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The Different Magnetic Relaxation Behaviors in $[Fe(CN)_6]^{3-}$ or $[Co(CN)_6]^{3-}$ Bridged 3d-4f Heterometallic Compounds

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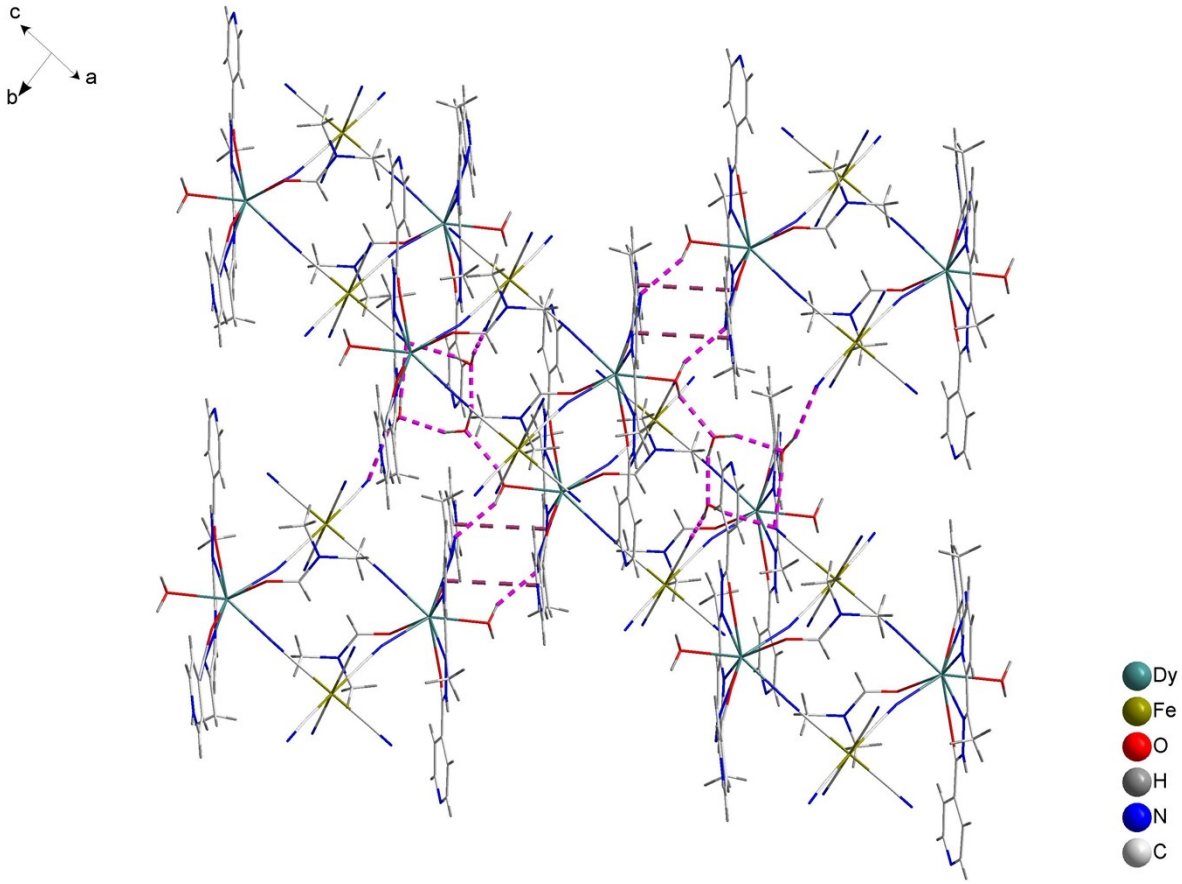

Figure S1 Crystal packing diagram of complex $\mathbf{1}_{DyFe}$

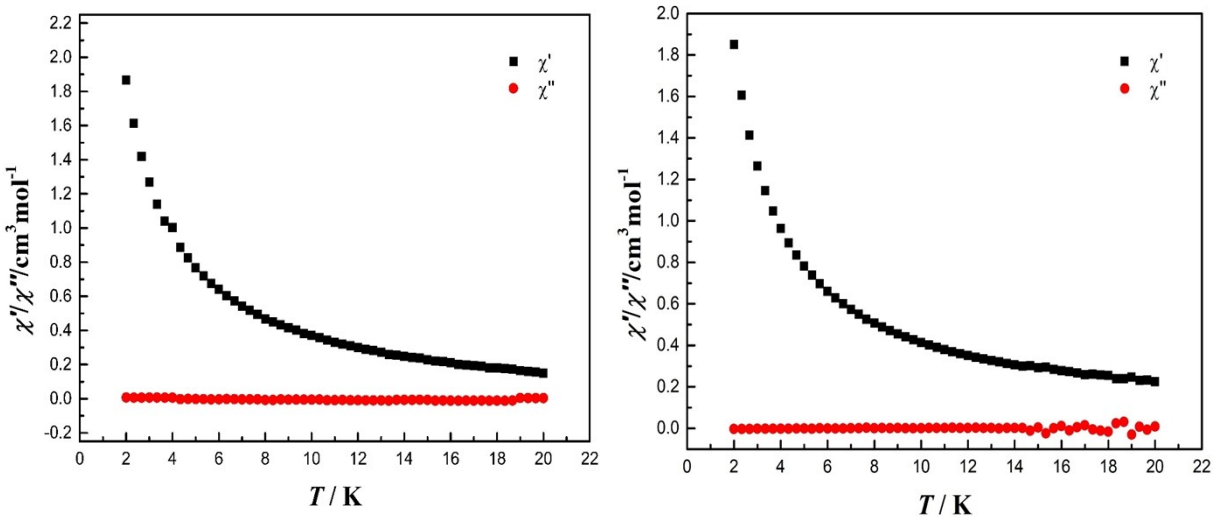

Figure S2 (left) Temperature dependence of the χ' and χ'' ac magnetic susceptibility for $\mathbf{1}_{\mathbf{DyFe}}$ and (right) $\mathbf{4}_{\mathbf{DyCo}}$ in 940 Hz under zero dc field

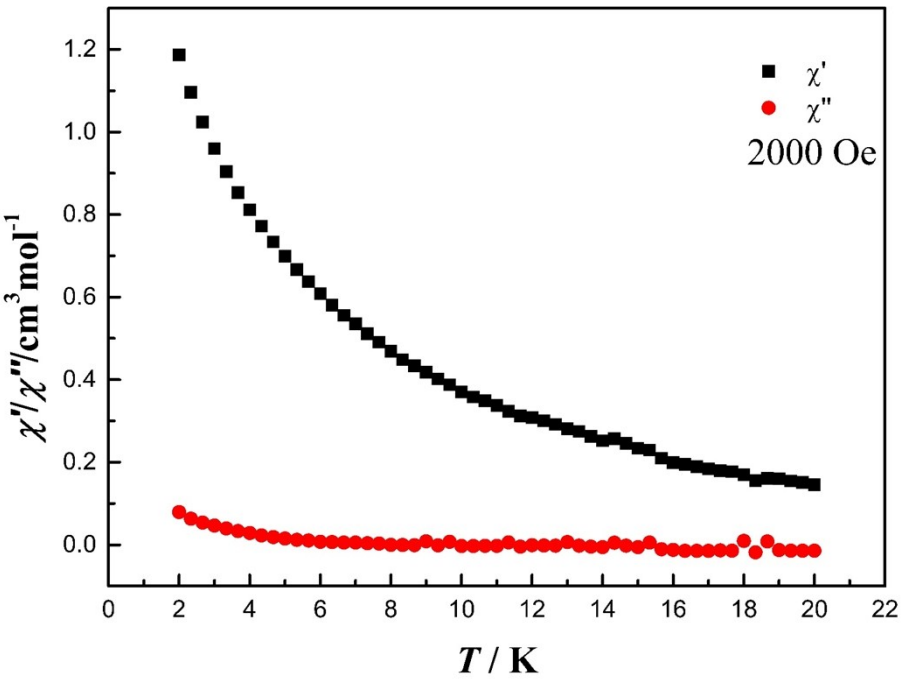

Figure S3 Temperature dependence of the χ' and χ'' ac magnetic susceptibility for $\mathbf{1}_{\mathbf{DyFe}}$ in 940 Hz under 2000 Oe dc field

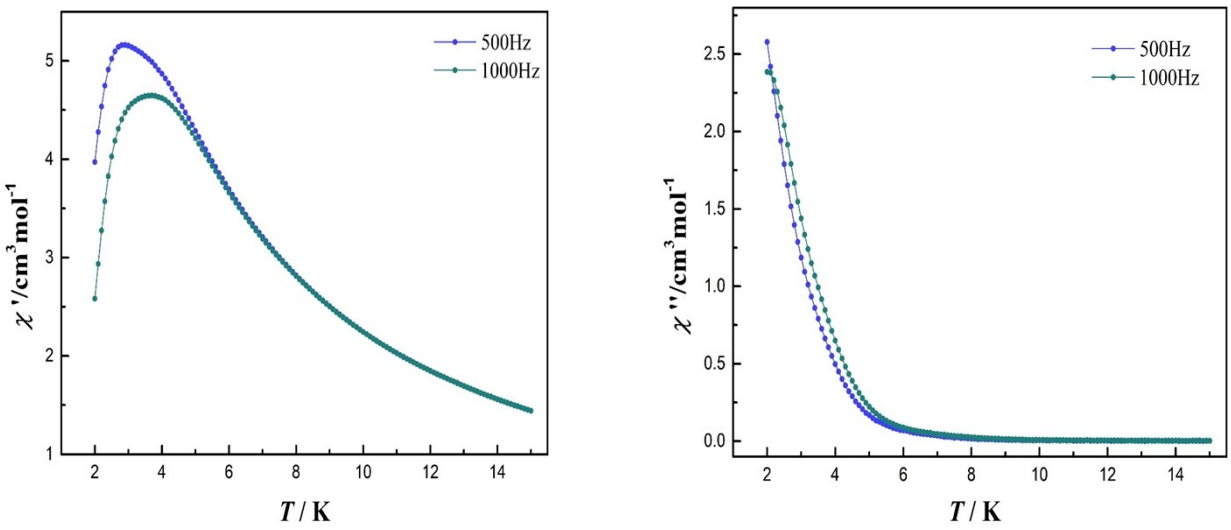

Figure S4 Temperature dependence of the χ' and χ'' ac magnetic susceptibility for $\mathbf{4_{DyCo}}$ under 1000 Oe dc field

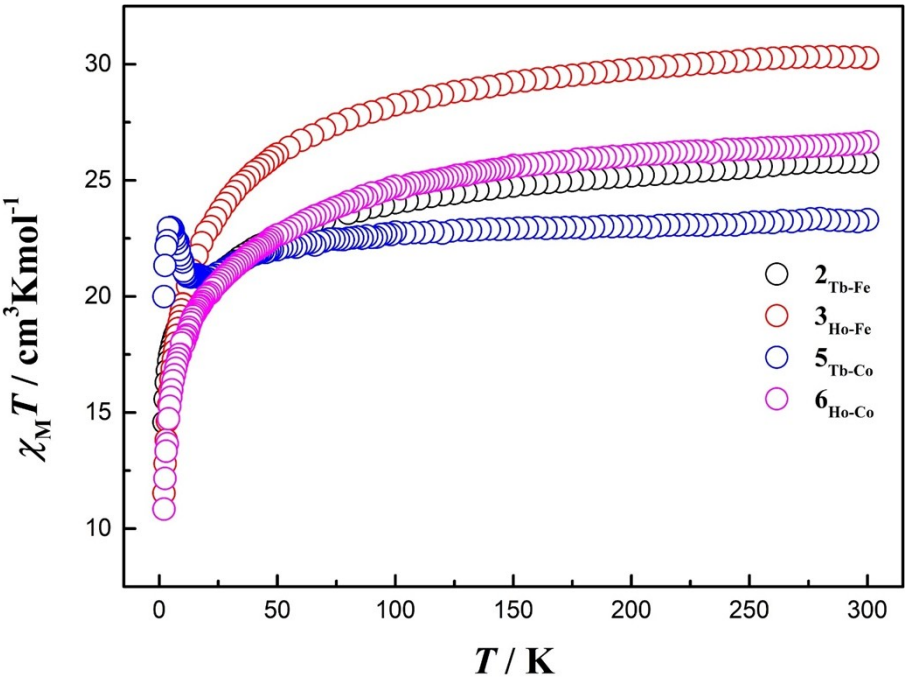

Figure S5 Temperature dependence of $\chi_M T$ for complexes $\mathbf{2_{TbFe}}$, $\mathbf{3_{HoFe}}$, $\mathbf{5_{TbCo}}$ **and** $\mathbf{6_{HoCo}}$ in the range of 2−300 K under 1000 Oe dc field

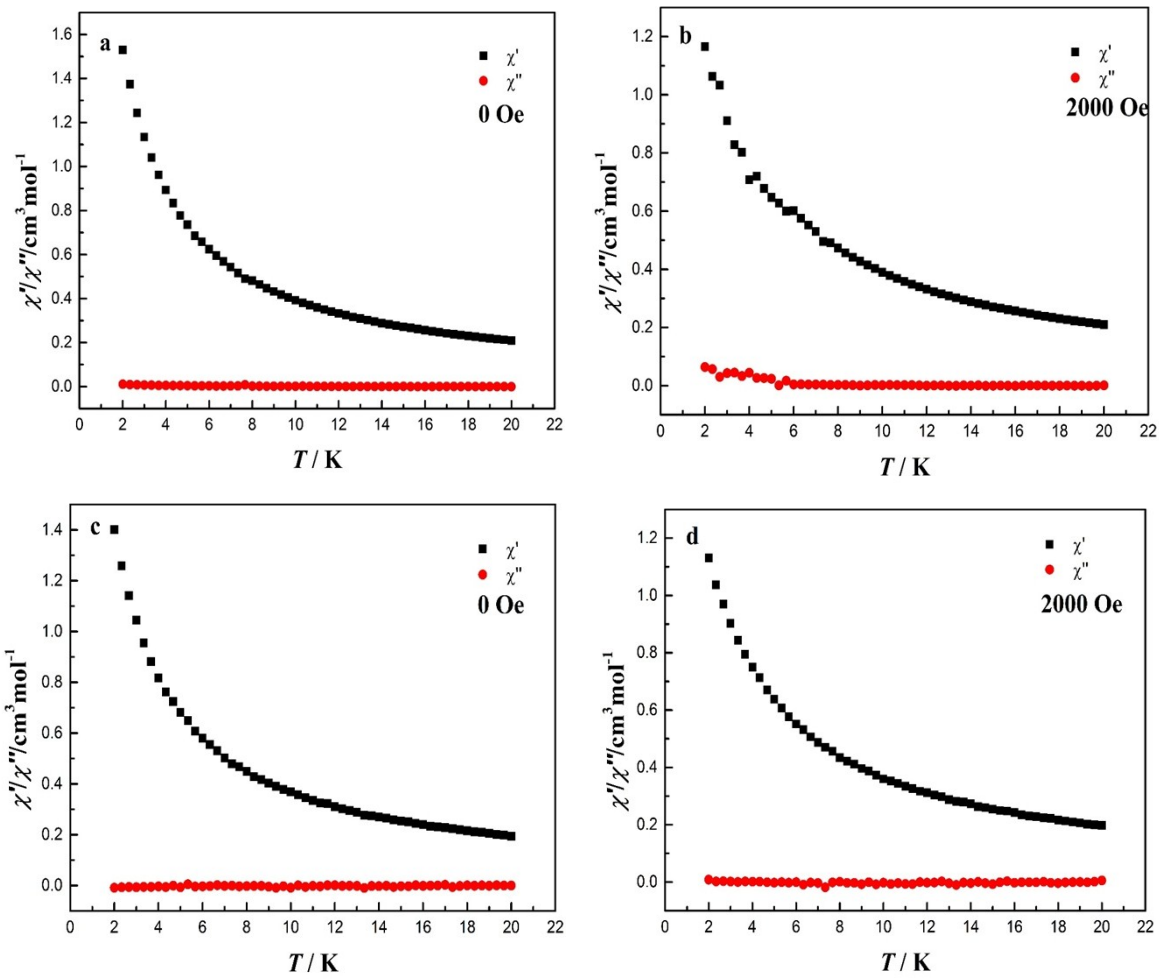

Figure S6 (a) and (b) Temperature dependence of $\chi'$and χ''ac magnetic susceptibility for $\mathbf{2}_{\mathbf{TbFe}}$ in 940 Hz under 0 and 2000 Oe dc field. (c) and (d) Temperature dependence of $\chi'$and χ''ac magnetic susceptibility for $\mathbf{5}_{\mathbf{TbCo}}$ in 940 Hz under 0 and 2000 Oe dc field

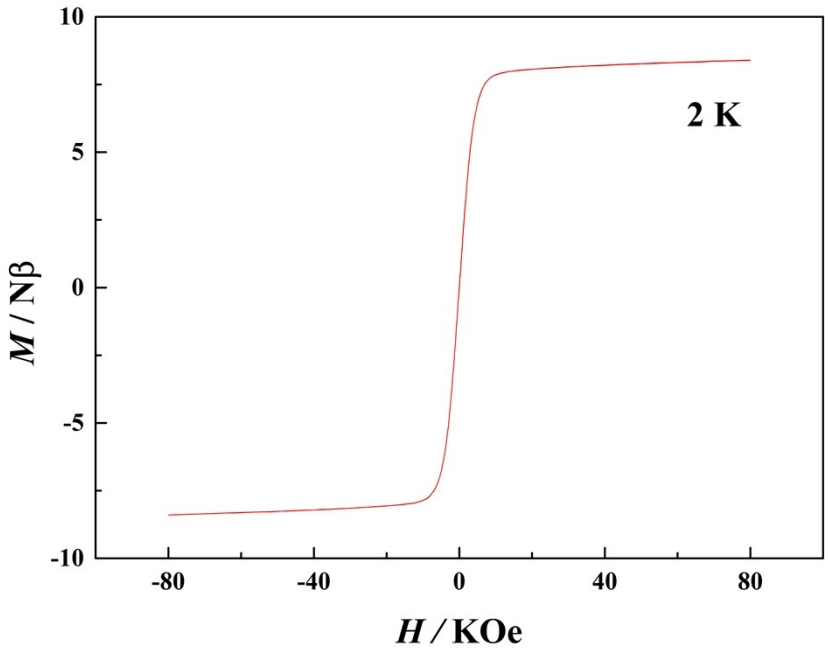

Figure S7 Magnetization curve versus applied field measured at 2 K for complex $\mathbf{4}_{\mathbf{DyCo}}$

Table S1 Ln^{III} ion geometry analysis by SHAPE software for all the six complexes.

Complexes	*Cs*-Muffin	C_{4v}-CSAPR	D_{3h}-TCTPR
$\mathbf{1}_{\mathbf{DyFe}}$	2.434	2.541	2.562
$\mathbf{2}_{\mathbf{TbFe}}$	2.427	2.572	2.631
$\mathbf{3}_{\mathbf{HoFe}}$	2.340	2.469	2.474
$\mathbf{4}_{\mathbf{DyCo}}$	2.412	2.513	2.534
$\mathbf{5}_{\mathbf{TbCo}}$	2.478	2.558	2.614
$\mathbf{6}_{\mathbf{HoCo}}$	2.366	2.463	2.466

Table S2 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{1}_{\mathbf{DyFe}}$

Bond Lengths			
Dy1-O3	2.365(3)	Dy1-O4	2.331(3)
Dy1-O1	2.451(3)	Dy1-O2	2.358(3)
Dy1-N3	2.622(4)	Dy1-N5	2.564(4)
Dy1-N4	2.570(4)	Dy1-N8	2.442(4)
Dy1-N9	2.470(4)	Fe1-C22	1.923(5)
Fe1-C25	1.930(5)	Fe1-C27	1.936(6)
Fe1-C26	1.943(6)	Fe1-C24	1.953(6)
Fe1-C23	1.939(5)	O4-H4A…N6	2.781(5)
O4-H4B…O1	2.849(5)	O4-H4B…O6	2.652(6)
O5-H5A…N11	3.008(1)	O5-H5B…N13	2.968(1)
O6-H6A…O7	2.688(7)	O6-H6B…O5	2.690(1)
N7-H7A…N13	2.788(7)	N7-H7B…N12	2.785(7)
Bond angles			
O1-Dy1-N4	120.69(11)	O4-Dy1-O3	126.90(12)
O1-Dy1-N5	148.42(11)	O4-Dy1-N3	74.11(11)
O1-Dy1-N9	79.27(12)	O4-Dy1-N4	82.83(12)
O2-Dy1-O1	102.73(11)	O4-Dy1-N5	76.23(11)
O2-Dy1-O3	72.79(11)	O4-Dy1-N8	142.84(13)
O2-Dy1-N3	151.28(12)	O4-Dy1-N9	136.58(12)
O2-Dy1-N4	124.46(12)	N4-Dy1-N3	59.82(13)
O2-Dy1-N5	63.40(12)	N5-Dy1-N3	116.26(13)
O2-Dy1-N8	84.06(12)	N5-Dy1-N4	61.49(13)
O2-Dy1-N9	141.30(12)	N8-Dy1-O1	143.37(12)
O3-Dy1-O1	71.28(11)	N8-Dy1-N3	123.29(13)
O3-Dy1-N3	118.64(12)	N8-Dy1-N4	80.66(13)
O3-Dy1-N4	149.89(11)	N8-Dy1-N5	66.62(12)
O3-Dy1-N5	124.40(12)	N8-Dy1-N9	73.88(13)
O3-Dy1-N8	76.77(13)	N9-Dy1-N3	63.36(12)
O3-Dy1-N9	71.44(12)	N9-Dy1-N4	83.35(13)
O4-Dy1-O1	73.06(11)	N9-Dy1-N5	129.98(14)
O4-Dy1-O2	78.29(11)	C25-Fe1-C24	92.8(2)
C22-Fe1-C23	89.30(19)	C25-Fe1-C26	91.1(2)
C22-Fe1-C24	90.2(2)	C25-Fe1-C27	87.2(2)
C22-Fe1-C25	92.6(2)	C26-Fe1-C24	176.1(2)
C22-Fe1-C26	88.9(2)	C27-Fe1-C23	90.9(2)
C22-Fe1-C27	179.6(2)	C27-Fe1-C24	90.2(2)
C23-Fe1-C24	91.5(2)	C27-Fe1-C26	90.7(2)
C23-Fe1-C26	84.7(2)	C25-Fe1-C23	175.4(2)

Table S3 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{2}_{\mathbf{TbFe}}$

Bond Lengths			
Tb1-O4	2.365(5)	Tb1-O3	2.382(5)
Tb1-N4	2.569(5)	Tb1-N2	2.640(6)
Tb1-O2	2.360(5)	Tb1-N3	2.588(6)
Tb1-O1	2.468(5)	Tb1-N9	2.502(6)
Tb1-N10	2.471(6)	Fe1-C25	1.929(7)
Fe1-C26	1.923(7)	Fe1-C27	1.941(8)
Fe1-C28	1.937(9)	Fe1-C29	1.946(8)
Fe1-C30	1.933(7)	O4-H4A…O7	2.669(1)
O4-H4B…N5	2.809(8)	O5-H5B…N12	3.090(2)
O5-H5A…N14	3.060(2)	O6-H6B…N12	2.792(1)
O6-H6A…N13	2.793(1)	O7-H7A…O5	2.680(2)
O7-H7B…O6	2.689(1)	N6-H6…N14	3.060(2)
Bond angles			
O1-Tb1-N2	61.13(16)	O4-Tb1-N10	142.59(18)
O1-Tb1-N3	119.95(17)	N3-Tb1-N2	59.75(17)
O1-Tb1-N4	147.36(17)	N4-Tb1-N2	115.91(17)
O1-Tb1-N9	79.38(19)	N4-Tb1-N3	61.33(17)
O1-Tb1-N10	143.92(18)	N9-Tb1-N2	63.61(18)
O2-Tb1-O1	103.30(16)	N9-Tb1-N3	83.95(19)
O2-Tb1-O3	73.21(17)	N9-Tb1-N4	130.6(2)
O2-Tb1-O4	77.61(18)	N10-Tb1-N2	123.90(19)
O2-Tb1-N2	150.96(18)	N10-Tb1-N3	81.44(19)
O2-Tb1-N3	123.70(17)	N10-Tb1-N4	67.21(18)
O2-Tb1-N4	62.80(17)	N10-Tb1-N9	74.2(2)
O2-Tb1-N9	141.61(18)	C25-Fe1-C27	92.7(3)
O2-Tb1-N10	83.60(19)	C25-Fe1-C28	90.8(3)
O3-Tb1-O1	72.01(17)	C25-Fe1-C29	84.8(3)
O3-Tb1-N2	118.85(17)	C25-Fe1-C30	175.1(3)
O3-Tb1-N3	150.46(18)	C26-Fe1-C25	89.5(3)
O3-Tb1-N4	124.66(18)	C26-Fe1-C27	90.0(3)
O3-Tb1-N9	71.39(18)	C26-Fe1-C28	179.60(3)
O3-Tb1-N10	76.48(19)	C26-Fe1-C29	89.70(3)
O4-Tb1-O1	72.63(16)	C26-Fe1-C30	92.20(3)
O4-Tb1-O3	126.63(18)	C27-Fe1-C29	177.40(3)
O4-Tb1-N2	74.33(18)	C28-Fe1-C27	89.80(3)
O4-Tb1-N3	82.58(18)	C28-Fe1-C29	90.50(3)
O4-Tb1-N4	75.43(17)	C30-Fe1-C27	91.90(3)
O4-Tb1-N9	136.98(18)	C30-Fe1-C28	87.40(3)
C30-Fe1-C29	90.70(3)		

Table S4 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{3_{HoFe}}$

Bond Lengths			
Ho1-O1	2.440(5)	Ho1-O2	2.347(5)
Ho1-O3	2.361(5)	Ho1-O4	2.337(5)
Ho1-N2	2.624(5)	Ho1-N3	2.564(5)
Ho1-N4	2.546(5)	Ho1-N9	2.477(6)
Ho1-N10	2.431(6)	Fe2-C25	1.929(7)
Fe2-C26	1.926(7)	Fe2-C27	1.940(8)
Fe2-C28	1.930(8)	Fe2-C29	1.937(8)
Fe2-C30	1.936(8)	O4-H4A…O7	2.676(1)
O4-H4B…N5	2.809(8)	O5-H5A…N14	3.020(2)
O5-H5B…N12	3.090(2)	N6-H6…N14	2.731(1)
O6-H6A…N13	2.799(1)	O6-H5B…N12	2.810(1)
O7-H7A…O5	2.670(2)	O7-H7B…O6	2.685(1)
Bond angles			
O1-Ho1-N2	61.46(16)	N4-Ho1-N2	116.37(17)
O1-Ho1-N3	120.82(16)	N4-Ho1-N3	61.62(17)
O1-Ho1-N4	147.23(17)	N9-Ho1-N2	63.69(18)
O1-Ho1-N9	79.77(18)	N9-Ho1-N3	83.57(18)
O2-Ho1-O1	101.79(16)	N9-Ho1-N4	130.67(19)
O2-Ho1-O3	72.80(16)	N10-Ho1-O1	143.35(17)
O2-Ho1-N2	150.25(17)	N10-Ho1-N2	124.44(19)
O2-Ho1-N3	124.56(16)	N10-Ho1-N3	81.51(19)
O2-Ho1-N4	63.37(16)	N10-Ho1-N4	67.48(18)
O2-Ho1-N9	141.56(18)	N10-Ho1-N9	74.08(19)
O2-Ho1-N10	84.11(19)	C25-Fe1-C27	92.3(3)
O3-Ho1-O1	71.20(17)	C25-Fe1-C28	90.6(3)
O3-Ho1-N2	118.46(17)	C25-Fe1-C29	84.8(3)
O3-Ho1-N3	150.28(17)	C25-Fe1-C30	174.7(3)
O3-Ho1-N4	124.69(17)	C26-Fe1-C25	89.7(3)
O3-Ho1-N9	71.51(18)	C26-Fe1-C27	90.0(3)
O3-Ho1-N10	76.36(18)	C26-Fe1-C28	179.6(3)
O4-Ho1-O1	72.65(16)	C26-Fe1-C29	89.7(3)
O4-Ho1-O2	77.48(17)	C26-Fe1-C30	92.3(3)
O4-Ho1-O3	126.41(18)	C28-Fe1-C27	89.7(3)
O4-Ho1-N2	74.06(17)	C28-Fe1-C29	90.6(3)
O4-Ho1-N3	82.94(17)	C28-Fe1-C30	87.4(3)
O4-Ho1-N4	75.52(17)	C29-Fe1-C27	177.1(3)
O4-Ho1-N9	136.87(18)	C30-Fe1-C27	92.6(3)
O4-Ho1-N10	142.94(18)	C30-Fe1-C29	90.3(3)
N3-Ho1-N2	60.22(17)		

Table S5 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{4_{DyCo}}$

Bond Lengths			
Dy1-O4	2.356(3)	Dy1-N8	2.451(3)
Dy1-O3	2.368(3)	Dy1-O1	2.356(3)
Dy1-O2	2.449(3)	Dy1-N5	2.630(3)
Dy1-N4	2.576(3)	Dy1-N3	2.563(3)
Dy1-N9	2.490(3)	Co1-C22	1.888(4)
Co1-C25	1.898(4)	Co1-C26	1.905(5)
Co1-C27	1.887(4)	Co1-C23	1.890(4)
Co1-C24	1.900(5)	O4-H4A…N2	2.810(4)
O4-H4B…O6	2.676(6)	O5-H5A…N13	2.819(7)
O5-H5B…N10	2.795(7)	O6-H6A…O5	2.700(7)
O6-H6B…O7	2.691(1)	O7-H7A…N11	3.046(1)
N1-H1…N11	2.740(7)	O7-H7B…N13	3.089(1)
Bond angles			
O3-Dy1-N4	150.45(10)	N8-Dy1-N5	124.03(11)
O3-Dy1-N3	124.46(10)	N8-Dy1-N9	74.39(11)
O3-Dy1-N8	76.41(11)	N9-Dy1-N4	84.06(11)
O3-Dy1-N5	118.87(10)	N9-Dy1-N3	131.05(11)
O3-Dy1-N9	71.41(11)	N9-Dy1-N5	63.55(11)
O3-Dy1-O2	71.74(10)	O2-Dy1-N4	120.41(10)
O4-Dy1-O3	126.63(11)	O2-Dy1-N3	147.25(10)
O4-Dy1-N4	82.56(11)	O2-Dy1-N8	143.69(10)
O4-Dy1-O1	77.79(11)	O2-Dy1-N5	61.37(9)
O4-Dy1-N3	75.82(10)	O2-Dy1-N9	79.26(11)
O4-Dy1-N8	143.13(10)	C25-Co1-C26	91.4(2)
O4-Dy1-N5	73.72(10)	C25-Co1-C24	90.6(2)
O4-Dy1-N9	136.26(11)	C22-Co1-C25	91.34(18)
O4-Dy1-O2	72.31(10)	C22-Co1-C23	90.04(16)
N4-Dy1-N5	59.94(10)	C22-Co1-C26	90.04(18)
O1-Dy1-O3	72.86(10)	C22-Co1-C24	89.78(17)
O1-Dy1-N4	124.23(10)	C27-Co1-C25	88.1(2)
O1-Dy1-N3	63.21(10)	C27-Co1-C22	179.29(19)
O1-Dy1-N8	84.26(11)	C27-Co1-C23	90.58(18)
O1-Dy1-N5	150.35(10)	C27-Co1-C26	89.6(2)
O1-Dy1-N9	141.68(11)	C27-Co1-C24	90.60(19)
O1-Dy1-O2	102.21(9)	C23-Co1-C25	176.12(19)
N3-Dy1-N4	61.50(10)	C23-Co1-C26	92.26(18)
N3-Dy1-N5	116.15(10)	C23-Co1-C24	85.80(18)
N8-Dy1-N4	81.41(11)	C24-Co1-C26	178.05(18)
N8-Dy1-N3	67.34(10)		

Table S6 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{5_{TbCo}}$

Bond Lengths			
Tb1-O3	2.368(5)	Tb1-O4	2.347(5)
Tb1-N4	2.581(6)	Tb1-O1	2.366(5)
Tb1-N3	2.570(5)	Tb1-N8	2.467(6)
Tb1-N5	2.637(6)	Tb1-N9	2.480(6)
Tb1-O2	2.459(5)	Co1-C25	1.891(8)
Co1-C22	1.894(7)	Co1-C27	1.888(7)
Co1-C23	1.886(7)	Co1-C26	1.906(7)
Co1-C24	1.898(7)	O4-H4A…N2	2.774(8)
O4-H4B…O6	2.657(1)	O5-H5A…N13	2.807(1)
O5-H5B…N10	2.772(1)	O6-H6A…O5	2.686(1)
O6-H6B…O7	2.800(2)	O7-H7A…N11	3.101(2)
N1-H1A…N11	2.742(1)	O7-H7B…N13	2.936(2)
Bond angles			
O3-Tb1-N4	149.76(17)	N8-Tb1-N5	123.46(19)
O3-Tb1-N3	123.95(17)	N8-Tb1-N9	73.97(19)
O3-Tb1-N8	76.12(18)	N9-Tb1-N4	83.99(19)
O3-Tb1-N5	119.18(17)	N9-Tb1-N3	130.29(19)
O3-Tb1-N9	71.11(18)	N9-Tb1-N5	63.69(18)
O3-Tb1-O2	72.31(16)	O2-Tb1-N4	120.49(17)
O4-Tb1-O3	126.92(17)	O2-Tb1-N3	148.00(16)
O4-Tb1-N4	83.05(18)	O2-Tb1-N8	143.77(17)
O4-Tb1-O1	78.26(17)	O2-Tb1-N5	61.44(16)
O4-Tb1-N3	76.34(17)	O2-Tb1-N9	79.32(18)
O4-Tb1-N8	142.99(17)	C25-Co1-C22	91.3(3)
O4-Tb1-N5	74.19(17)	C25-Co1-C26	91.3(3)
O4-Tb1-N9	136.83(17)	C25-Co1-C24	91.2(3)
O4-Tb1-O2	72.44(16)	C22-Co1-C26	90.4(3)
N4-Tb1-N5	59.92(17)	C22-Co1-C24	89.1(3)
O1-Tb1-O3	72.70(16)	C27-Co1-C25	88.1(3)
O1-Tb1-N4	123.96(17)	C27-Co1-C22	179.3(3)
O1-Tb1-N3	63.10(16)	C27-Co1-C26	90.0(3)
O1-Tb1-N8	83.61(19)	C27-Co1-C24	90.5(3)
O1-Tb1-N5	151.46(17)	C23-Co1-C25	176.9(3)
O1-Tb1-N9	140.94(18)	C23-Co1-C22	90.0(3)
O1-Tb1-O2	103.16(16)	C23-Co1-C27	90.5(3)
N3-Tb1-N4	61.25(17)	C23-Co1-C26	91.5(3)
N3-Tb1-N5	116.13(17)	C23-Co1-C24	86.0(3)
N8-Tb1-N4	80.80(19)	C24-Co1-C26	177.4(3)
N8-Tb1-N3	66.69(18)		

Table S7 Selected bond lengths [Å] and-angles [°] for complex $\mathbf{6_{HoCo}}$

Bond Lengths			
Ho1-O3	2.348(4)	Ho1-O2	2.439(4)
Ho1-O4	2.344(5)	Ho1-N4	2.555(6)
Ho1-N5	2.622(5)	Ho1-O1	2.350(4)
Ho1-N3	2.542(5)	Ho1-N9	2.479(6)
Ho1-N8	2.439(6)	Co1-C23	1.887(7)
Co1-C22	1.887(7)	Co1-C25	1.885(8)
Co1-C24	1.905(8)	Co1-C27	1.893(8)
Co1-C26	1.910(8)	O4-H4A…N2	2.806(8)
O4-H4B…O6	2.671(1)	O5-H5A…N13	2.816(1)
O5-H5B…N10	2.792(1)	O6-H6A…O5	2.699(1)
O6-H6B…O7	2.700(2)	O7-H7A…N11	3.026(2)
N1-H1A…N11	2.751(1)	O7-H7B…N13	3.060(2)
Bond angles			
O3-Ho1-N4	150.27(18)	N8-Ho1-N5	124.10(19)
O3-Ho1-O1	72.72(17)	N8-Ho1-N9	74.2(2)
O3-Ho1-N3	124.27(17)	N9-Ho1-N4	83.84(19)
O3-Ho1-N8	76.40(19)	N9-Ho1-N3	131.11(19)
O3-Ho1-N5	118.85(17)	N9-Ho1-N5	63.71(18)
O3-Ho1-N9	71.45(19)	O2-Ho1-N4	120.90(16)
O3-Ho1-O2	71.35(16)	O2-Ho1-N3	147.22(17)
O4-Ho1-O3	126.61(18)	O2-Ho1-N8	143.39(17)
O4-Ho1-N4	82.77(18)	O2-Ho1-N5	61.68(16)
O4-Ho1-O1	77.70(18)	O2-Ho1-N9	79.47(18)
O4-Ho1-N3	75.69(17)	C25-Co1-C22	91.4(3)
O4-Ho1-N8	143.10(17)	C25-Co1-C27	87.7(3)
O4-Ho1-N5	73.73(17)	C25-Co1-C23	176.4(3)
O4-Ho1-N9	136.47(18)	C25-Co1-C26	91.6(3)
O4-Ho1-O2	72.57(16)	C25-Co1-C24	90.7(3)
N4-Ho1-N5	60.07(17)	C22-Co1-C27	179.0(3)
O1-Ho1-N4	124.47(17)	C22-Co1-C26	90.3(3)
O1-Ho1-N3	63.11(17)	C22-Co1-C24	89.7(3)
O1-Ho1-N8	84.41(19)	C27-Co1-C26	89.2(3)
O1-Ho1-N5	150.20(17)	C27-Co1-C24	90.9(3)
O1-Ho1-N9	141.58(18)	C23-Co1-C22	90.0(3)
O1-Ho1-O2	101.75(16)	C23-Co1-C27	90.9(3)
N3-Ho1-N4	61.81(17)	C23-Co1-C26	91.7(3)
N3-Ho1-N5	116.39(17)	C23-Co1-C24	86.0(3)
N8-Ho1-N4	81.24(19)	C24-Co1-C26	177.6(3)
N8-Ho1-N3	67.44(18)		

Table S8. Relaxation fitting parameters from the Cole-Cole plots of $\mathbf{4_{DyCo}}$ under 2.0 K-4.0 K according to the generalized Debye model

T / K	χ_0 / cm^3 K mol^{-1}	χ_s / cm^3 K mol^{-1}	α
2.0 K	0.01984	7.91332	0.25573
2.2 K	0.03342	7.64786	0.31364
2.4 K	0.05097	7.28297	0.31607
2.7 K	0.17211	6.90405	0.36394
3.0 K	0.21314	6.53746	0.40939
3.2 K	0.42117	6.28899	0.42524
3.5 K	0.98630	5.86159	0.40912
4.0 K	1.49607	5.33725	0.42354