Impact of anionic co-ligands on nuclearity and single-molecule magnetism in a $\{Co^{III}_2Dy^{III}\}$ trimeric and two $\{Co^{III}_2Dy^{III}_2\}$ tetrameric complexes

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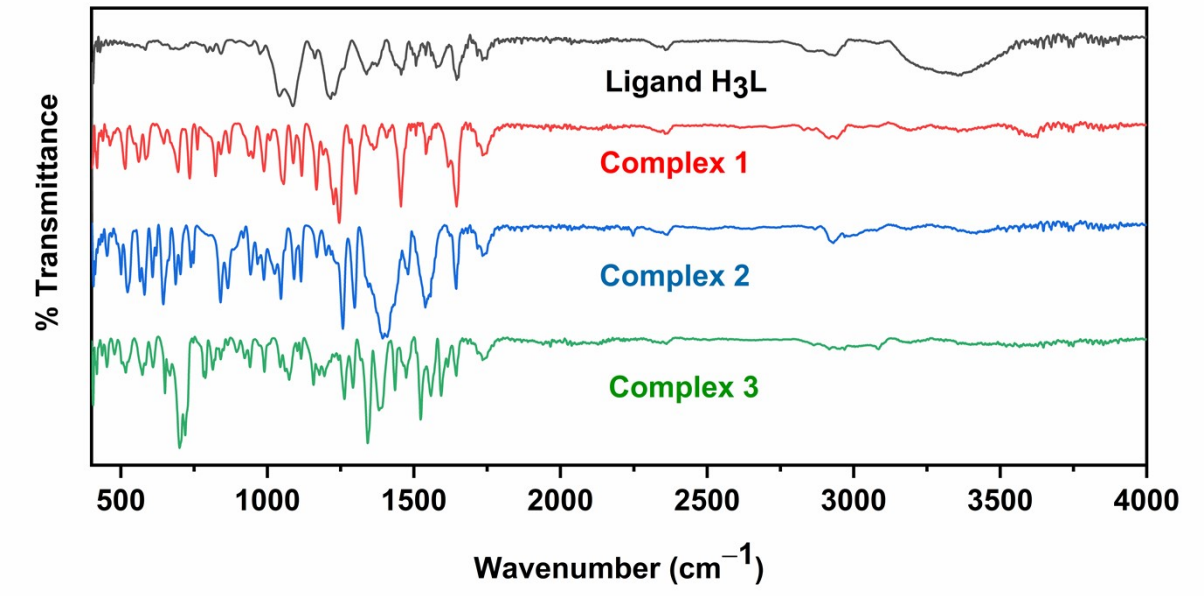

Fig. S1. IR spectra of Schiff base H_3L and complexes **1–3**.

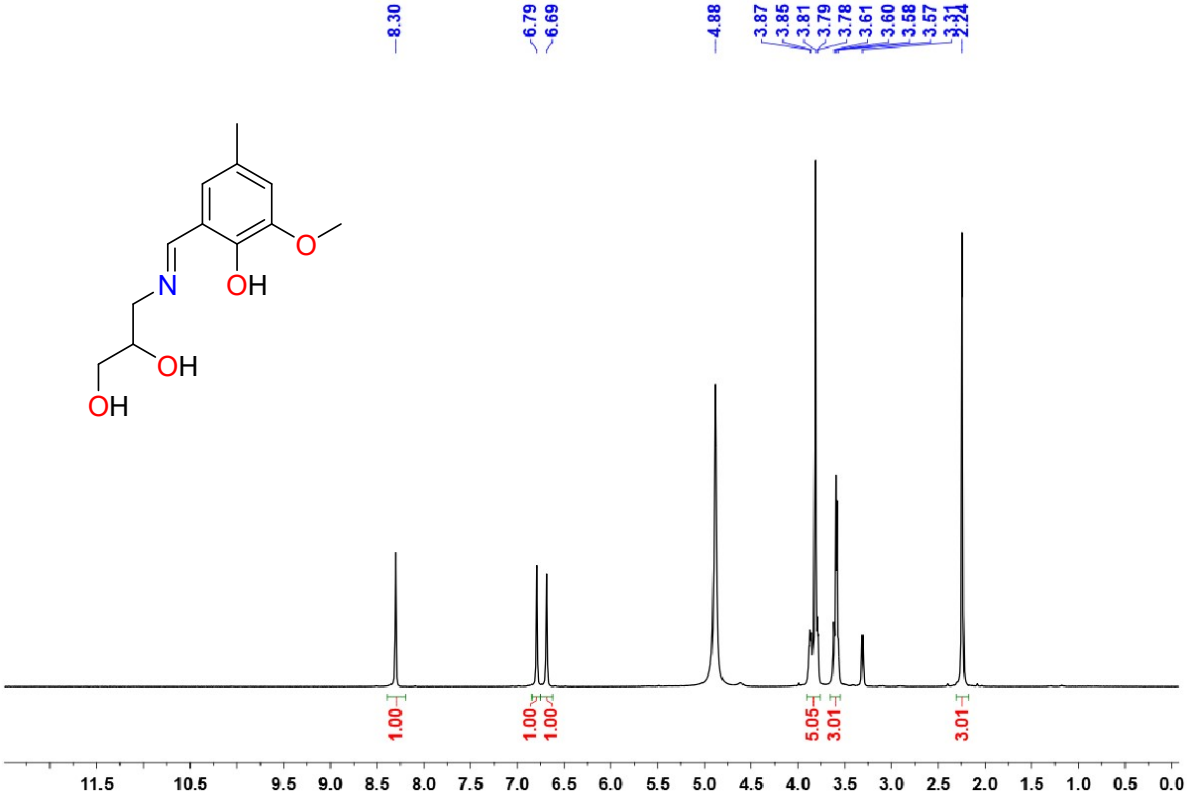

Fig. S2. ^{1}H-NMR spectrum of Schiff base ligand H_3L in CD_3OD.

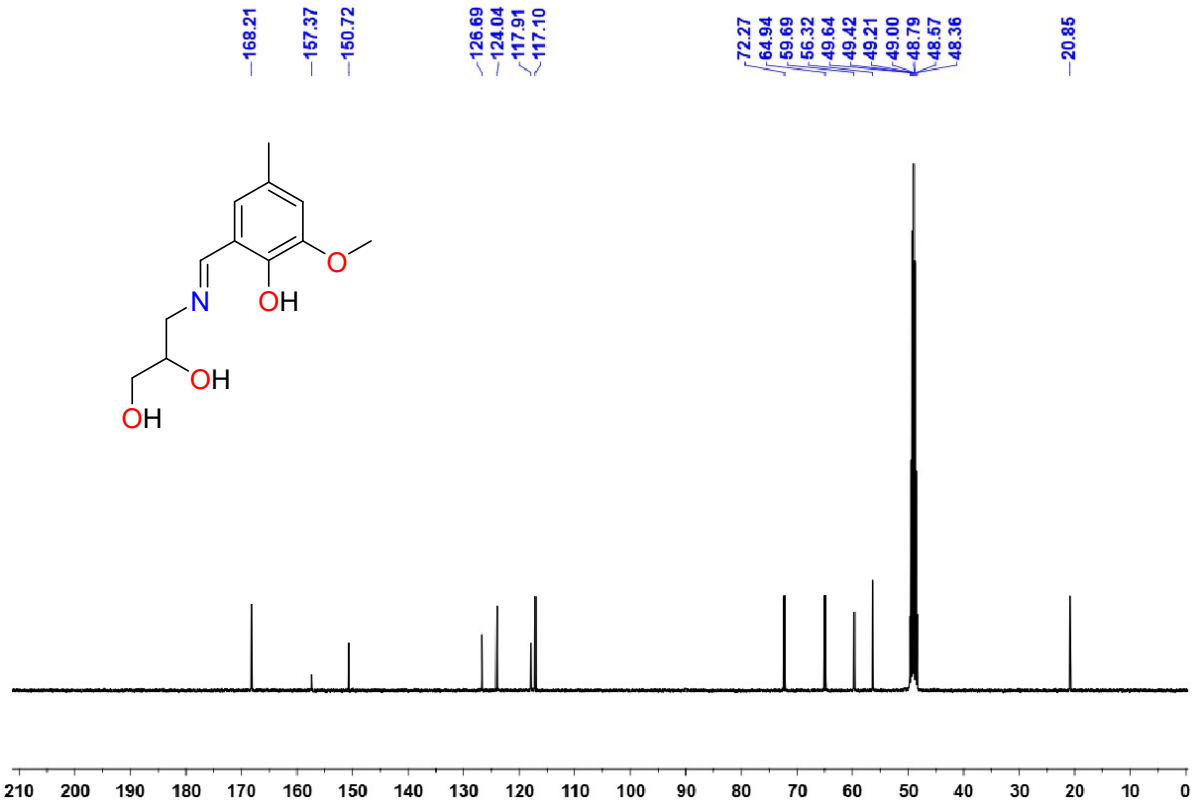

Fig. S3. ^{13}C-NMR spectrum of Schiff base ligand H_3L in CD_3OD.

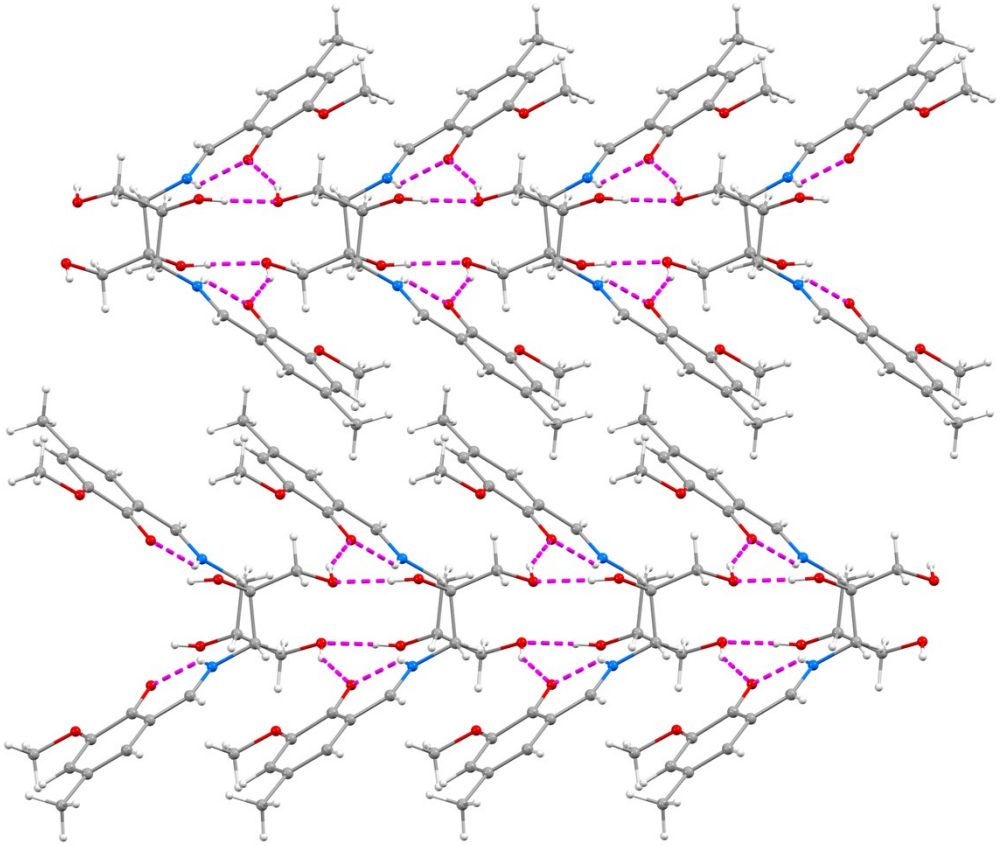

Fig. S4. Hydrogen bonded structure of ligand H_3L.

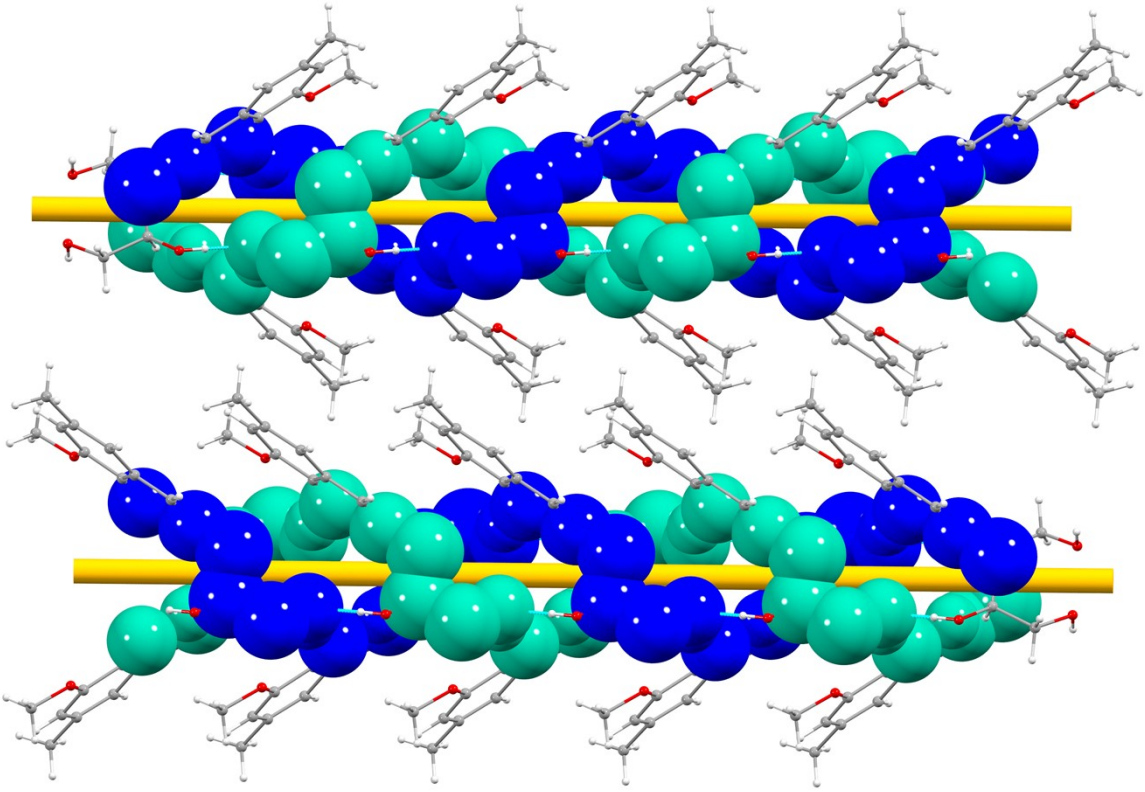

Fig. S5. The alternating hydrogen-bonded helical chain structures of ligand H_3L.

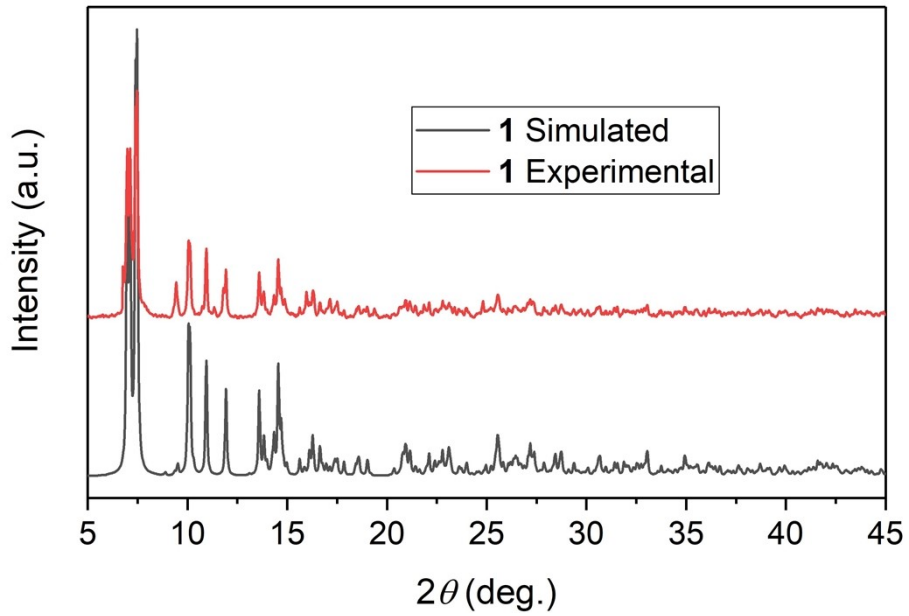

Fig. S6. Simulated and experimental PXRD data of complex **1**.

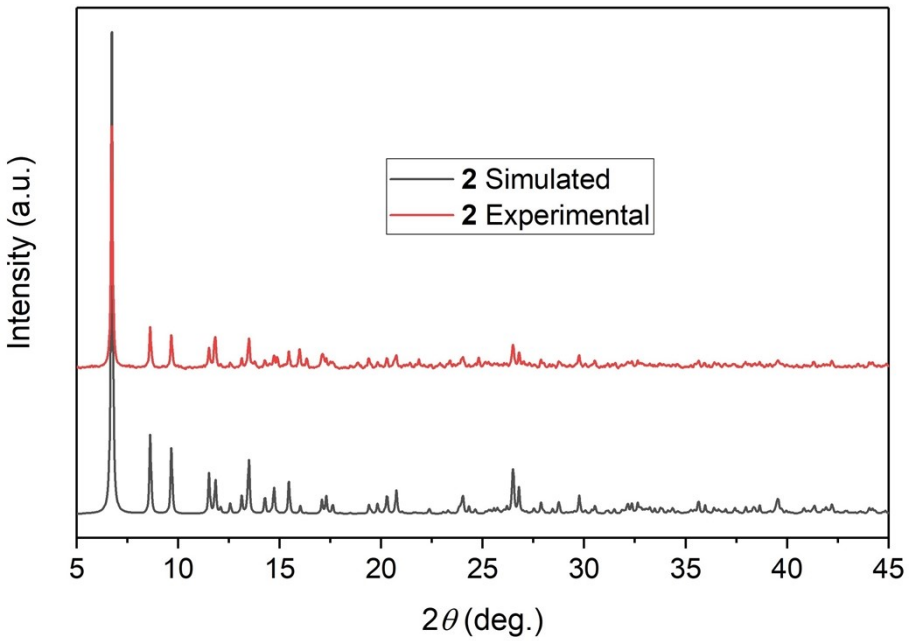

Fig. S7. Simulated and experimental PXRD data of complex **2**.

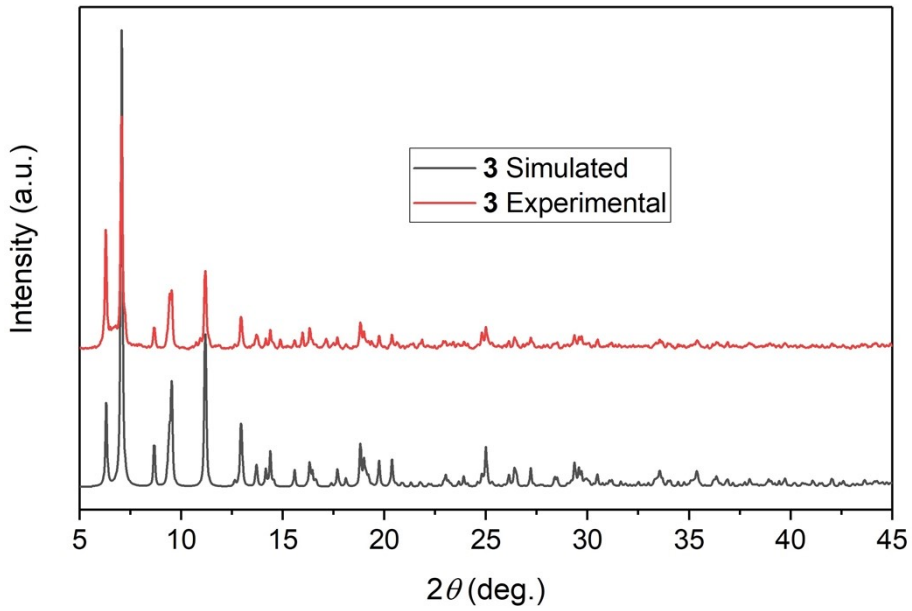

Fig. S8. Simulated and experimental PXRD data of complex **3**.

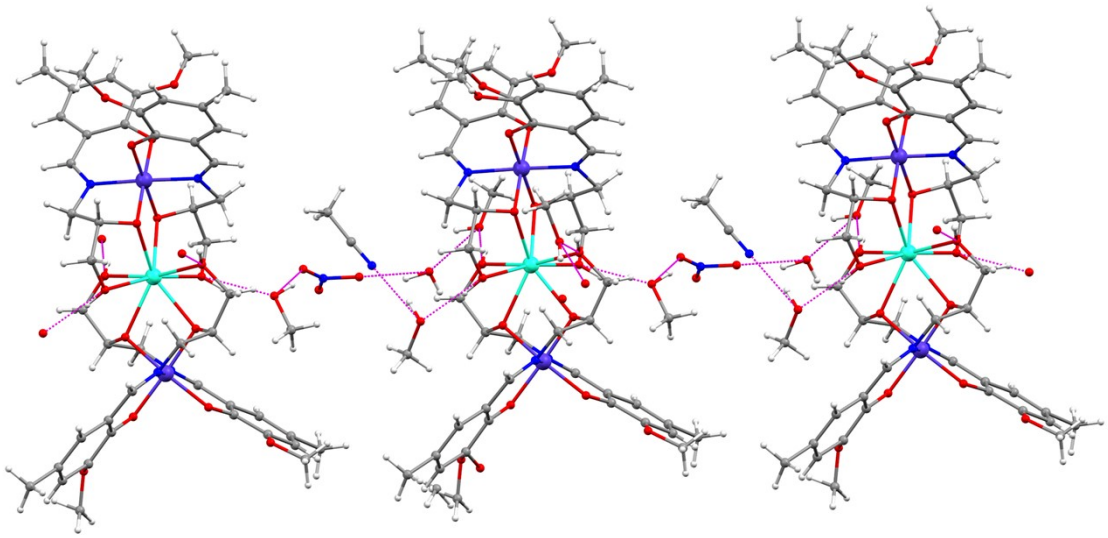

Fig. S9. A part of crystal packing of **1** showing hydrogen bonding interaction

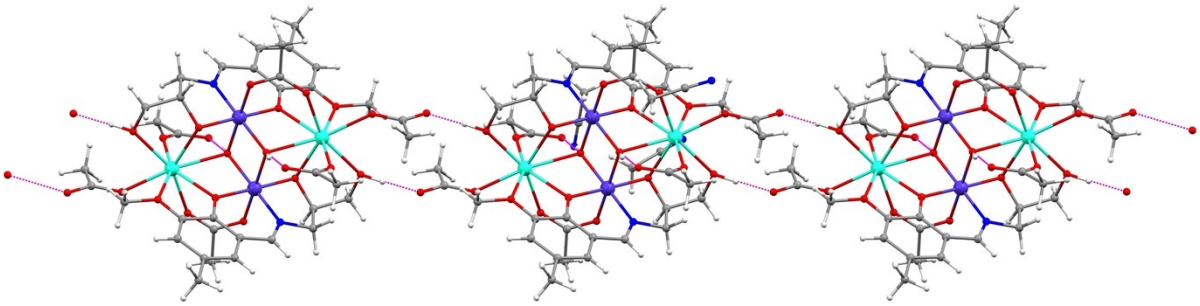

Fig. S10. A part of crystal packing of **2** showing hydrogen bonding interaction

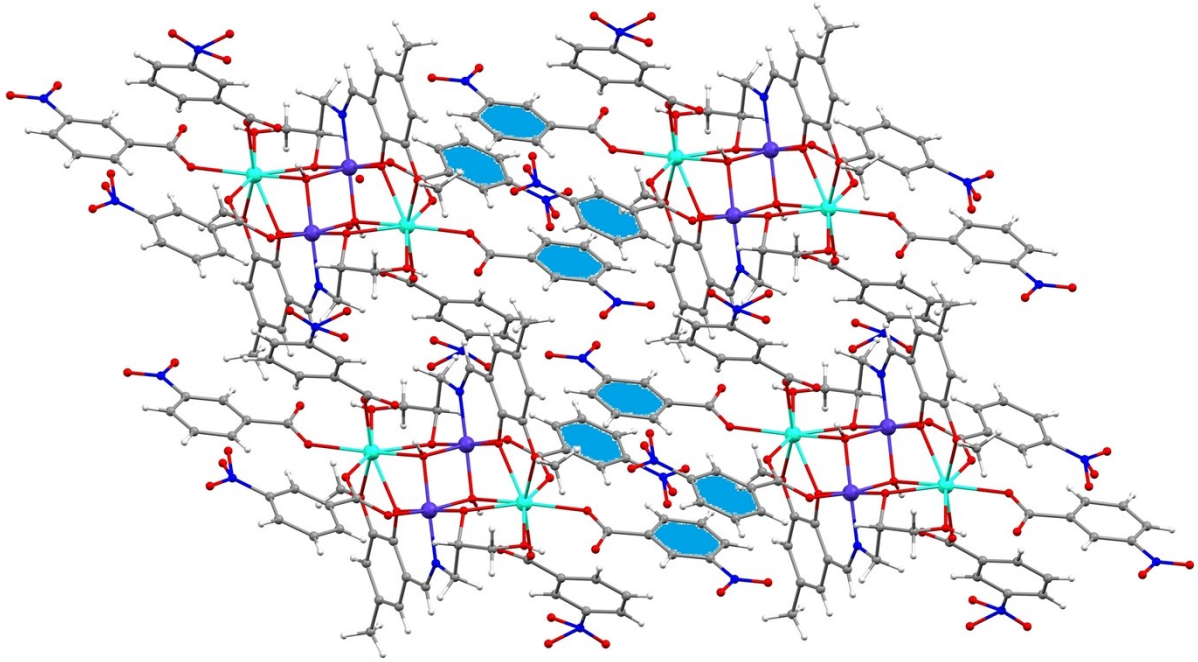

Fig. S11. A part of crystal packing of **3** showing π–π stacking interaction

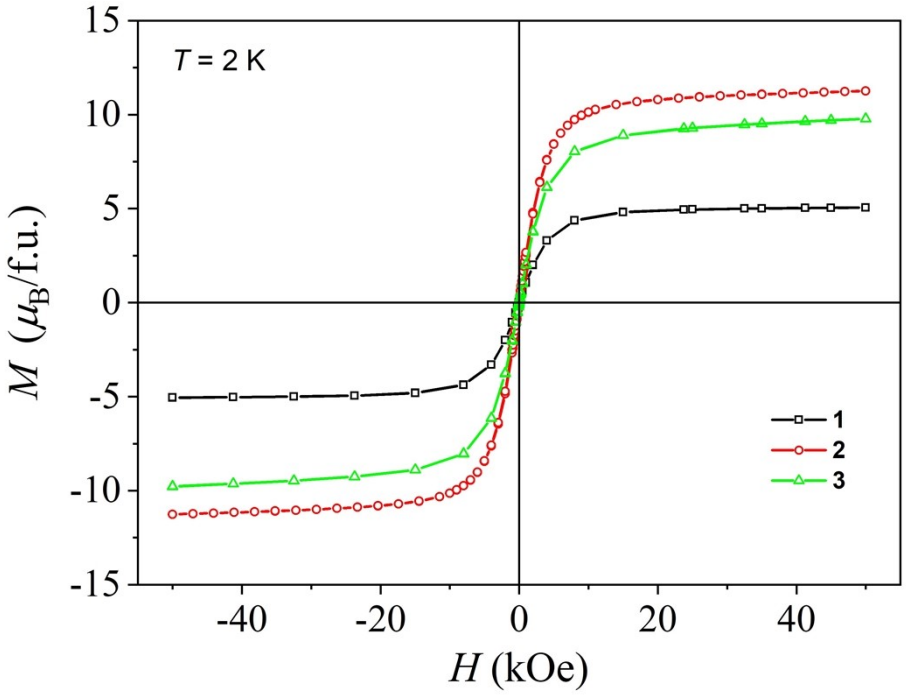

Fig. S12. Isothermal magnetization at temperature 2 K for complexes **1–3**.

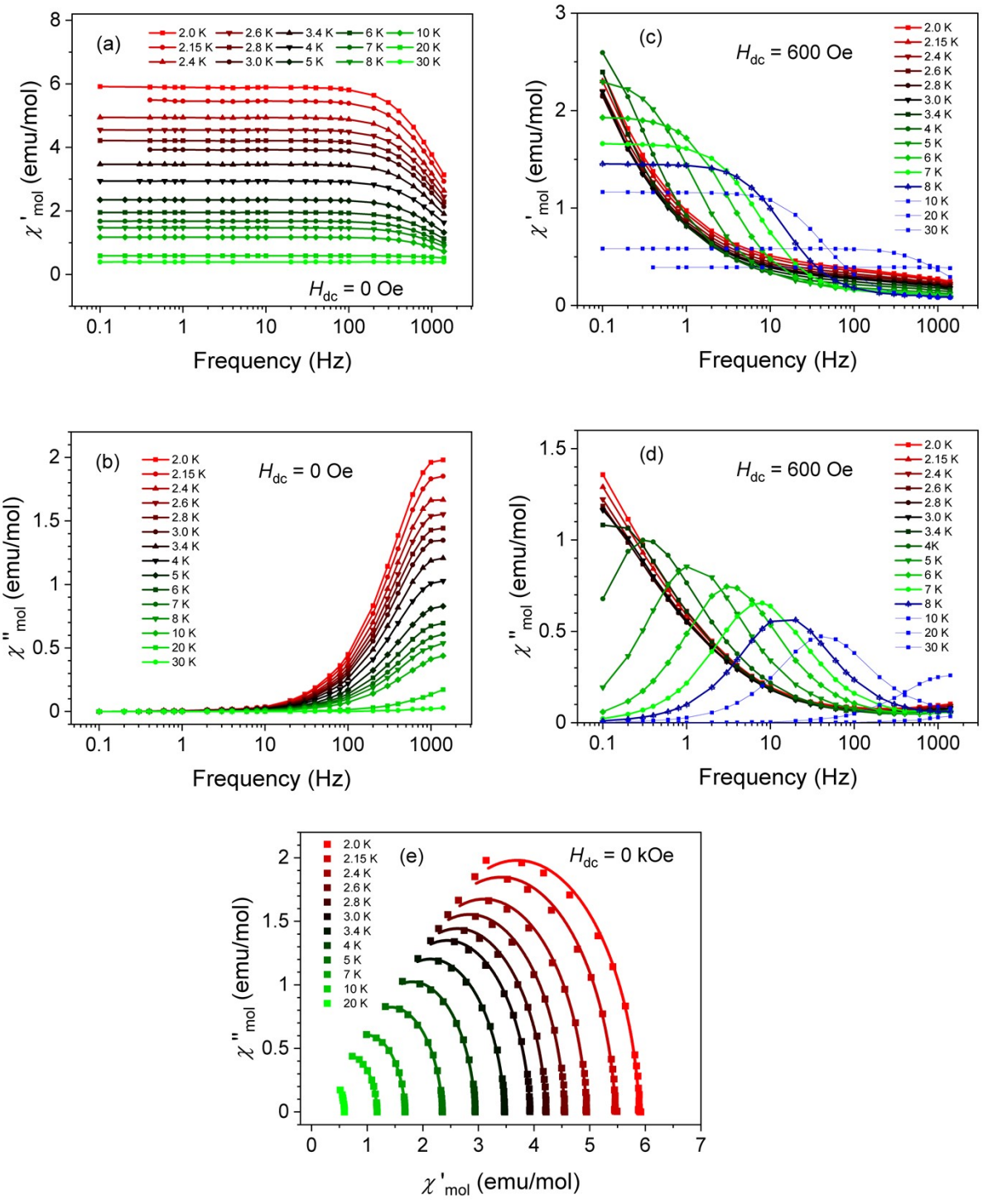

Fig. S13. Frequency dependent in-phase (a) and out-of-phase (b) ac susceptibility plots for complex **1** at zero dc field, and corresponding plots at 600 Oe dc field (c, d) with selected frequencies for clarity. Cole-Cole plots at zero dc field (e).

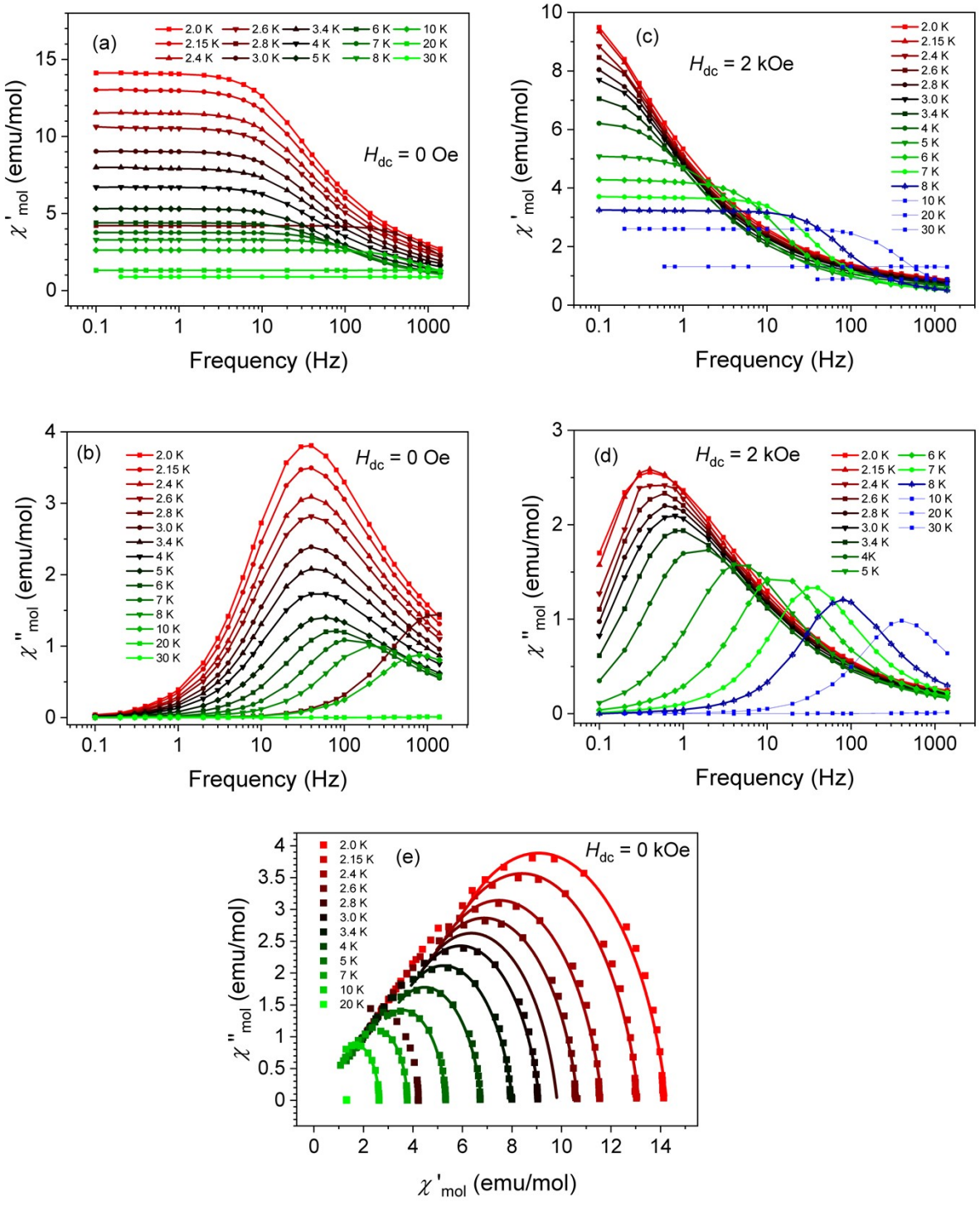

Fig. S14. Frequency dependent in-phase (a) and out-of-phase (b) ac susceptibility plots for complex **2** at zero dc field, and corresponding plots at 2 kOe dc field (c, d) with selected frequencies for clarity. Cole-Cole plots at zero dc field (e).

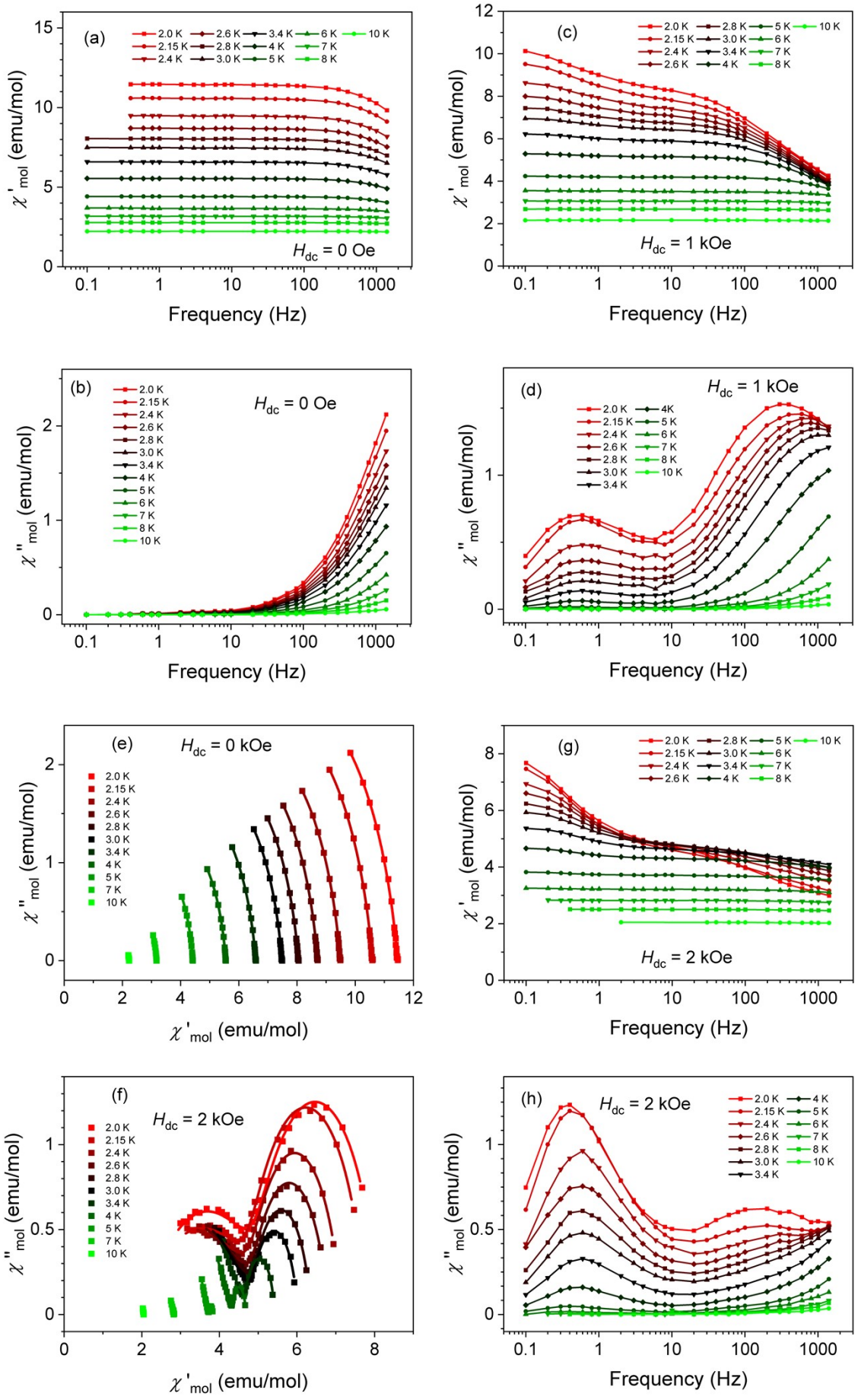
(a)
2.0 K 2.6 K 3.4 K 6 K 10 K
2.15 K 2.8 K 4 K 7 K
2.4 K 3.0 K 5 K 8 K
H_{dc} = 0 Oe
χ'_{mol} (emu/mol)
Frequency (Hz)
(c)
2.0 K 2.8 K 5 K 10 K
2.15 K 3.0 K 6 K
2.4 K 3.4 K 7 K
2.6 K 4 K 8 K
H_{dc} = 1 kOe
χ'_{mol} (emu/mol)
Frequency (Hz)
(b)
2.0 K
2.15 K
2.4 K
2.6 K
2.8 K
3.0 K
3.4 K
4 K
5 K
6 K
7 K
8 K
10 K
H_{dc} = 0 Oe
χ''_{mol} (emu/mol)
Frequency (Hz)
(d)
H_{dc} = 1 kOe
2.0 K 4K
2.15 K 5 K
2.4 K 6 K
2.6 K 7 K
2.8 K 8 K
3.0 K 10 K
3.4 K
χ''_{mol} (emu/mol)
Frequency (Hz)
(e)
H_{dc} = 0 kOe
2.0 K
2.15 K
2.4 K
2.6 K
2.8 K
3.0 K
3.4 K
4 K
5 K
7 K
10 K
χ''_{mol} (emu/mol)
χ'_{mol} (emu/mol)
(g)
2.0 K 2.8 K 5 K 10 K
2.15 K 3.0 K 6 K
2.4 K 3.4 K 7 K
2.6 K 4 K 8 K
H_{dc} = 2 kOe
χ'_{mol} (emu/mol)
Frequency (Hz)
(f)
H_{dc} = 2 kOe
2.0 K
2.15 K
2.4 K
2.6 K
2.8 K
3.0 K
3.4 K
4 K
5 K
7 K
10 K
χ''_{mol} (emu/mol)
χ'_{mol} (emu/mol)
(h)
H_{dc} = 2 kOe
2.0 K 4 K
2.15 K 5 K
2.4 K 6 K
2.6 K 7 K
2.8 K 8 K
3.0 K 10 K
3.4 K
χ''_{mol} (emu/mol)
Frequency (Hz)

Fig. S15. Frequency dependent in-phase (a) and out-of-phase (b) ac susceptibility plots for complex **1** at zero dc field, and corresponding plots at 1 and 2 kOe dc fields (c, d, g and h) with selected frequencies for clarity. Cole-Cole plots at zero (e) and 2 kOe filed (f).

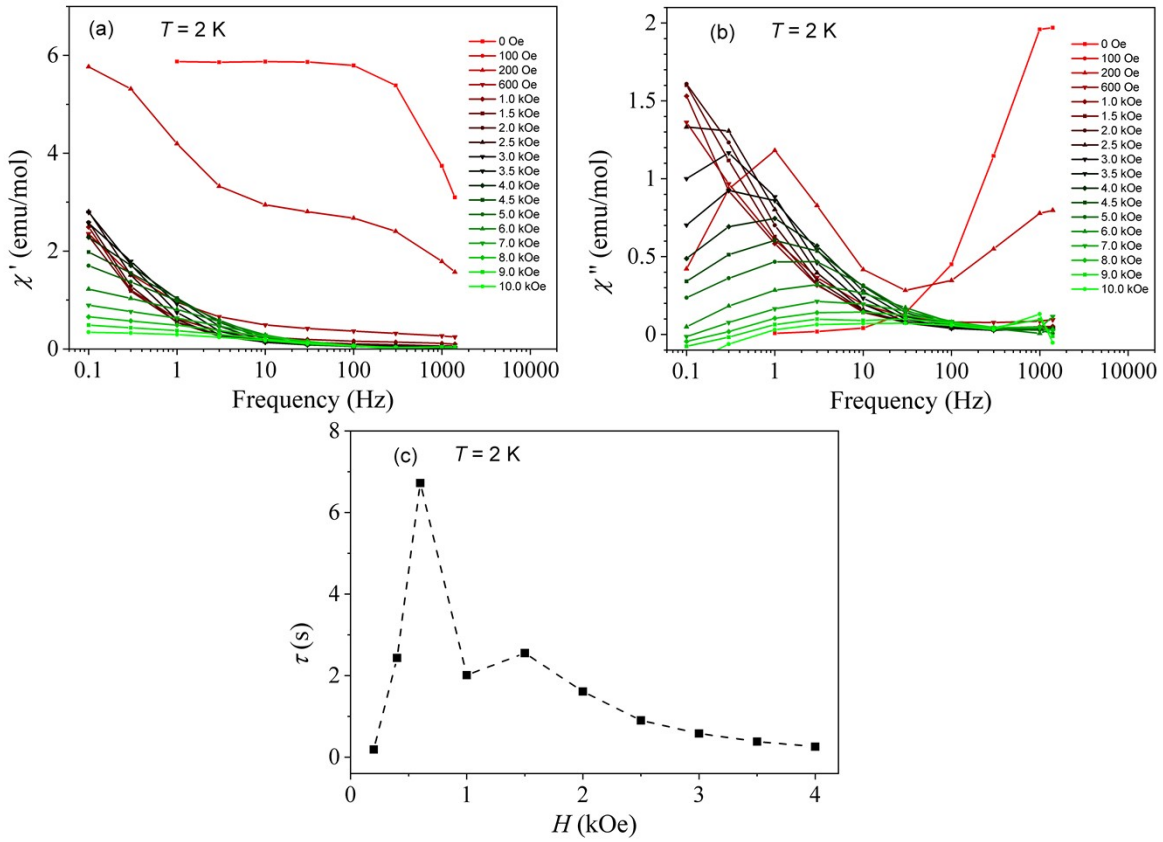

Fig. S16. Field dependence AC magnetic data for complex **1**

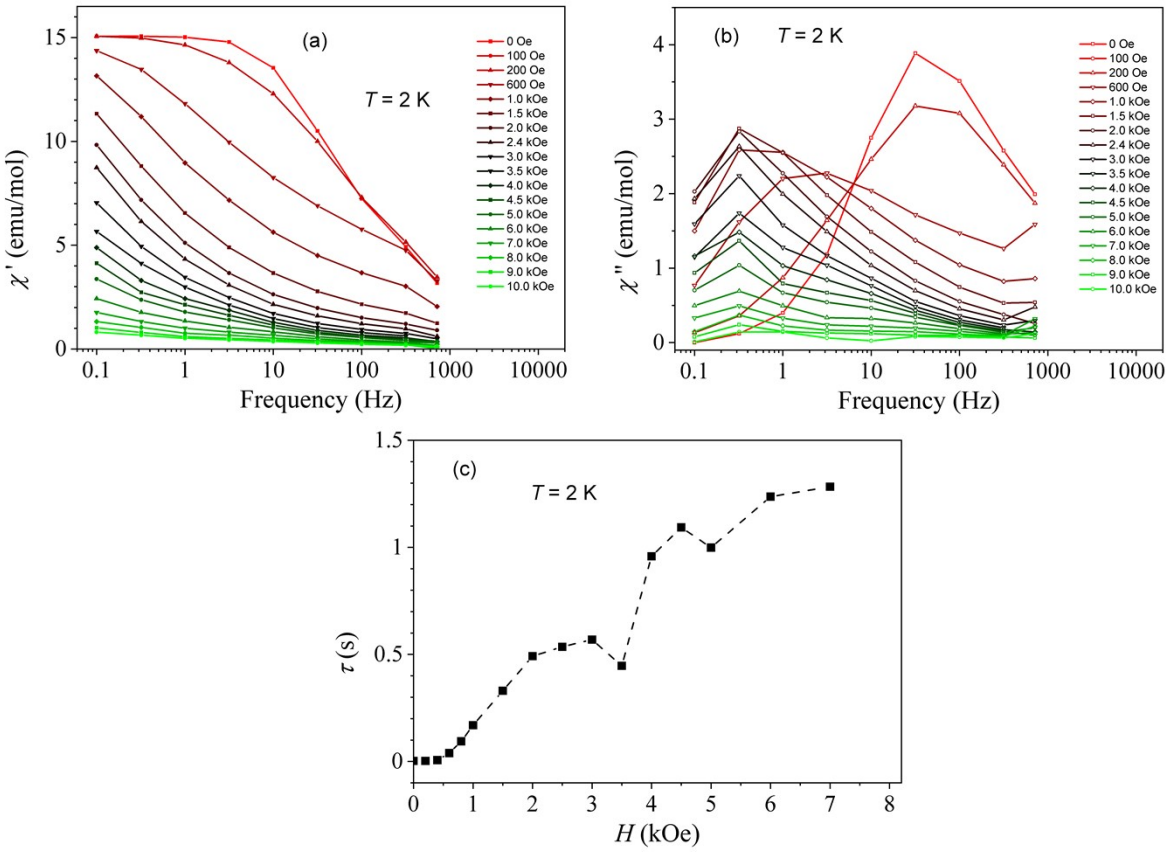

Fig. S17. Field dependence AC magnetic data for complex **2**

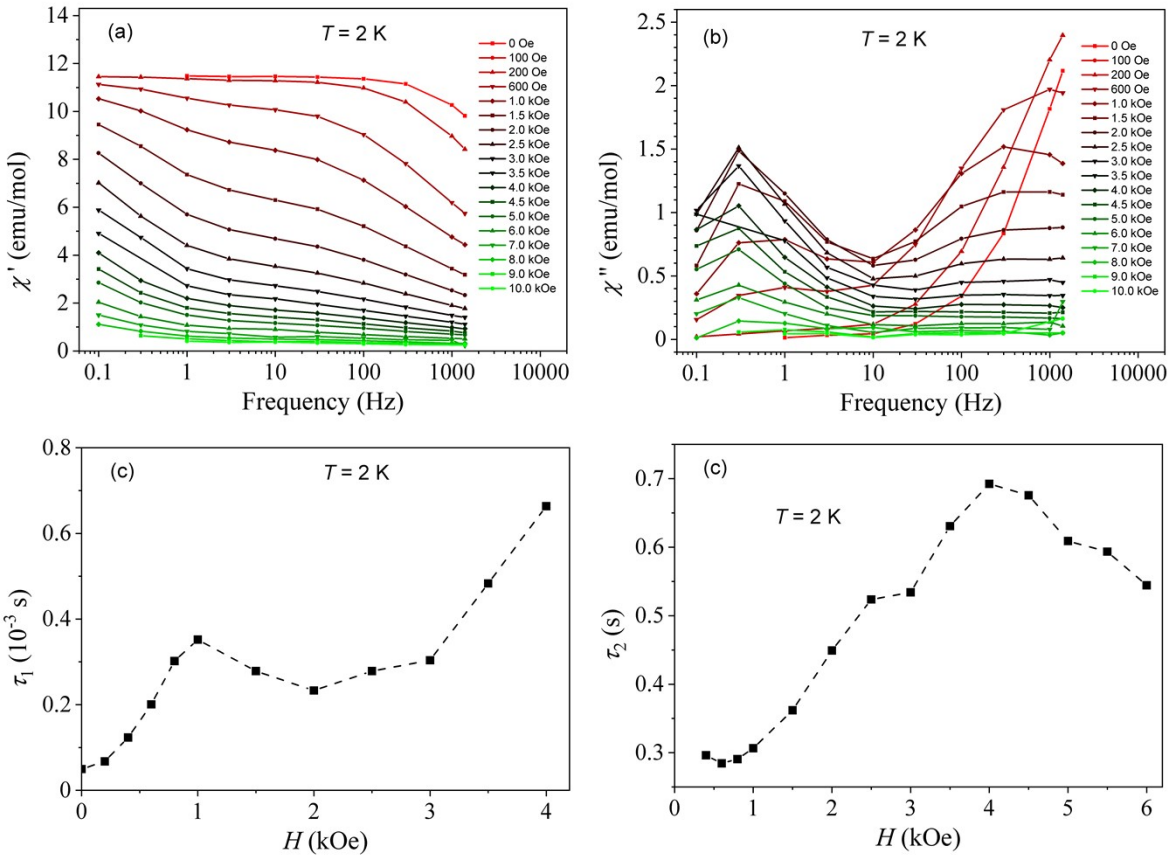

Fig. S18. Field dependence AC magnetic data for complex **3**.

Table S1. X-ray crystallographic data and refinement parameters for ligand H_3L and complexes **1-3**.

	H_3L	**1**	**2**	**3**
Empirical formula	$C_{12}H_{17}NO_4$	$C_{54}H_{83}Co_2DyN_6O_{25}$	$C_{48}H_{68}Co_2Dy_2N_8O_{22}$	$C_{66}H_{56}Co_2Dy_2N_8O_{36}$
Formula weight	239.26	1496.62	1551.96	1980.04
Temperature/K	150.01(10)	100.15	293(2)	200.15
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2/c$	$P\bar{1}$	$P2_1/c$	C2/c
a/Å	9.5116(3)	12.9113(3)	14.0030(5)	27.9723(9)
b/Å	5.7815(2)	13.2394(3)	14.0934(4)	10.8697(3)
c/Å	21.9120(7)	19.7653(4)	15.8785(5)	24.8686(6)
α/°	90	102.619(2)	90	90
β/°	97.532(3)	101.993(2)	109.288(4)	90.025(2)
γ/°	90	97.689(2)	90	90
Volume/Å^3	1194.57(7)	3167.72(13)	2957.73(18)	7561.3(4)
Z	4	2	2	4
ρ_{calc} g/cm^3	1.330	1.569	1.743	1.739
μ/mm^{-1}	0.830	1.769	3.130	2.483
$F(000)$	512.0	1538.0	1548.0	3928.0
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	8.14 to 155.512	3.39 to 61.364	3.968 to 61.04	4.02 to 61.18
Reflections collected	7554	62909	28769	33460
Independent reflections	2454 [R_{int} = 0.0476, R_{sigma} = 0.0480]	15455 [R_{int} = 0.0721, R_{sigma} = 0.0611]	7310 [R_{int} = 0.0545, R_{sigma} = 0.0494]	8981 [R_{int} = 0.0415, R_{sigma} = 0.0363]
Data/restraints/parameter	2454/0/158	15455/137/876	7310/0/383	8981/19/542
Goodness-of-fit on F^2	1.057	1.026	1.030	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0547, wR_2 = 0.1565	R_1 = 0.0474, wR_2 = 0.1105	R_1 = 0.0325, wR_2 = 0.0734	R_1 = 0.0319, wR_2 = 0.0854
Final R indexes [all data]	R_1 = 0.0616, wR_2 = 0.1634	R_1 = 0.0753, wR_2 = 0.1264	R_1 = 0.0412, wR_2 = 0.0779	R_1 = 0.0395, wR_2 = 0.0893
Largest diff. peak/hole / e Å^{-3}	0.32/-0.27	1.75/-1.31	1.41/-1.00	1.28/-0.52

Table S2. Selected bond distances around the Co^{III} centers in complexes **1-3**.

1				**2**		**3**	
Co1–O7	1.917(3)	Co2–O10	1.895(3)	Co1–O11	1.912(2)	Co1–O11[1]	1.937(2)
Co1–O3	1.906(3)	Co2–O11	1.909(3)	Co1–O11[1]	1.931(2)	Co1–O11	1.899(2)
Co1–O6	1.908(3)	Co2–O15	1.916(3)	Co1–O2	1.895(2)	Co1–O2	1.902(2)
Co1–O2	1.922(3)	Co2–O14	1.895(3)	Co1–O3	1.893(2)	Co1–O3	1.898(2)
Co1–N1	1.891(3)	Co2–N4	1.902(3)	Co1–O5	1.902(2)	Co1–O5	1.907(2)
Co1–N2	1.903(3)	Co2–N3	1.897(4)	Co1–N1	1.885(2)	Co1–N1	1.890(3)
Co1---Dy1	3.407(1)	Co2---Dy1	3.384(1)	Co---Dy	3.405(1)	Co---Dy	3.405(1)

Symmetry code: [1] = 1-X,1-Y,1-Z

Table S3. Selected bond distances around the Dy^{III} centers in complexes **1-3**.

1		**2**		**3**	
Dy1– O7	2.359(3)	Dy1–O11[1]	2.402(2)	Dy1– O11[1]	2.417(2)
Dy1– O3	2.364(3)	Dy1–O2	2.332(2)	Dy1– O2	2.305(2)
Dy1– O8	2.425(3)	Dy1–O3[1]	2.372(2)	Dy1– O1	2.537(2)
Dy1– O12	2.412(3)	Dy1–O8	2.279(2)	Dy1– O3[1]	2.373(2)
Dy1– O11	2.342(3)	Dy1–O4[1]	2.384(2)	Dy1– O4[1]	2.356(2)
Dy1– O4	2.369(3)	Dy1–O1	2.556(2)	Dy1– O6	2.330(2)
Dy1– O15	2.344(3)	Dy1–O6	2.351(2)	Dy1– O9	2.310(2)
Dy1– O16	2.391(3)	Dy1–O9	2.256(2)	Dy1– O7	2.276(2)

Symmetry code: [1] = 1-X,1-Y,1-Z

Table S4. Shape analysis around the Co^{III} centers in complexes **1-3**.

Label	Shape	Symmetry	**1**		**2**	**3**
			Co1	Co2	Co1	Co1
HP-6	Hexagon	D_{6h}	29.167	28.933	28.220	28.817
D6h	Pentagonal pyramid	C_{5v}	27.260	27.432	25.766	24.992
OBPY-10	Octahedron	Oh	0.294	0.282	0.518	0.548
PPY-6	Trigonal prism	D_{3h}	15.379	15.504	14.019	13.661
OC-6	Johnson pentagonal pyramid J2	C_{5v}	30.897	30.895	29.317	28.675

Table S5. Shape analysis around the Dy^{III} centers in complexes **1-3**.

Label	**Shape**	**Symmetry**	**1**	**2**	**3**
OP-8	Octagon	D_{8h}	34.778	31.487	30.041
HPY-8	Heptagonal pyramid	C_{7v}	24.490	23.999	23.728
HBPY-8	Hexagonal bipyramid	D_{6h}	8.474	14.526	14.578
CU-8	Cube	Oh	12.797	11.465	10.278
SAPR-8	Square antiprism	D_{4d}	9.056	**1.963**	**1.393**
TDD-8	Triangular dodecahedron	D_{2d}	6.890	**1.478**	**2.264**
JGBF-8	Johnson gyrobifastigium J26	D_{2d}	**4.519**	13.593	14.315
JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	25.115	27.435	26.396
JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	8.372	2.741	2.489
BTPR-8	Biaugmented trigonal prism	C_{2v}	7.600	**2.236**	**1.929**
JSD-8	Snub diphenoid J84	D_{2d}	7.694	3.996	4.628
TT-8	Triakis tetrahedron	Td	13.557	11.977	10.774
ETBPY-8	Elongated trigonal bipyramid	D_{3h}	20.892	23.726	22.597

Table S6. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **1** by the single-component generalized Debye model at H_{dc} = 0 Oe and H_{dc} = 600 Oe.

H_{dc} = 0 Oe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2
2	1.49981	4.39307	1.51E-04	0.06584
2.15	1.34467	4.11944	1.48E-04	0.06899
2.4	1.25856	3.68363	1.51E-04	0.06024
2.6	1.11974	3.42977	1.47E-04	0.06229
2.8	1.02613	3.19059	1.46E-04	0.06358
3	0.94458	2.98376	1.44E-04	0.06353
3.2	0.85947	2.82555	1.41E-04	0.06568
3.4	0.80164	2.6692	1.40E-04	0.06567
3.6	0.74253	2.53275	1.38E-04	0.06831
3.8	0.69459	2.40912	1.37E-04	0.06841
4	0.67276	2.27052	1.38E-04	0.06516

4.2	0.64485	2.1568	1.38E-04	0.06482
4.4	0.60521	2.06815	1.36E-04	0.06691
4.6	0.56343	1.99376	1.34E-04	0.06813
4.8	0.54136	1.90924	1.33E-04	0.06745
5	0.51069	1.84132	1.32E-04	0.06967
5.5	0.45117	1.6849	1.28E-04	0.07183
6	0.41225	1.54442	1.27E-04	0.0696
6.5	0.36182	1.44778	1.23E-04	0.07128
7	0.33226	1.34933	1.20E-04	0.06985
7.5	0.30426	1.26567	1.17E-04	0.07002
8	0.27222	1.19977	1.14E-04	0.0729
8.5	0.25602	1.12959	1.13E-04	0.06865
9	0.24927	1.06007	1.12E-04	0.06616
9.5	0.20683	1.03342	1.06E-04	0.07186
10	0.20283	0.97521	1.05E-04	0.0653
12	0.13079	0.84516	9.09E-05	0.06243
14	0.11939	0.71975	8.37E-05	0.04452
16	0.08056	0.65499	6.85E-05	0.03926
18	0.06489	0.59009	5.53E-05	0.02173
20	0.04967	0.54036	4.22E-05	0.02739

H_{dc} = 600 Oe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2
2	0.31985	6.9452	6.01E+00	0.4607
2.15	0.30077	6.55979	5.76E+00	0.46267
2.4	0.27296	6.16834	5.51E+00	0.46442
2.6	0.2541	5.84604	5.03E+00	0.4606
2.8	0.24195	5.53647	4.33E+00	0.45023
3	0.23733	5.04721	3.19E+00	0.42689
3.2	0.23522	4.53079	2.19E+00	0.39693
3.4	0.23553	4.00955	1.42E+00	0.35831
3.6	0.23133	3.58488	9.47E-01	0.3209
3.8	0.22854	3.23658	6.55E-01	0.28404
4	0.2237	2.9619	4.68E-01	0.25122
4.2	0.21623	2.75693	3.48E-01	0.22561
4.4	0.20889	2.58363	2.63E-01	0.2032
4.6	0.19686	2.44859	2.04E-01	0.18779
4.8	0.19003	2.32183	1.60E-01	0.17149
5	0.1819	2.21405	1.26E-01	0.1586
5.5	0.16334	1.98874	7.36E-02	0.13443
6	0.1459	1.8147	4.56E-02	0.12012

6.5	0.13078	1.67569	2.99E-02	0.11019
7	0.11806	1.55645	2.03E-02	0.10413
7.5	0.11016	1.4503	1.43E-02	0.09695
8	0.09796	1.36425	1.03E-02	0.09605
8.5	0.09057	1.28542	7.62E-03	0.09334
9	0.08262	1.21656	5.76E-03	0.09278
9.5	0.07302	1.15856	4.44E-03	0.09688
10	0.06714	1.10227	3.49E-03	0.09601
10.5	0.06356	1.05002	2.79E-03	0.09437
11	0.05864	1.00416	2.25E-03	0.09351
11.5	0.05345	0.96372	1.83E-03	0.09302
12	0.04836	0.91951	1.46E-03	0.09253
12.5	0.04231	0.88898	1.21E-03	0.09491
13	0.04022	0.85843	0.00102	0.0958
13.5	0.03835	0.82708	8.55E-04	0.09248
14	0.03528	0.79973	7.23E-04	0.09203
16	0.02586	0.70551	3.87E-04	0.08604
18	0.01346	0.6371	2.14E-04	0.07563
20	0.00986	0.57542	1.21E-04	0.06612

Table S7. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **2** by the single-component generalized Debye model at H_{dc} = 0 Oe and H_{dc} = 2 kOe.

H_{dc} = 0 Oe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2
2	3.90093	10.33695	4.19E-03	0.17918
2.15	3.65999	9.46453	4.06E-03	0.17799
2.4	3.32343	8.30806	3.91E-03	0.1751
2.6	3.09128	7.5614	3.81E-03	0.17415
2.8	2.90609	6.91217	3.71E-03	0.17235
3	2.73579	6.36809	3.64E-03	0.17027
3.2	2.58414	5.92246	3.57E-03	0.16931
3.4	2.43849	5.57187	3.49E-03	0.17245
3.6	2.34462	5.1782	3.42E-03	0.16565
3.8	2.22749	4.89058	3.36E-03	0.16788
4	2.17002	4.58779	3.29E-03	0.16039
4.2	2.07341	4.34472	3.20E-03	0.15834
4.4	1.99575	4.1135	3.12E-03	0.15352
4.6	1.93949	3.89267	3.05E-03	0.14888
4.8	1.87873	3.69883	2.96E-03	0.14181
5	1.82271	3.52085	2.84E-03	0.13584

5.5	1.70014	3.13259	2.54E-03	0.11566
6	1.5894	2.82137	2.18E-03	0.09222
6.5	1.50903	2.55728	1.82E-03	0.06805
7	1.42071	2.34897	1.47E-03	0.04485
7.5	1.20171	2.31566	1.05E-03	0.05617
8	1.13469	2.15645	8.16E-04	0.04015
8.5	0.97402	2.12383	5.64E-04	0.05462
9	0.94789	1.97477	4.31E-04	0.03439
9.5	0.86432	1.90366	3.05E-04	0.03322
10	0.70613	1.92439	1.95E-04	0.05725
10.5	0.67809	1.82518	1.35E-04	0.04509
11	0.61219	1.77537	8.93E-05	0.03817
11.5	0.57281	1.71073	5.87E-05	0.03454
12	0.51681	1.65632	3.63E-05	0.02652
12.5	0.66166	1.42754	2.77E-05	0.01874

H_{dc} = 2 kOe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2
2	2.76603	8.17272	3.57E-01	0.28218
2.15	2.93785	7.5111	3.58E-01	0.22656
2.4	2.8072	6.80319	2.99E-01	0.20272
2.6	2.92278	6.16568	2.81E-01	0.16982
2.8	1.45759	7.67828	1.89E-01	0.34344
3	1.44689	7.12338	1.68E-01	0.32527
3.2	1.43002	6.66806	1.52E-01	0.30982
3.4	1.41638	6.23238	1.37E-01	0.2912
3.6	1.39782	5.84383	1.21E-01	0.27294
3.8	1.39203	5.48566	1.06E-01	0.2501
4	1.35529	5.15285	8.91E-02	0.23217
4.2	0.96299	5.34272	6.66E-02	0.28001
4.4	0.90618	5.09197	5.42E-02	0.26733
4.6	0.8836	4.82102	4.43E-02	0.24578
4.8	0.85812	4.58175	3.59E-02	0.22586
5	0.7654	4.45417	2.84E-02	0.22168
5.5	0.7188	3.99791	1.68E-02	0.17797
6	0.65805	3.65704	1.01E-02	0.14699
6.5	0.62705	3.3589	6.43E-03	0.11958
7	0.59635	3.10839	4.20E-03	0.0975
7.5	0.50541	2.96387	2.70E-03	0.1041
8	0.48886	2.76672	1.81E-03	0.09209
8.5	0.48299	2.58443	1.23E-03	0.07992

9	0.47379	2.42587	8.35E-04	0.07104
9.5	0.46284	2.28529	5.59E-04	0.06443
10	0.46075	2.15069	3.70E-04	0.05592
10.5	0.44678	2.03514	2.37E-04	0.05282
11	0.42094	1.95267	1.48E-04	0.05384
11.5	0.43157	1.84301	9.40E-05	0.04792
12	0.4491	1.71754	5.58E-05	0.04656
12.5	0.44648	1.63684	3.58E-05	0.05115
13	0.07185	1.93423	1.75E-05	0.07405
13.5	0.06612	1.86653	1.13E-05	0.07099

Table S8. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **2** by the single-component generalized Debye model at H_{dc} = 0 Oe and the double-component generalized Debye model with two relaxation times at H_{dc} = 1 kOe.

H_{dc} = 0 kOe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2
2	4.58641	6.86917	4.70E-05	0.17137
2.15	4.19933	6.39339	4.58E-05	0.17236
2.4	3.89842	5.58766	4.70E-05	0.1665
2.6	3.56954	5.13665	4.61E-05	0.16537
2.8	3.2236	4.82326	4.42E-05	0.1666
3	3.03404	4.44546	4.41E-05	0.16303
3.2	2.86049	4.13917	4.36E-05	0.16167
3.4	2.63252	3.94834	4.17E-05	0.16444
3.6	2.4234	3.77408	3.99E-05	0.1612
3.8	2.3235	3.53443	3.93E-05	0.15826
4	2.46853	3.08012	4.33E-05	0.14738
4.2	2.46427	2.81189	4.43E-05	0.1431
4.4	2.49108	2.53857	4.57E-05	0.13539
4.6	2.24256	2.5653	4.03E-05	0.1383
4.8	2.06249	2.54171	3.60E-05	0.14275
5	1.9228	2.49462	3.26E-05	0.14392
5.5	1.61425	2.39083	2.52E-05	0.14176
6	1.12296	2.54295	1.66E-05	0.14317
6.5	2.00258	1.40876	2.77E-05	0.12413
7	1.86299	1.30835	2.11E-05	0.13854
7.5	1.8475	1.11503	1.76E-05	0.15602
8	1.34104	1.43845	8.12E-06	0.19717

8.5	1.59085	1.02725	9.09E-06	0.19878

H_{dc} = 1 Oe

T (K)	χ_S (emu/mol)	$\Delta\chi_2$ (emu/mol)	τ_2(s)	α_2	$\Delta\chi_1$ (emu/mol)	τ_1 (s)	α_1
2	2.4947	1.59289	3.65E-01	0.14766	6.22246	4.30E-04	0.41344
2.15	2.20219	1.45092	3.14E-01	0.12475	5.99667	3.20E-04	0.42028
2.4	2.03156	1.03864	2.93E-01	0.12186	5.64996	2.58E-04	0.40283
2.6	1.96653	0.74315	2.95E-01	0.08604	5.33915	2.24E-04	0.38745
2.8	1.94579	0.5526	3.00E-01	0.06376	4.97961	1.97E-04	0.36776
3	1.9335	0.38989	2.92E-01	0.01799	4.64316	1.74E-04	0.35198
3.2	1.94702	0.30875	3.01E-01	0	4.3041	1.54E-04	0.33466
3.4	2.00216	0.25276	3.18E-01	0	3.96692	1.38E-04	0.31406
3.6	2.03376	0.19539	3.33E-01	0	3.67524	1.22E-04	0.29447
3.8	2.05725	0.15076	3.55E-01	0	3.38058	1.08E-04	0.27241
4	2.07908	0.11433	3.74E-01	0	3.10473	9.71E-05	0.25295
4.2	2.11349	0.09014	3.75E-01	0	2.84311	8.76E-05	0.23461
4.4	2.10142	0.06954	4.04E-01	0	2.64237	7.70E-05	0.21881
4.6	2.03875	0.05887	4.10E-01	0	2.50851	6.56E-05	0.20783
4.8	1.9971	0.04824	4.03E-01	0	2.37016	5.64E-05	0.19501
5	1.91665	0.03841	4.24E-01	0	2.28383	4.71E-05	0.18856
5.5	1.59537	0.02455	4.07E-01	0	2.23244	2.77E-05	0.17506
6	0.86555	0	0.00E+00	0	2.65029	1.27E-05	0.17575
6.5	1.94007	0	0.00E+00	0	1.33963	2.11E-05	0.15834
7	2.05212	0	0.00E+00	0	1.0034	1.89E-05	0.16417

Table S9. Structural and magnetic data of all the structurally characterized $Co^{III}_2Dy^{III}_2$ tetramers following Orbach relaxation mechanism.[b]

Complex	Core structure	Topology	Dy^{III} geometry	U_{eff} [K]	H_{DC} [Oe]	Ref.
$[Co_2Dy_2(valdien)_2(CH_3COO)_4(OH)_2(H2O)_2]^{2+}$	Co-Dy-Dy-Co	linear	TCTPR-9	33.8	0	31
$[Co_2Dy_2(OH)_2(teaH)_2(acac)_6]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	71 (SR)	0	
				45 (FR)	0	
$[Co_2Dy_2(OH)_2(bdea)_2(acac)_6]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	27	0	32
				38	500	
$[Co_2Dy_2(OH)_2(edea)_2(acac)_6]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	16	1000	
$[Co_2Dy_2(OH)_2(bdea)_2(acac)_2(NO_3)_4]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	169	0	33
$[Co_2Dy_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4]^{2+}$ and $[Co_2Dy_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	88.8	0	34
$[Co_2Dy_2(OMe)_2(O_2CPh\text{-}2\text{-}Cl)_4(bdea)_2(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	115.8	0	
$[Co_2Dy_2(OMe)_2(O_2CPh\text{-}4\text{-}^tBu)_4(bdea)_2(NO_3)(MeOH)_3]^+$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	110.7	0	
				137.7	0	35
$[Co_2Dy_2(OMe)(OH)(O_2CPh2\text{-}Cl)_4(bdea)_2(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	126.9	0	
$[Co_2Dy_2(mdea)_4(hfacac)_3(O_2CCF_3)(H_2O)]$	$CoDy_2Co$	Butterfly, Type-II	CSAPR-9	32.5	0	
$[Co_2Dy_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4]^{2+}$ and $[Co_2Dy_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]$	CoDy2Co	Butterfly, Type-II	SAPR-8	87.8	0	
$[Co_2Dy_2(OMe)_2(dea)_2(O_2CPh)_4(MeOH)_4]^{2+}$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	103.7	0	36
$[Co_2Dy_2(OMe)_2(mdea)_2(O_2CPh)_4(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	79.2	0	
$[Co_2Dy_2(OMe)_2(bdea)_2(O_2CPh)_4(MeOH)_4]^{2+}$ and $[Co_2Dy_2(OMe)_2(bdea)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	115.2	0	
$[Co_2Dy_2(\mu_3\text{-}OH)_2(ortho\text{-}toluene)_4(mdea)_2(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	116.9	0	37
$[Co_2Ln_2(L^3)_2(pdm)_2(CH_3COO)_2(CH_3OH)_2](NO_3)_2$	CoDyDyCo	linear	MFF-9	64.6	0	38
				64.0	2000	
{Co_2Ln_2} with [CpCo{P(]O)(OEt)$_2$]$_3$] as a metallo-ligand	CoDyDyCo	Linear-like	COC-7	7	2000	39
$[Co_2Dy_2(OMe)_2(teaH)_2(acac)_4(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	27	0	
				35	3000	
$[Co_2Dy_2(OH)_2(teaH)_2(acac)_4(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	28	0	40
$[Co_2Dy_2(OMe)_2(mdea)_2(acac)_4(NO_3)_2]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	38	0	
$[Co_2Dy_2(OR)_2(teaH)_2(piv)_6]$	$CoDy_2Co$	Butterfly, Type-II	SAPR-8	51 (FR)	0	41
				127 (SR)	0	
$[(L_{OEt})_2Dy_2(L^4)]$	CoDyDyCo	Linear like	COC-7	56.53	2500	42
$[(L_{OEt})_2Dy_2(L^5)]$	CoDyDyCo	Linear like	CTPR-7	45.76	2500	
$[Co_2Dy_2(\mu_3\text{-}OH)_2(HL^2)_2(OAc)_6]$	$DyCo_2Dy$	Butterfly, Type-I	SAPR-8	27.7 (FR)	0	
				43.9 (SR)	0	43
				27.7 (FR)	500	
				43.9 (SR)	500	
2	$DyCo_2Dy$	Butterfly, Type-I	SAPR-8	125	0	
				200	2000	This
3	$DyCo_2Dy$	Butterfly, Type-I	TDD-8	21	0	work
				28	1000	

[b] Abbreviations: H_2valdien= N1,N3-bis(3-methoxysalicylidene)diethylenetriamine, $teaH_3$ = triethanolamine, $bdeaH_2$ = *N*-n-butyldiethanolamine, $edeaH_2$ = *N*-ethyldiethanolamine, acacH = acetylacetone, $mdeaH_2$ = *N*-methyldiethanolamine, piv = pivalate, $pdmH_2$ = 2,6-pyridinedimethanol, $(L_4)^{4-}$ = 2,2′,2″,2‴-[1,2,4,5-benzenetetrayltetrakis-(nitrilomethylidyne)]tetrakisphenolate; $(L_5)^{4-}$ = 2,2′,2″,2‴-[[1,1′-biphenyl]-3,3′,4,4′-tetrayltetrakis(nitrilomethylidyne)] tetrakis(4-chlorophenolate); L_{OEt} = [CpCo{P(O)(OEt)$_2$}$_3$]$^-$, H_3L^2 = 3-[(2-hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol, TCTPR-9 = tricapped trigonal prism, SAPR-8 = square antiprism, CSAPR-9 = capped square antiprism, MFF-9 = Muffin, COC-7 = capped octahedron, CTPR-7 = capped trigonal prism, COC-7=capped octahedron, CTPR-7=capped trigonal prism;

Table S10. Magneto-structural data for heterometallic $\{Co^{III}_2Dy\}$ core complexes displaying slow relaxation of magnetization.[a]

Complex	Topology	Dy^{III} geometry	U_{eff}/K	H_{DC}/Oe	Ref.
$[Co_2Dy(valdien)_2(OCH_3)_2(chp)_2](ClO_4)$	bent	SAPR-8	74.1	2000	44
$[Co_2Dy(hmb)_2(OMe)_2(O_2CCH_3)_3]$	triangular	MFF-9	5.5	500	45
			6.4	1250	
$[Co_2Dy(L^1)_2(O_2CCH_3)_2(H_2O)_3](NO_3)$	bent	TCTPR-9	88	1000	46
$[Co_2Dy(HL^2)_4](NO_3)$	linear	JGBF-8	40.2	3400	43
$[Co_2Dy(OMe)_2(naph)_2(O_2CMe)_3(MeOH)_2]$	triangular	SAPR-8	85.7	400	47
$[Dy(L_{OEt})_2](PF6)$	linear	OC-6	25.9	600	48
$[Dy(L_{OiPr})_2](PF6)$	linear	OC-6	13.0	750	
1	linear	JGBF-8	12	0	This work
			32	600	

[a] Abbreviations: H_2valdien= *N*1,*N*3-bis(3-methoxysalicylidene)diethylenetriamine, Hchp = 6-chloro-2- hydroxypyridine, H_2hmb = 2-hydroxy-3-methoxybenzylidene benzohydrazide, H_3L^1 = 2-methoxy-6-[{2-(2-hydroxyethylamino)ethylimino}methyl]phenol, H_3L^2 = 3-[(2-hydroxy-3-methoxy-benzylidene)-amino]-propane-1,2-diol, L_{OEt} = $[CpCo\{P(O)(OEt)_2\}_3]^-$, L_{OiPr} = $[CpCo\{P(O)(OiPr)_2\}_3]^-$, SAPR-8 = Square antiprism, MFF-9 = Muffin, TCTPR-9 = Spherical tricappedtrigonal prism, JGBF-8 = Johnson gyrobifastigium, OC-6 = Octahedron.

Table S11. CASSCF calculated energy and g-values for the 8 Kramers' doublets belonging to the ground $^6H_{15/2}$ multiplet for **1-3**.

Complex	E (cm^{-1})	g_x	g_y	g_z
1	0.0	0.001	0.013	19.672
	278.5	1.130	1.592	15.441
	354.5	1.407	3.105	12.299
	380.9	2.075	7.421	9.306
	437.4	2.885	6.412	7.720
	514.8	4.910	5.419	9.203
	612.5	0.603	1.800	16.681
	666.7	0.424	1.263	18.549
2	0.0	0.028	0.039	19.673
	178.2	0.538	0.699	16.141
	248.6	0.044	0.762	13.985
	298.8	2.509	3.211	10.550
	364.5	0.873	5.745	8.781
	428.4	2.631	4.345	10.754
	478.5	1.228	2.820	17.214
	646.5	0.038	0.043	19.540
3	0.0	0.150	0.237	19.167
	91.0	0.368	0.382	17.283
	143.3	1.979	3.565	13.372
	181.6	2.063	2.850	10.415
	246.1	2.776	4.551	9.537
	310.8	3.473	3.939	13.061
	377.7	0.470	0.647	18.834
	557.0	0.001	0.016	19.533