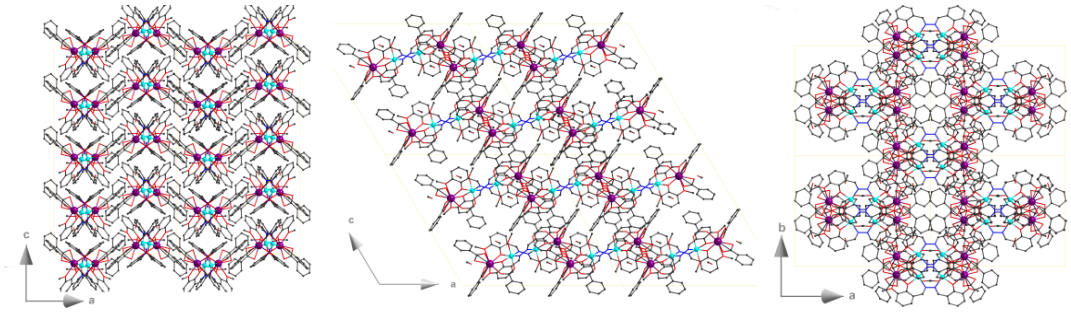

Fig. S3 Packing model of compound **3**.

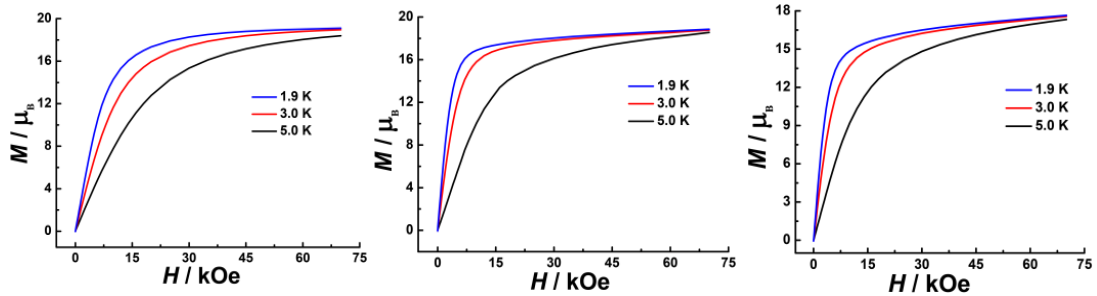

Fig. S4 Molar magnetization (*M*) vs magnetic field (*H*) for compounds [Gd_2Co_2] (left), [Tb_2Co_2] (middle), [Dy_2Co_2] (right) at 1.9, 3.0, and 5.0 K.

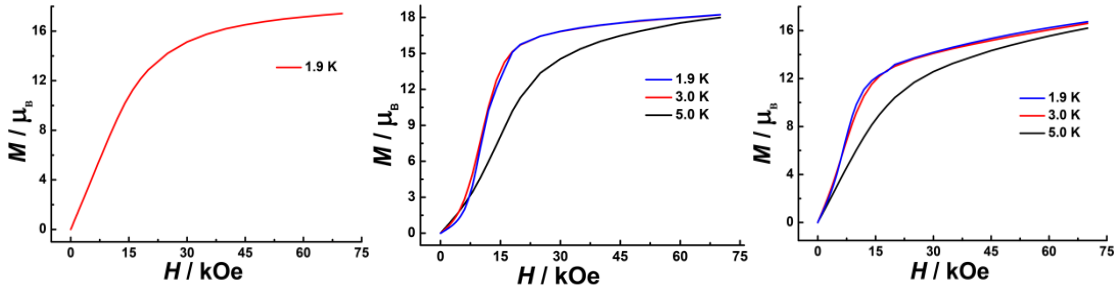

Fig. S5 Molar magnetization (*M*) vs magnetic field (*H*) for compounds [Gd_2Ni_2] (left), [Tb_2Ni_2] (middle), [Dy_2Ni_2] (right) at 1.9, 3.0, and 5.0 K.

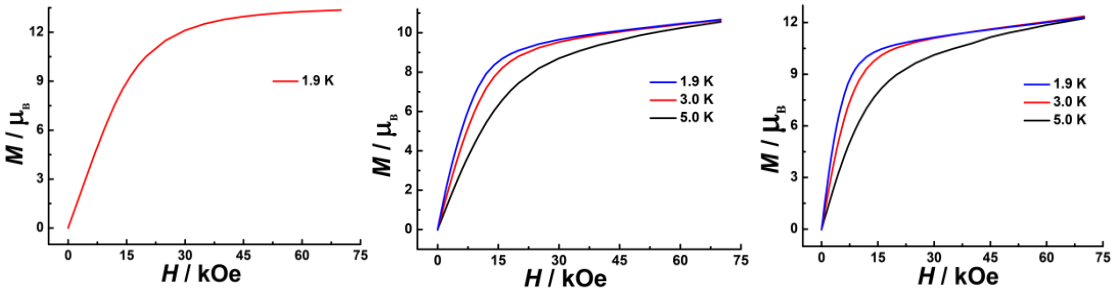

Fig. S6 Molar magnetization (*M*) vs magnetic field (*H*) for compounds [Gd_2Cu_2] (left), [Tb_2Cu_2] (middle), [Dy_2Cu_2] (right) at 1.9, 3.0, and 5.0 K.

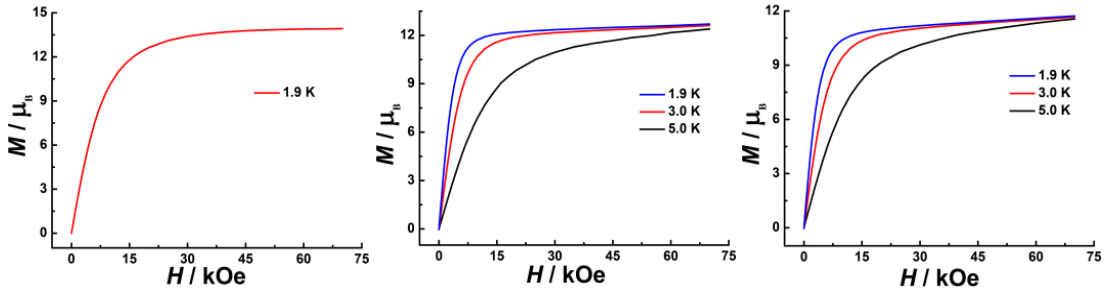

Fig. S7 Molar magnetization (M) vs magnetic field (H) for compounds [Gd_2Zn_2] (left), [Tb_2Zn_2] (middle), [Dy_2Zn_2] (right) at 1.9, 3.0, and 5.0 K.

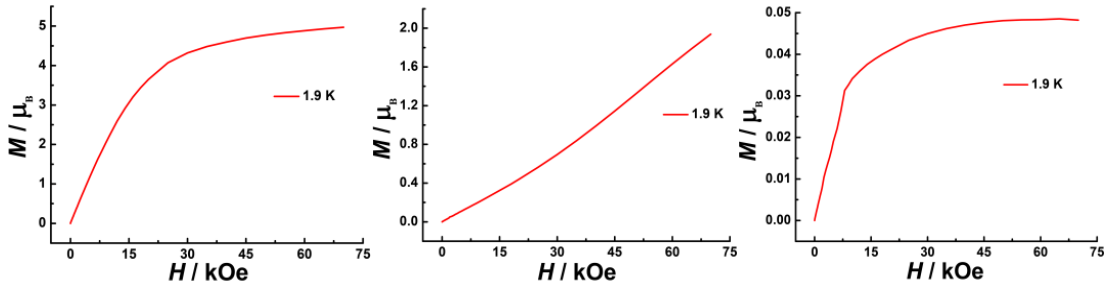

Fig. S8 Molar magnetization (M) vs magnetic field (H) for compounds [Y_2Co_2] (left), [Y_2Ni_2] (middle), [Y_2Cu_2] (right) at 1.9 K.

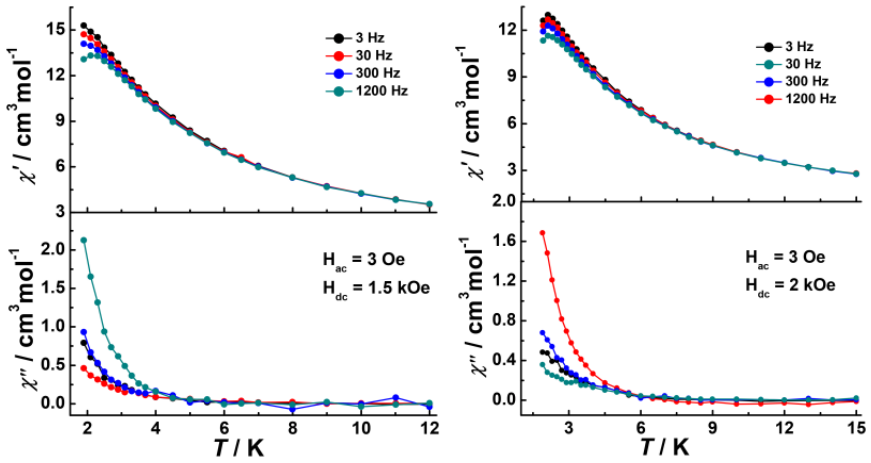

Fig. S9 Temperature-dependent ac susceptibility for [Tb_2Co_2] (left), [Dy_2Co_2] (right).

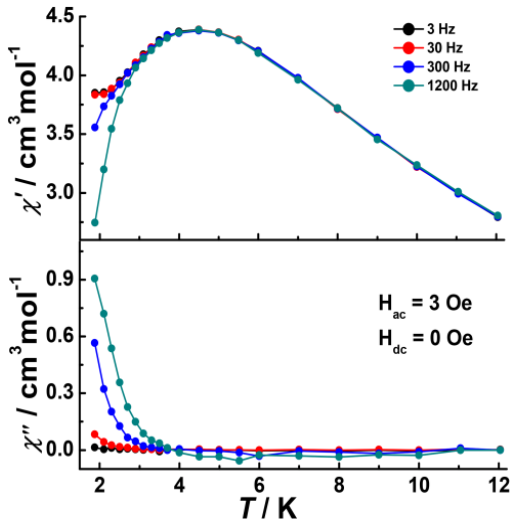

Fig. S10 Temperature-dependent ac susceptibility for [Dy_2Ni_2].

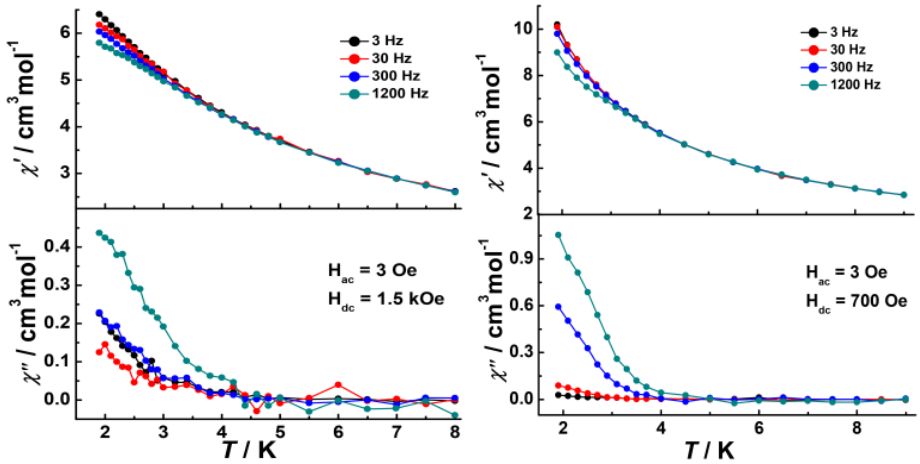

Fig. S11 Temperature-dependent ac susceptibility for [Tb_2Cu_2] (left), [Dy_2Cu_2] (right).

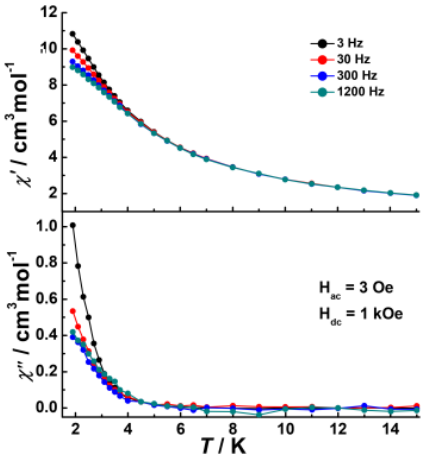

Fig. S12 Temperature-dependent ac susceptibility for [Tb_2Zn_2]