Supporting Information

Odd-numbered cyclic single-molecule magnets: from heptanuclear to dimer of heptanuclear dysprosium clusters

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Experimental Section

Synthetic procedures

1-naphthylphosphonic acid ($C_{10}H_7PO_3H_2$) was prepared according to the literature method.[1] All chemicals were of reagent grade and were used without any further purification.

Synthesis of (*E*)-N'-(2-hyborxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide (H₂opch). Pyrazine-2-carbohydrazide (3 mmol, 0.414 g) was suspended together with *o*-vanillin (3 mmol, 0.456 g) in methanol (20 mL), and the resulting mixture was stirred at the room temperature overnight. The pale yellow solid was collected by filtration (yield: 0.84 g, 83%). Elemental analysis (%) calcd for $C_{13}H_{12}N_4O_3$: C, 57.35, H, 4.44, N, 20.58: found C, 58.64, H, 4.59, N, 20.39. IR (KBr, cm^{-1}): 3415(w), 3258(w), 1677(vs), 1610(s), 1579(m). 1530(s), 1464(s), 1363(m), 1255(vs), 1153(s), 1051(w), 1021(s), 986(w), 906(m), 938(w), 736(s), 596(m), 498(w).

Synthesis of (*N',N''E,N',N''E*)-N',N''-(ethane-1,2-diylidene)dipyrazine-2-carbo hydrazide (H₂EDDC). Pyrazine-2-carbohydrazide (20 mmol, 2.764 g) was suspended together with glyoxal (10 mmol, 0.582 g) in methanol (40 ml), and the resulting mixture was stirred at the room temperature overnight. The pure white solid was collected by filtration (yield: 2.76 g, 64%). Elemental analysis (%) calcd for $C_{12}H_{10}N_8O_2$: C, 48.32, H, 3.38, N, 37.57: found C, 47.00, H, 3.65, N, 36.34. IR (KBr, cm^{-1}): 3420(m), 3241(w), 1678(vs), 1579(m), 1529(s), 1474(m), 1407(m), 1316(m), 1282(w), 1157(w), 1058(w), 1021(s), 950(w), 917(w), 868(m), 772(m), 648(w), 422(m).

Synthesis of [Dy₇(EDDC)(opch)₄(O₃PC₁₀H₇)₃(OAc)₅(MeOH)₂]·4MeOH (1). To a slurry of H₂EDDC (59.6 mg, 0.20 mmol) and triethylamine (0.14 ml, 1.0 mmol) in

methanol (20 mL), solid $Dy(OAc)_3 \cdot 4H_2O$ (164.8 mg, 0.40 mmol) was added. After stirring for 24 h, the H_2opch (108.0 mg, 0.40 mmol) and $C_{10}H_7PO_3H_2$ (20.8 mg, 0.10 mmol) were added to the resulting pale yellow solution. Then the mixture was stirred for another 24 h, followed by filtration. Next, the resultant yellow solution was transferred to a 25 mL glass ware and sealed. The glass ware was keep into a drying oven and the reaction mixture was heated at 100 °C. Red single crystals, suitable for X-ray diffraction analysis, were formed after for 48 h as single-phase product. Yield: 67 mg (43%, based on Dy). Elemental analysis (%) calcd for $C_{110}H_{108}Dy_7N_{24}O_{39}P_3$: C, 36.49, H, 3.00, N, 9.28: found C, 35.97, H, 2.86, N, 9.74. IR (KBr, cm^{-1}): 3419(m), 2972(w), 1604(vs), 1565(m), 1522(w), 1450(m), 1345(w), 1239(m), 1220(m), 1160(m), 1136(m), 1074(m), 1033(m), 1009(m), 969(m), 922(m), 862(w), 802(w), 776(w), 741(w),676(w), 646(w), 599w), 548(m), 553(w), 511(w), 424(w). Thermal analysis reveals a weight loss of 5.2% in the temperature range 30-250°C, in agreement with the removal of six methanol molecules (calcd. 5.3%).

Synthesis of $[Dy_{14}(EDDC)_4(opch)_4(O_3PC_{10}H_7)_{10}(OAc)_6(H_2O)_4] \cdot xH_2O$ (2). To a slurry of H_2EDDC (59.6 mg, 0.20 mmol) and triethylamine (0.14 mL, 1.0 mmol) in methanol (20 mL), solid $Dy(OAc)_3 \cdot 4H_2O$ (164.8 mg, 0.40 mmol) was added. After stirring for 24 h, the H_2opch (108.0 mg, 0.40 mmol) and $C_{10}H_7PO_3H_2$ (41.6 mg, 0.20 mmol) were added to the resulting pale yellow solution. Then the mixture was stirred for another 24 h, followed by filtration. Next, the resultant yellow solution was transferred to a 25 mL glass ware and sealed. The glass ware was kept into a drying oven and the reaction mixture was heated at 100 °C. Red single crystals, suitable for X-ray diffraction analysis, were formed after for 48 h as single-phase product. Yield: 85 mg (54%, based on Dy). Elemental analysis (%) calcd for $C_{212}H_{168}Dy_{14}N_{48}O_{66}P_{10} \cdot 9H_2O$: C, 35.38, H, 2.59, N, 9.35: found C, 35.30, H, 2.83, N, 9.18. IR (KBr, cm^{-1}): 3416(m), 2968(w), 1609(vs), 1562(m), 1544(w), 1521(w), 1452(s), 1419(w), 1377(w), 1346(m), 1289(w), 1241(m), 1217(s), 1159(m), 1105(w), 1048(w), 1029(w), 1020(w), 971(w), 925(w), 860(w), 785(w), 770(w), 743(m), 708(w), 642(w), 532(w), 484(w), 425(m). Thermal analysis reveals a weight loss of 3.3% in the temperature range 30-260°C, in agreement with the removal of thirteen water molecules (calcd. 3.3%).

Single-Crystal Structure Determination

Single crystals of dimensions $0.30 \times 0.30 \times 0.35$ mm^3 for **1** and $0.25 \times 0.25 \times 0.30$ mm^3 for **2** were mounted on a glass rod. The crystal data were collected on a Bruker SMART APEX II diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å) at 123(2) K for **1** and **2**. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL.[2] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were either put in calculated positions or found from the difference Fourier maps and refined isotropically. Selected bond lengths and angles are given in Table S2. CCDC 1424266 (**1**)-1424267 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical measurements

Elemental analyses for C, N and H were determined with a Perkin Elmer 240C elemental analyzer. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer with KBr pellets in the range of 400-4000 cm^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu-Kα) over the 2θ range of 5 to 50° at room temperature. Magnetic susceptibility measurements were performed in the temperature range 1.8–300 K using a vibrating sample magnetometer (VSM) of Quantum Design MPMS SQUID-VSM system. The diamagnetic contribution of the sample itself was estimated from Pascal's constant.[3]

References:

1. I. P. Beletskaya, M. A. Kazankova, *Russian J. Org. Chem.*, 2002, **38**, 1391-692.

2. SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments Madison, WI, 1995.

3. O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.

Table S1. Summary of structural data of **1** and **2**.

Compound	1	2
formula	$C_{110}H_{108}Dy_7N_{24}O_{39}P_3$	$C_{212}H_{176}Dy_{14}N_{48}O_{70}P_{10}$
mol wt	3620.61	7100.71
T [K]	123（2）	123(2)
λ [Å]	0.71073	0.71073
crystal syst	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a [Å]	14.7481(15)	22.068(2)
b [Å]	33.056(3)	25.118(3)
c [Å]	25.607(3)	44.977(5)
α [deg]	90	90
β [deg]	104.153(2)	101.477(2)
γ [deg]	90	90
V [Å^3]	12105(2)	24432(5)
Z	4	4
ρ[g cm^{-3}]	1.987	1.930
2θ [deg]	0.962 – 28.307	0.998 – 26.000
GOF	1.064	1.063
$R1$	0.0796	0.1576
w$R2$	0.2131	0.3752
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/[e Å^{-3}]	5.68, -5.53	2.55, -2.65
CCDC number	1424266	1424267

Table S2. Selected bond lengths (Å) and angles (º) for compounds **1** and **2**.

| NO.	1	NO.	1	NO.	2	NO.	2
Dy1- O7	2.2698(2)	Dy6- N23	2.4940(2)	Dy1- O1	2.2789(2)	Dy7- O9	2.3156(2)
Dy1- O9	2.3699(2)	Dy7- O10	2.2109(2)	Dy1- O4	2.4154(2)	Dy7- O15	2.2007(2)
Dy1- O11	2.3927(2)	Dy7- O14	2.2958(2)	Dy1- O13	2.2299(2)	Dy7- O17	2.3221(2)
Dy1- O12	2.3620(2)	Dy7- O16	2.3520(2)	Dy1- O16	2.2795(2)	Dy1···Dy2	4.0733(3)
Dy1- O30	2.2815(2)	Dy7- O17	2.3677(2)	Dy1- O17	2.4092(2)	Dy2···Dy3	4.0263(3)
Dy1- N8	2.4393(2)	Dy7- O20	2.3502(3)	Dy1- O19	2.3588(2)	Dy3···Dy4	4.0496(3)
Dy2- O6	2.3712(2)	Dy7- O21	2.3711(2)	Dy2- O5	2.2525(2)	Dy4···Dy5	4.0634(3)
Dy2- O8	2.2154(2)	Dy1···Dy2	4.0363(3)	Dy2- O26	2.3627(3)	Dy5···Dy6	3.7897(4)
Dy2- O11	2.3706(2)	Dy2···Dy3	4.2607(3)	Dy2- O2w	2.4206(3)	Dy6···Dy7	3.7204(3)
Dy2- O25	2.3512(2)	Dy3···Dy4	3.8123(3)	Dy3- O2	2.2781(2)	Dy7···Dy1	3.8578(3)
Dy2- O26	2.4143(2)	Dy4···Dy5	3.8045(4)	Dy3- O10	2.2812(2)	Dy1···Dy7a	6.5639(6)
Dy2- O31	2.4244(2)	Dy5···Dy6	3.5894(3)	Dy3- O20	2.3337(3)	Dy7···Dy7a	6.5671(5)
Dy3- O9	2.3761(2)	Dy6···Dy7	3.8773(3)	Dy3- O21	2.3966(2)	Dy6···Dy1a	6.7732(5)
Dy3- O12	2.3220(2)	Dy7···Dy1	3.8675(3)	Dy3- O27	2.3693(2)	Dy1···Dy1a	8.1067(8)
Dy3- O13	2.3964(2)	Dy1–O4–Dy2	113.700(5)	Dy3- O30	2.3282(2)	Dy1–O1–Dy2	115.615(5)
Dy3- O15	2.24582)	Dy1–O34–Dy2	112.013(5)	Dy4- O7	2.2553(3)	Dy1–O19–Dy2	112.091(5)
Dy3- O28	2.4405(2)	Dy2–O1–Dy3	113.745(5)	Dy4- O11	2.4571(2)	Dy2–O2–Dy3	112.688(6)
Dy3- O29	2.3160(2)	Dy2–O2–Dy3	118.239(5)	Dy4- O31	2.2590(2)	Dy2–O20–Dy3	110.349(6)
Dy4- O4	2.4705(3)	Dy3–O16–Dy4	108.657(5)	Dy4- O1w	2.2753(2)	Dy3–O10–Dy4	115.478(5)
Dy4- O18	2.3897(2)	Dy3–O17–Dy4	108.097(5)	Dy5- O8	2.3743(2)	Dy3–O21–Dy4	108.141(5)
Dy4- O22	2.2215(2)	Dy4–O14–Dy5	99.918(5)	Dy5- O11	2.2816(2)	Dy4–O11–Dy5	108.033(4)
Dy4- O23	2.2461(2)	Dy4–O15–Dy5	104.228(5)	Dy5- O23	2.2845(2)	Dy4–O22–Dy5	108.882(4)
Dy4- O34	2.4683(2)	Dy5–O12–Dy6	100.043(5)	Dy5- O22	2.4038(2)	Dy5–O8–Dy6	108.076(7)
Dy5- O4	2.3499(2)	Dy5–O13–Dy6	99.470(5)	Dy5- O24	2.1384(2)	Dy5–O23–Dy6	110.077(7)
Dy5- O5	2.2242(2)	Dy6–O7–Dy7	104.511(5)	Dy5- O29	2.2299(3)	Dy6–O6–Dy7	103.679(6)
Dy5- O6	2.3340(2)	Dy6–O11–Dy7	108.975(5)	Dy5- N16	2.4496(2)	Dy6–O9–Dy7	97.658(5)
Dy5- O24	2.3047(2)	Dy7–O6–Dy1	110.561(5)	Dy6- O6	2.3622(2)	Dy7–O4–Dy1	107.409(5)
Dy5- O31	2.3511(2)	Dy7–O31–Dy1	108.151(5)	Dy6- O8	2.3075(3)	Dy7–O17–Dy1	109.237(6)
Dy5- O34	2.3998(2)	Dy1–Dy2–Dy3	111.752(3)	Dy6- O12	2.3642(2)	Dy1–Dy2–Dy3	117.387(4)
Dy5- N1	2.4666(3)	Dy2–Dy3–Dy4	88.883(3)	Dy6- O14	2.2360(3)	Dy2–Dy3–Dy4	126.882(4)
Dy6- O1	2.3920(2)	Dy3–Dy4–Dy5	126.286(3)	Dy6- O23	2.3396(3)	Dy3–Dy4–Dy5	115.718(3)
Dy6- O2	2.3760(2)	Dy4–Dy5–Dy6	113.765(3)	Dy6- O28	2.3891(2)	Dy4–Dy5–Dy6	86.811(3)
Dy6- O3	2.1709(2)	Dy5–Dy6–Dy7	117.196(3)	Dy7- O3	2.2408(2)	Dy5–Dy6–Dy7	127.448(4)
Dy6- O16	2.3408(2)	Dy6–Dy7–Dy1	121.730(3)	Dy7- O4	2.3710(2)	Dy6–Dy7–Dy1	133.896(4)
Dy6- O17	2.3417(2)	Dy7–Dy1–Dy2	94.928(3)	Dy7- O6	2.3694(2)	Dy7–Dy1–Dy2	82.239(3)

Symmetry codes: (a) 1-x, y, 0.5-z.

Table S3. Relaxation fitting parameters from least-squares fitting of $\chi(\omega)$ data for compound **1**.

T	$\chi_{s,\,tot}$	FR			SR		
		$\Delta\chi_1$	α_1	$\ln(\tau_1\,/\,s)$	$\Delta\chi_2$	α_2	$\ln(\tau_2\,/\,s)$
1.8	0.0213	2.137	0.312	-1.613	44.22	0.623	-7.897
2.6	0.0364	1.836	0.341	-1.639	39.62	0.611	-7.908
3.2	0.0452	1.794	0.329	-1.673	34.10	0.593	-7.914
3.8	0.0526	1.744	0.321	-1.698	30.14	0.580	-7.928
4.4	0.9427	1.675	0.315	-1.720	26.94	0.568	-7.939
5.0	1.4459	1.666	0.288	-1.743	24.02	0.552	-7.943
5.6	1.8360	1.665	0.258	-1.774	21.58	0.535	-7.951
6.2	2.3591	1.848	0.177	-1.775	18.08	0.499	-7.962
6.8	2.6610	1.940	0.131	-1.820	16.32	0.474	-7.970
7.4	2.8398	2.131	0.056	-1.856	14.86	0.448	-7.983
8.0	2.9404	2.207	0.049	-1.941	13.66	0.426	-7.994
8.6	2.9780	2.289	0.034	-2.072	12.64	0.405	-8.043
9.2	2.5424	2.322	0.078	-2.264	11.71	0.385	-8.166
9.8	2.9506	2.251	0.098	-2.521	11.01	0.372	-8.319
10.4	2.8091	2.110	0.095	-2.798	10.50	0.367	-8.492
11.0	2.6412	1.977	0.094	-3.073	10.10	0.368	-8.678
11.6	2.1966	1.752	0.069	-3.616	10.05	0.386	-9.190
12.2	1.8114	1.596	0.056	-4.135	9.83	0.401	-9.742
12.8	1.4268	1.402	0.027	-4.641	9.25	0.421	-10.333
13.4	1.3020	1.284	0.021	-5.127	8.27	0.431	-10.941
14.0	1.5077	1.193	0.010	-5.591	7.82	0.428	-11.533
14.6	2.8852	1.157	0.013	-6.040	6.96	0.409	-12.138
15.2	2.1990	1.097	0.014	-6.450	6.17	0.404	-12.759
15.8	2.6799	1.119	0.032	-6.803	5.86	0.377	-13.335
16.4	3.0993	1.110	0.037	-7.134	5.47	0.347	-13.953
17.0	3.1487	1.125	0.057	-7.486	4.85	0.332	-14.543
17.6	3.4236	1.179	0.066	-7.721	4.51	0.313	-15.132
18.2	3.5129	1.195	0.085	-7.968	5.63	0.271	-15.731
18.8	3.5237	1.197	0.096	-8.214	6.64	0.264	-16.321
19.4	3.5620	1.265	0.100	-8.467	6.71	0.227	-16.939
20.0	3.6917	1.301	0.114	-8.715	7.96	0.110	-17.214

Table S3. Relaxation fitting parameters from least-squares fitting of $\chi(\omega)$ data for compound **2**.

T	χ_T	χ_s	α	$ln(\tau/s)$
1.8	35.10	1.607	0.205	-8.311
2.0	32.10	1.000	0.188	-8.395
2.3	28.97	0.266	0.168	-8.470
2.6	26.00	0.274	0.155	-8.519
2.9	23.96	0.055	0.146	-8.537
3.2	21.54	0.523	0.140	-8.543
3.5	20.10	0.325	0.136	-8.547
3.8	18.49	0.480	0.131	-8.548
4.1	16.74	0.986	0.129	-8.549
4.4	15.09	1.440	0.124	-8.551
4.7	13.47	2.070	0.123	-8.559
5.0	11.85	2.646	0.117	-8.563
5.3	10.23	3.452	0.115	-8.569
5.6	8.50	4.387	0.113	-8.581
5.9	6.67	5.505	0.109	-8.598
6.2	4.83	6.631	0.106	-8.613
6.5	2.98	7.787	0.100	-8.623
6.8	1.21	8.914	0.095	-8.637
7.1	0.08	9.616	0.089	-8.652
7.4	1.39	10.481	0.087	-8.671
7.7	3.18	11.714	0.082	-8.909
8.0	5.51	13.479	0.074	-9.119
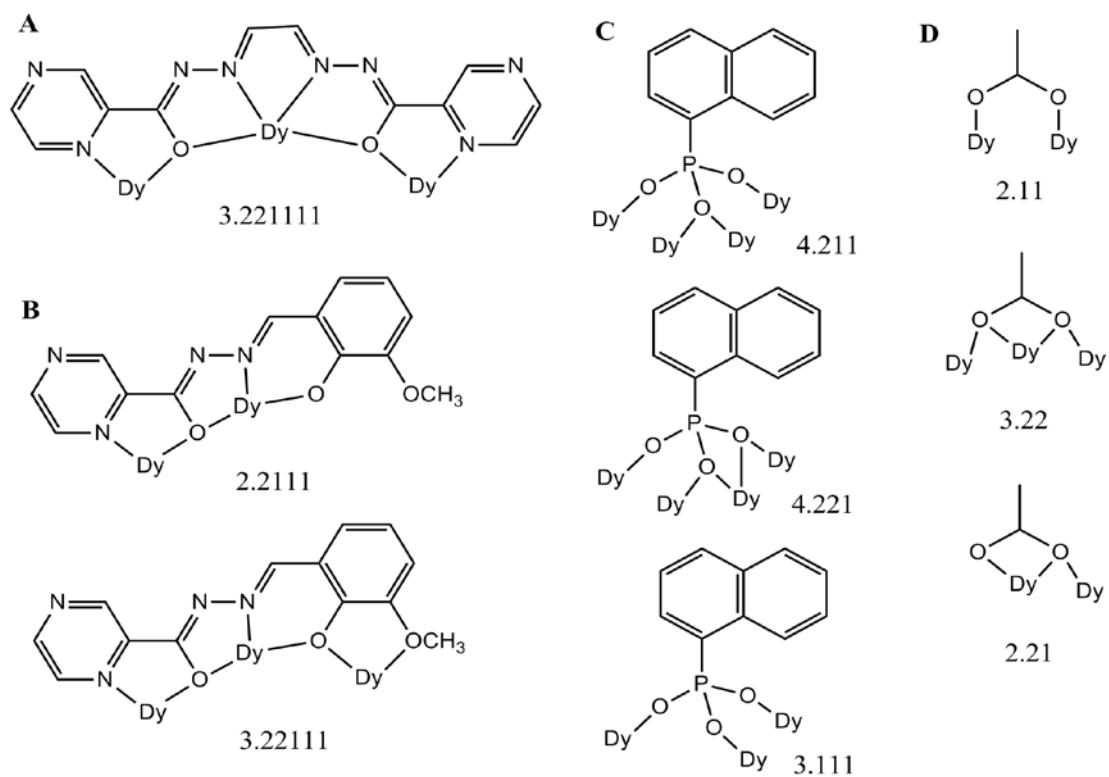
Scheme S1. The coordination modes of EDDC^{2-} (A), opch^{2-} (B), 1-naphthylphosphonate (C) and acetate (D) ligands.
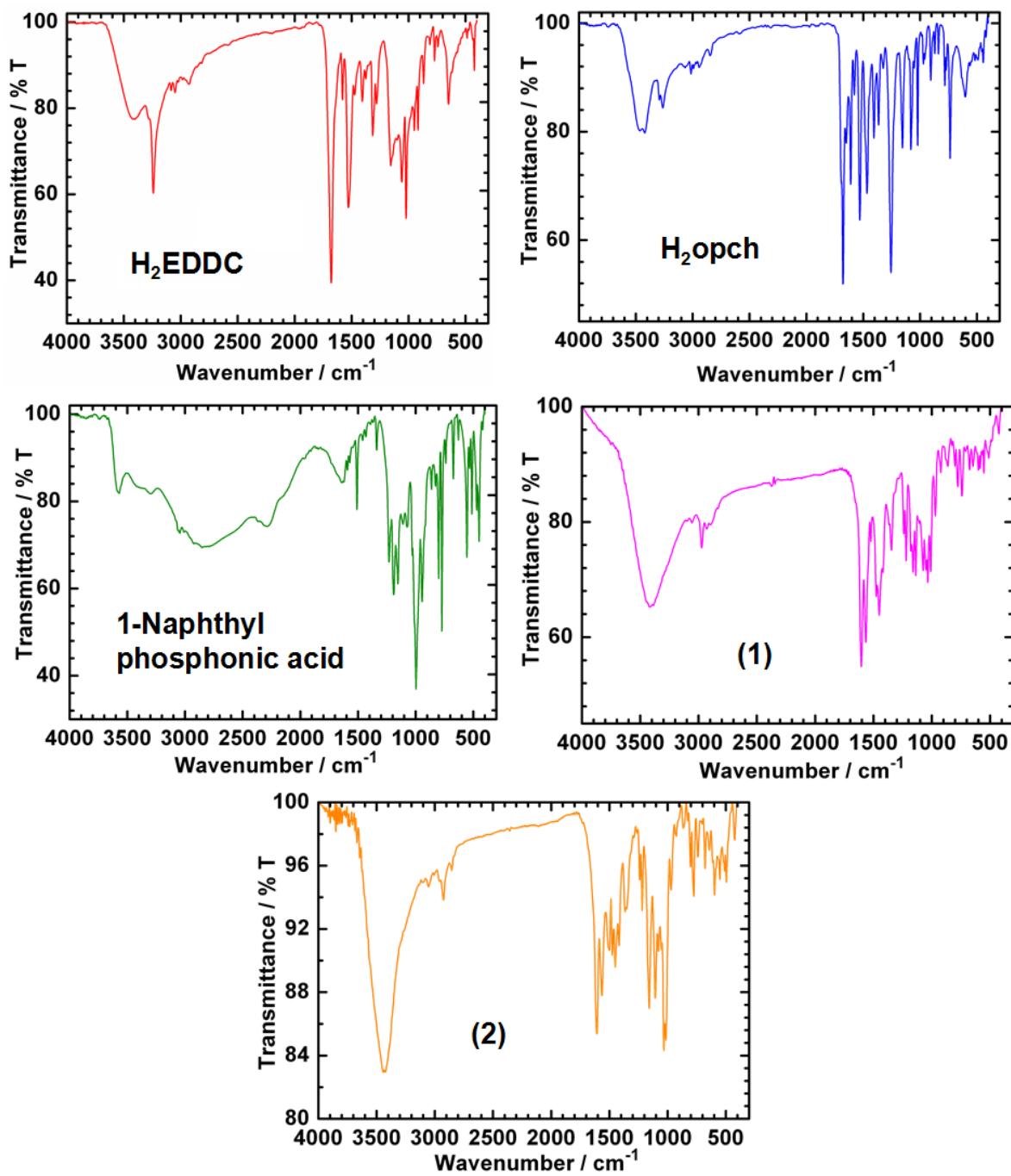
Figure S1. Infrared spectra of **H₂EDDC**, **H₂opch**, **1-naphthyl phosphonic acid**, compounds **1** and **2**.
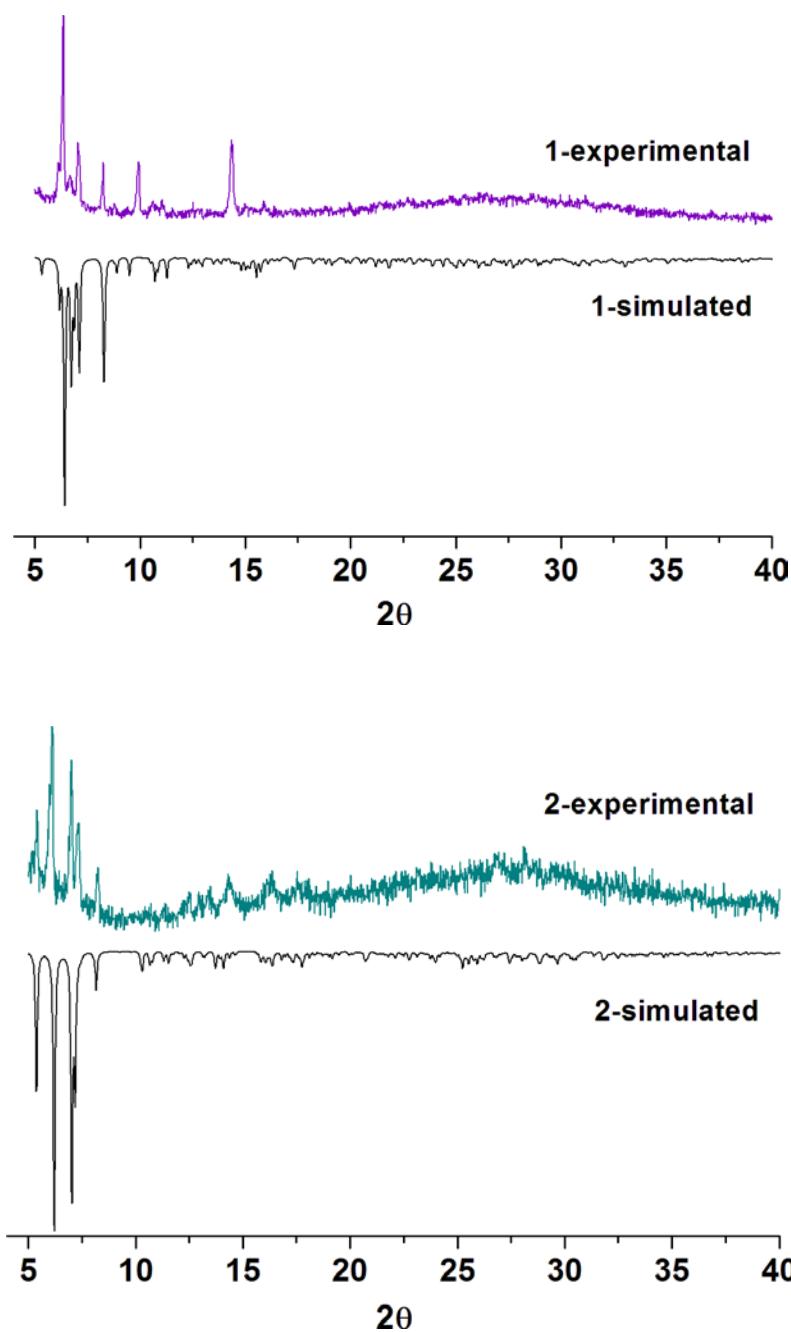
Figure S2. PXRD patterns of compounds **1** and **2**.
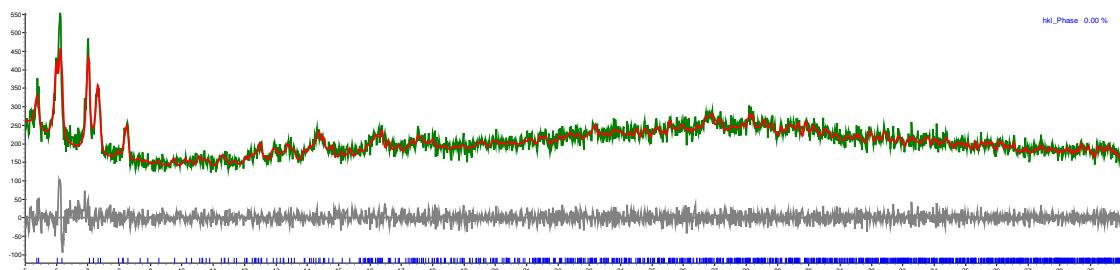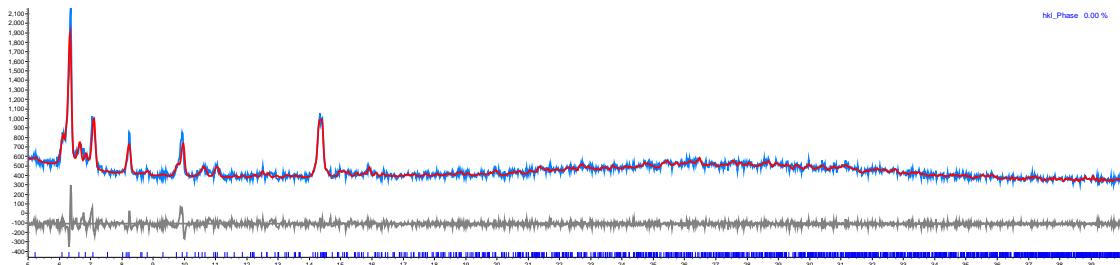
Figure S3. Pawley fit of the fresh sample of compounds **1** (top**)** and **2** (bottom) performed using Topas 4.2 program.

Cell parameters for **1**: $P2_1/c$, a = 14.89 Å, b = 33.79 Å, c = 25.62 Å, β = 103.1°, V = 12560.6 Å^3 (Rwp = 5.37).

Cell parameters for **2**: $C2/c$, a = 22.23 Å, b = 25.04 Å, c = 45.22 Å, β = 102.0°, V = 24626.5 Å^3 (Rwp = 6.85).
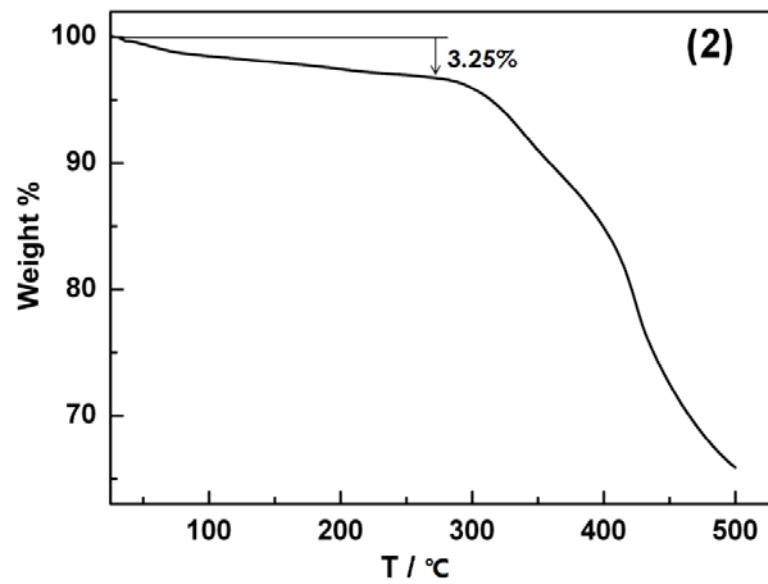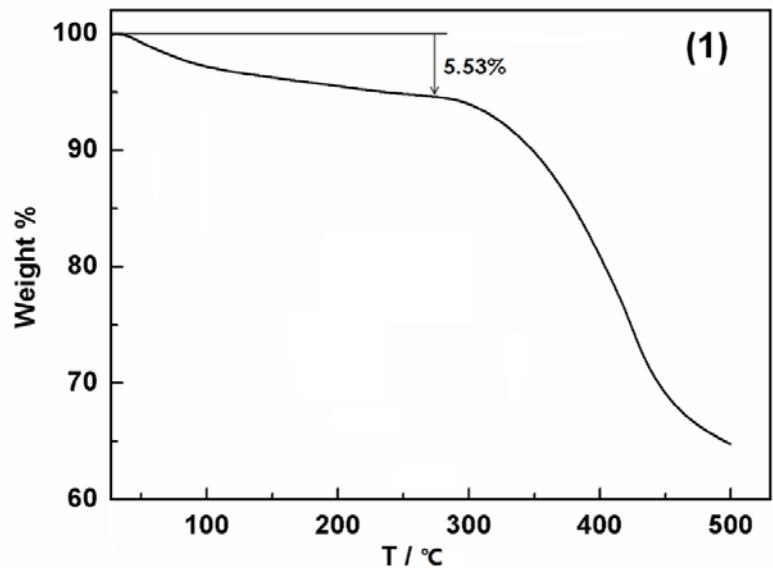
Figure S4. TG curves of compounds **1** (top**)** and **2** (bottom).
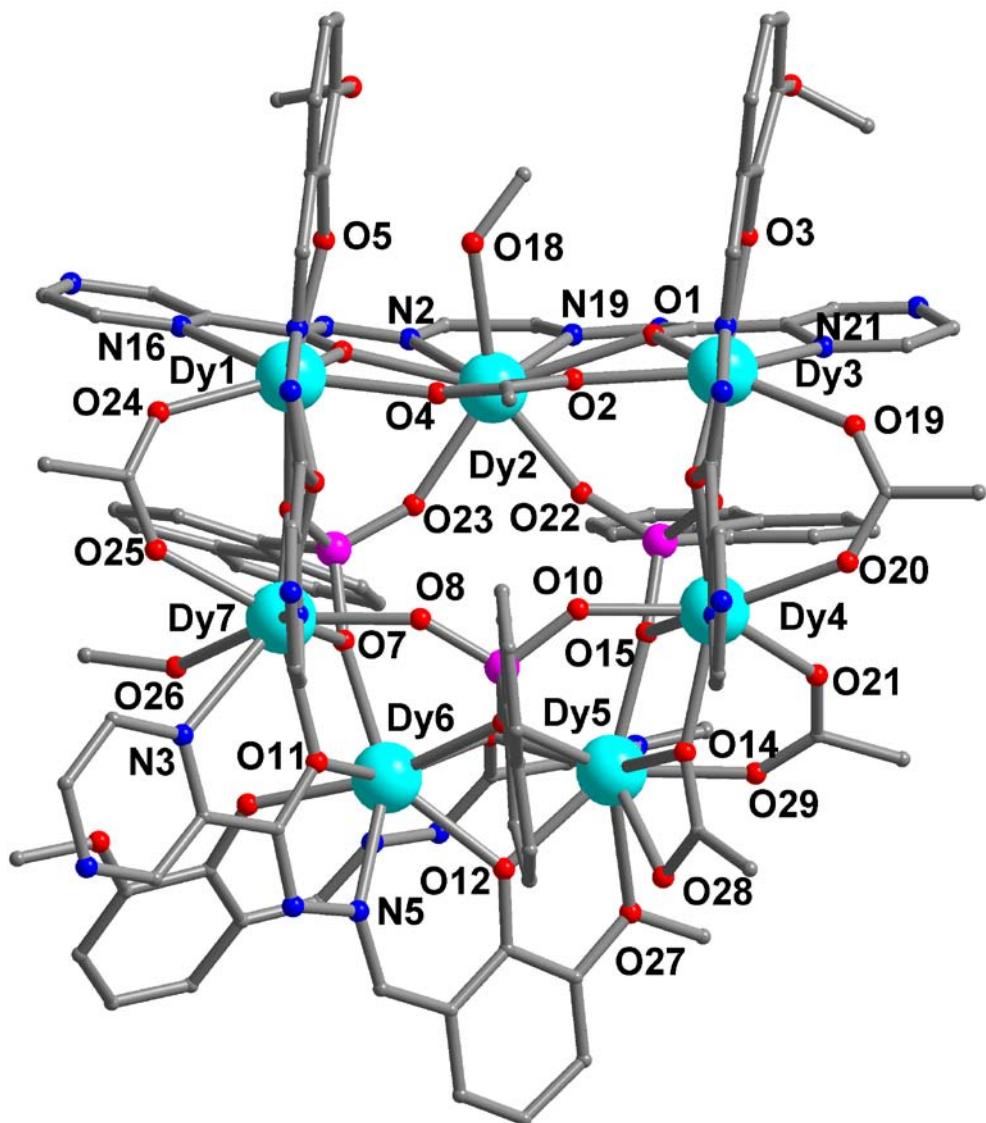
Figure S5. Partially labeled structure of compound **1**. Turquiose Dy, Red O, Blue N, purple P, grey C.
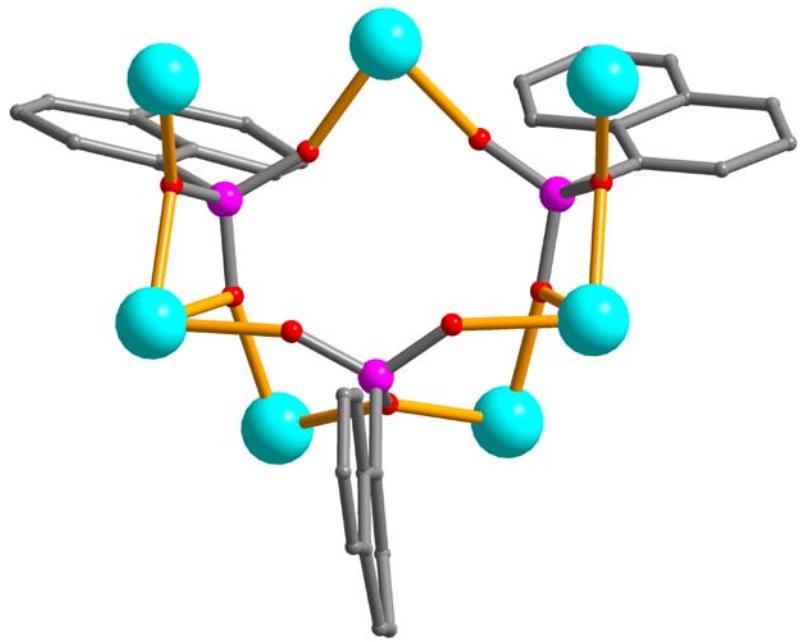
Figure S6. The $[Dy_7(C_{10}H_7PO_3)_3]^{15+}$ core for compound **1**. Turquiose Dy, Red O, Blue N, purple P, grey C.
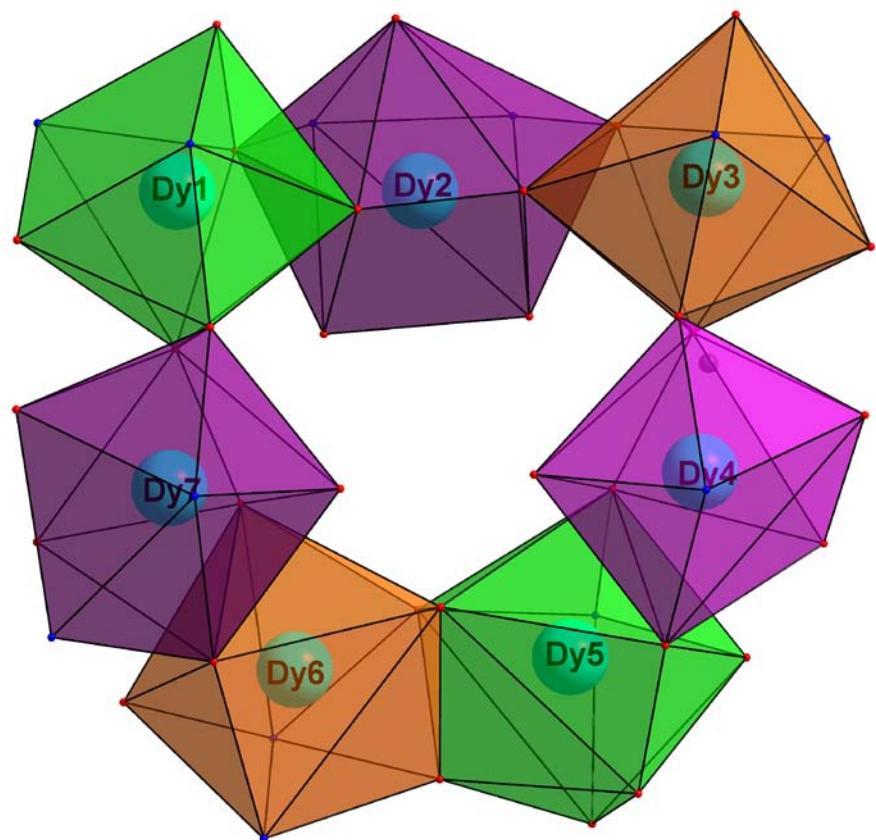
Figure S7. Coordination polyhedra observed for the metal centers in **1**.
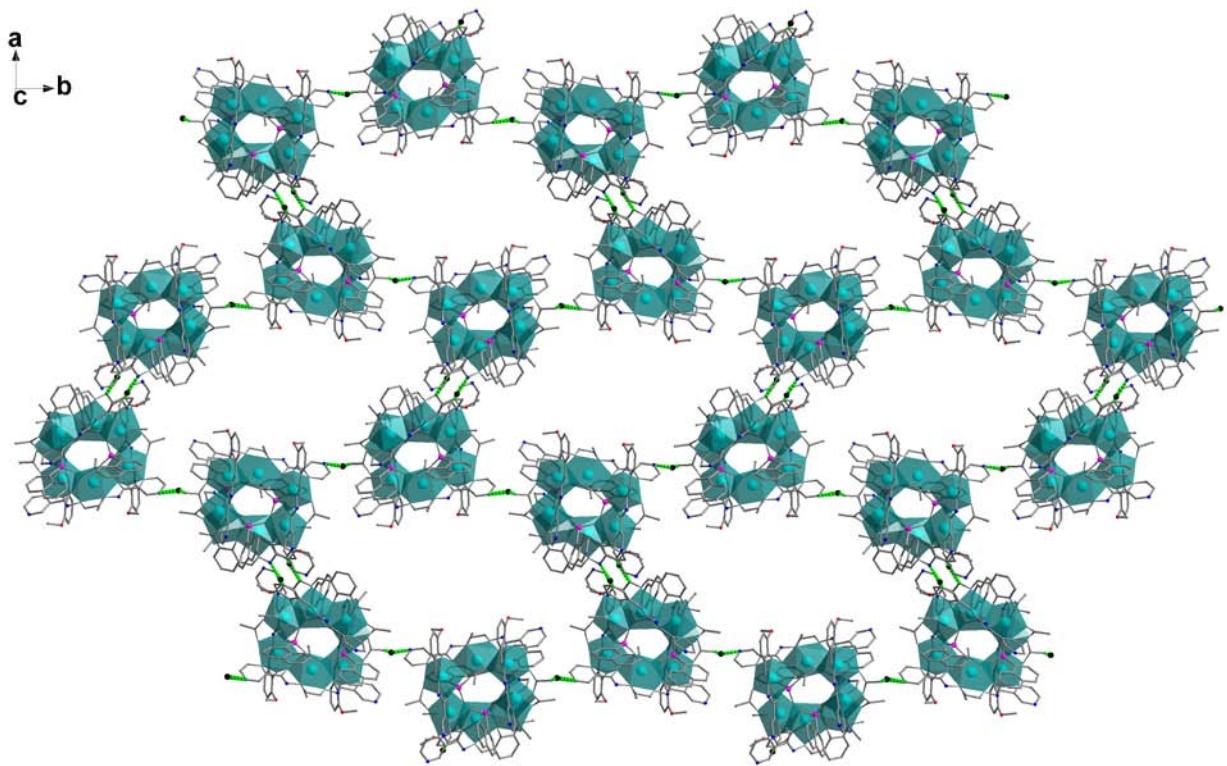
Figure S8. Illustration showing the hydrogen-bonding interactions (light green lines) and the circular hexagon packing arrangement of the molecules in compound **1**. Turquiose Dy, Red O, Blue N, purple P, grey C.
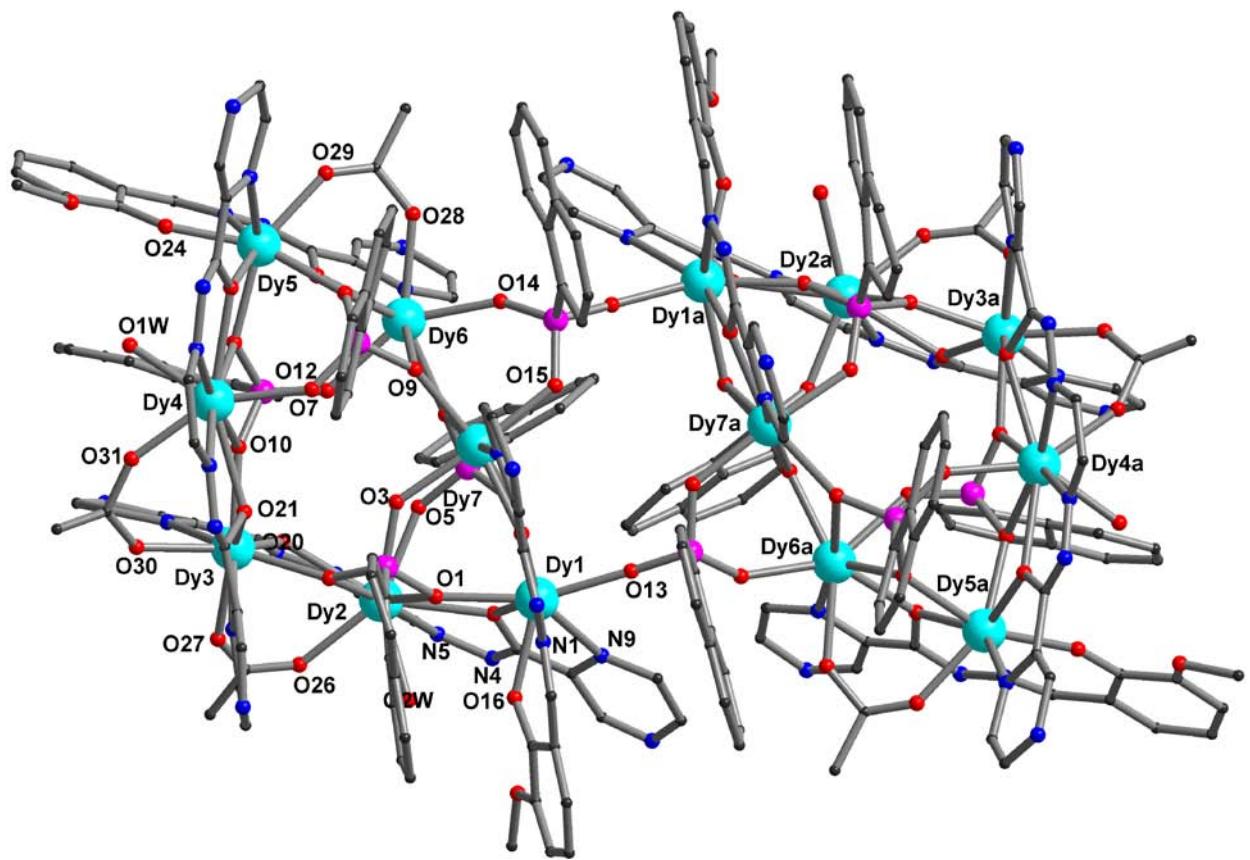
Figure S9. Partially labeled structure of compound **2**. Turquiose Dy, Red O, Blue N, purple P, grey C.
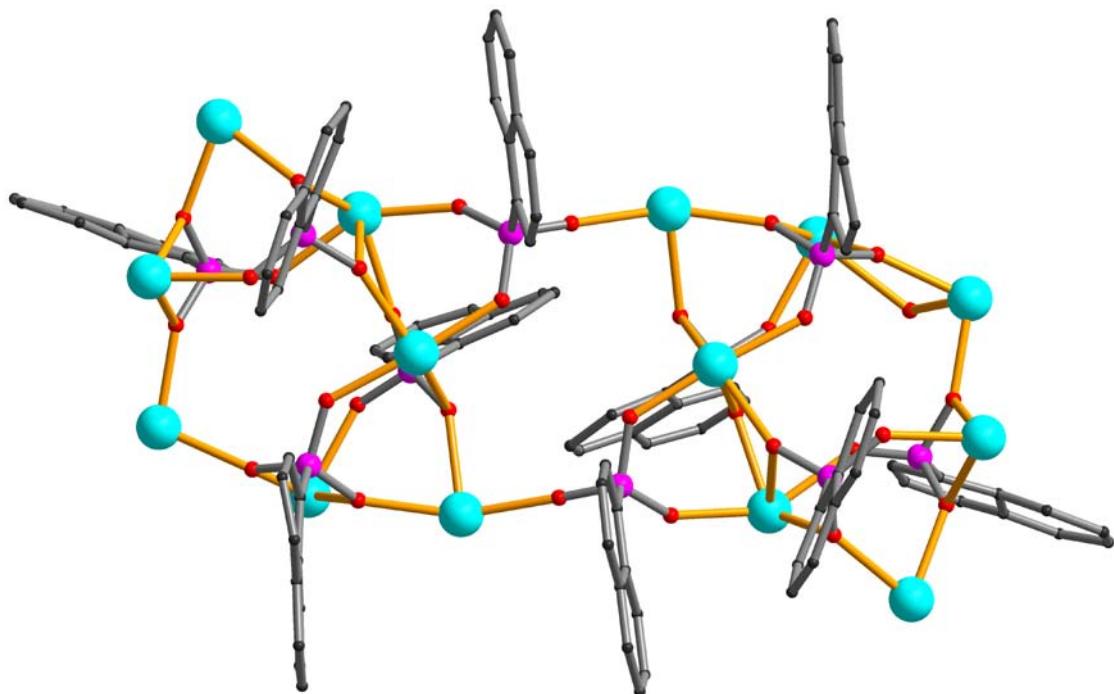
Figure S10. The [Dy$_{14}$(C$_{10}$H$_7$-PO$_3$)$_{10}$]$^{22+}$ core for compound **2**. Turquiose Dy, Red O, Blue N, purple P, grey C.
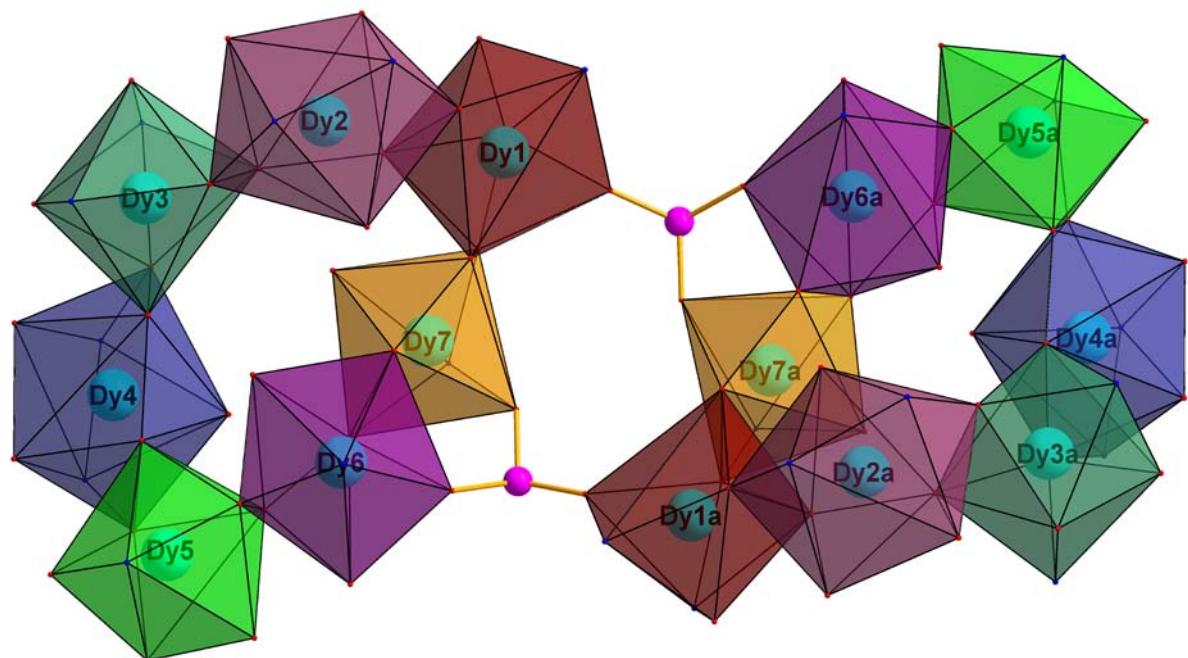
Figure S11. Coordination polyhedra observed for the metal center in **2**.
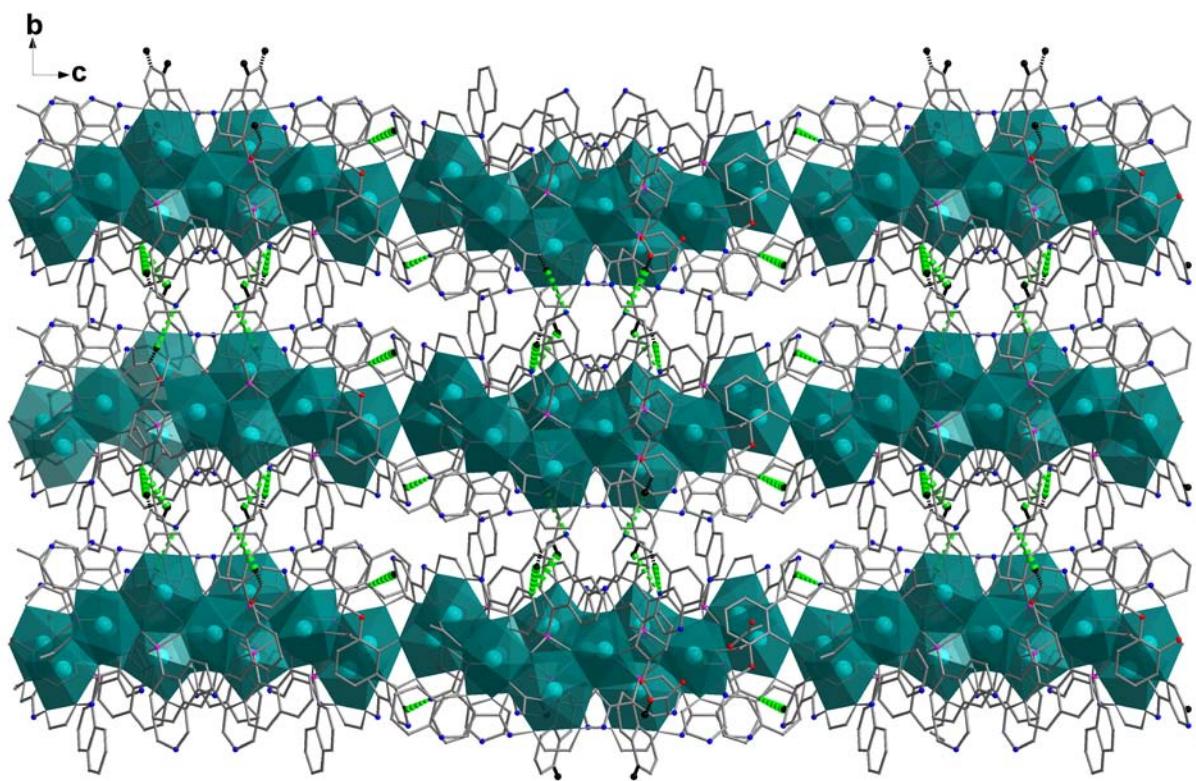
**Figure S12.** 3D hydrogen-bonded supramolecular structure of compound **2**. Turquiose Dy, Red O, Blue N, purple P, grey C.
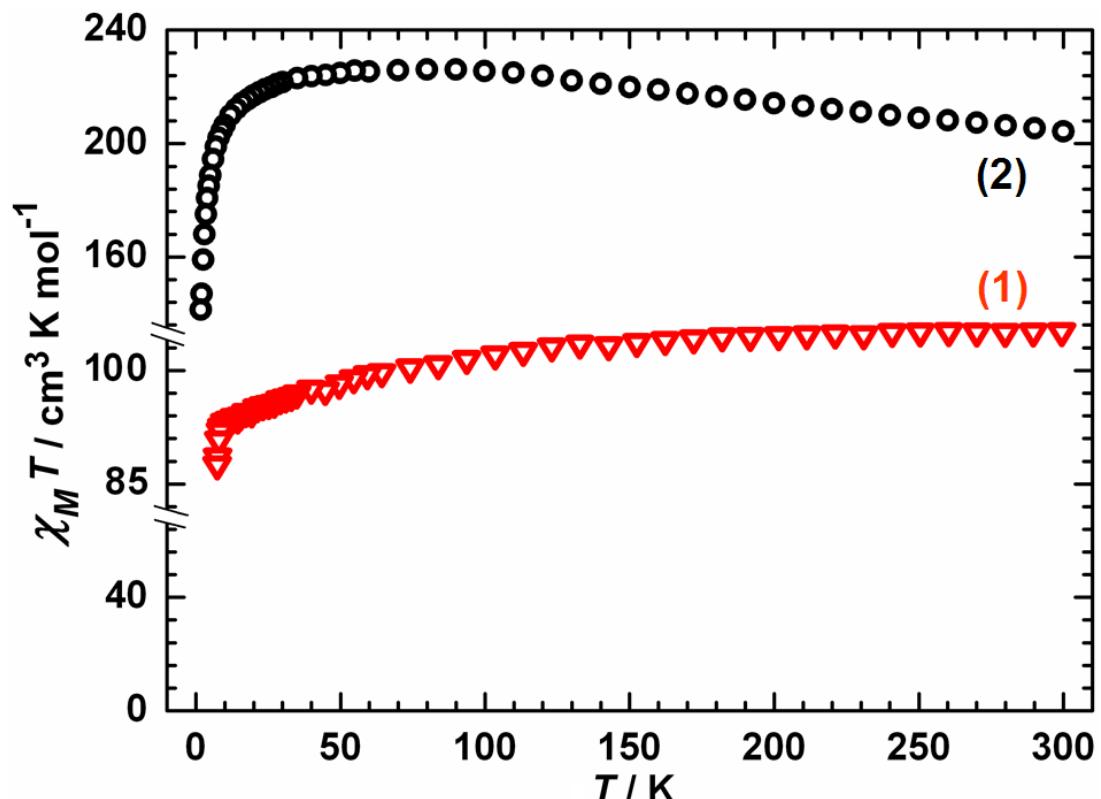
Figure S13. Temperature dependence of the $\chi_M T$ product at 1 kOe for **1** (bottom) and **2** (top).
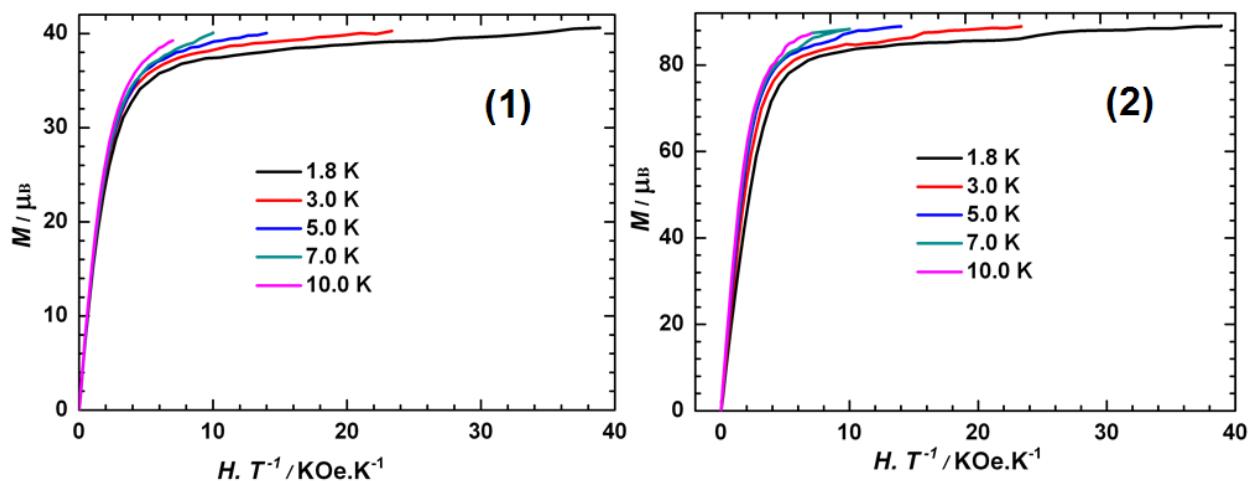
Figure S14. *M vs. H/T* plot at different temperatures below 10.0 K for **1** (left) and **2** (right).
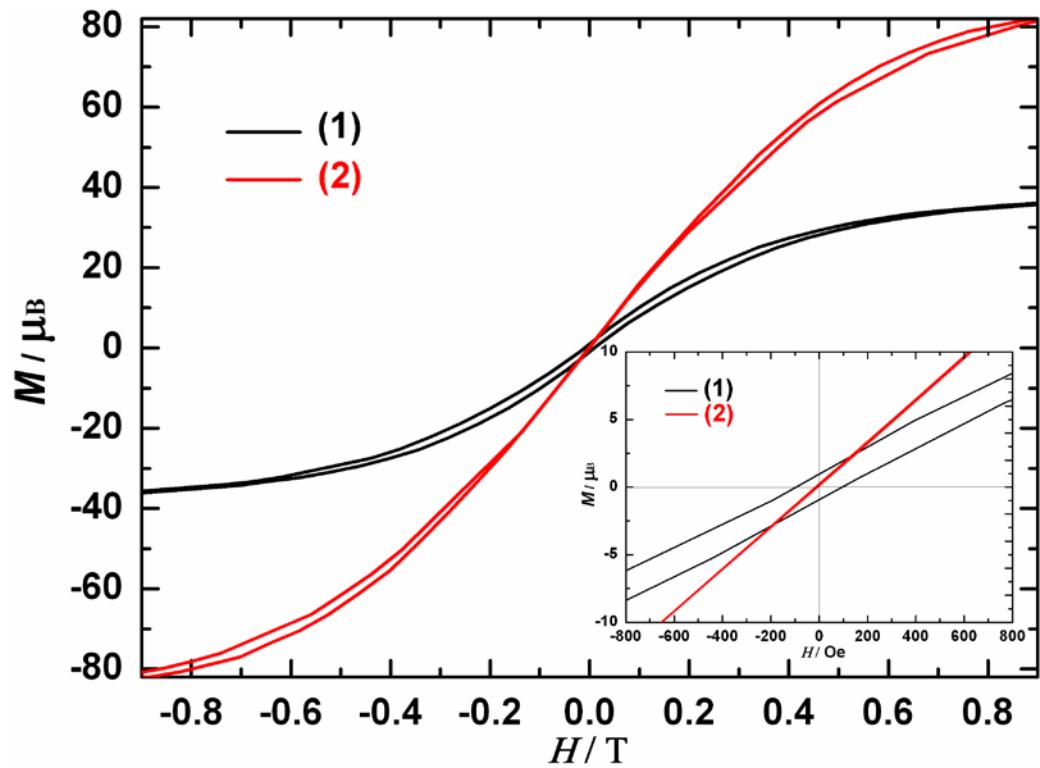
Figure S15. The hysteresis loops of compounds **1** (black lines) and **2** (red lines) at 1.8 K. Sweep rate: 600 Oe s^{-1}.
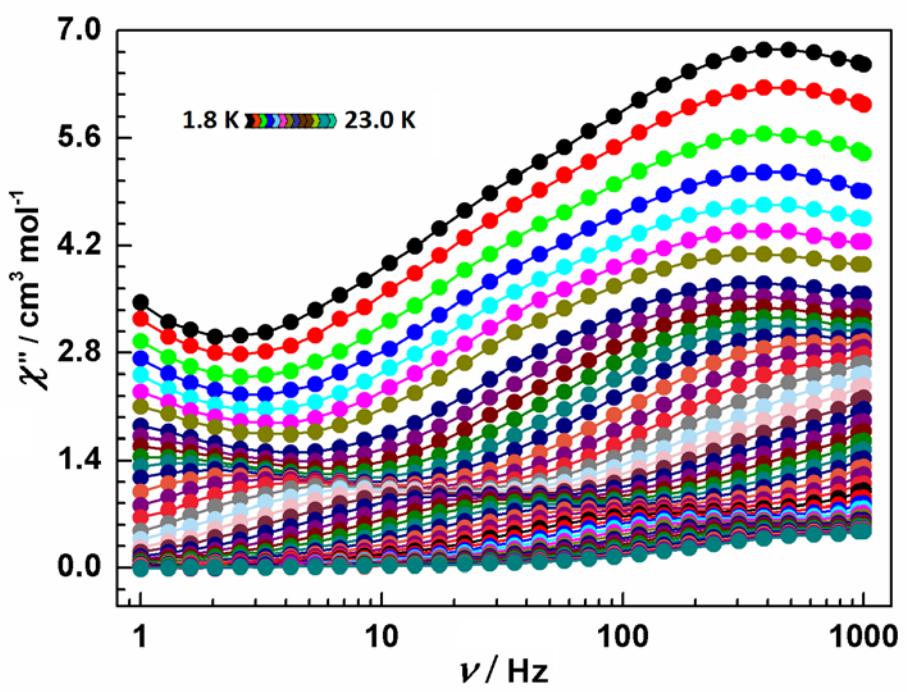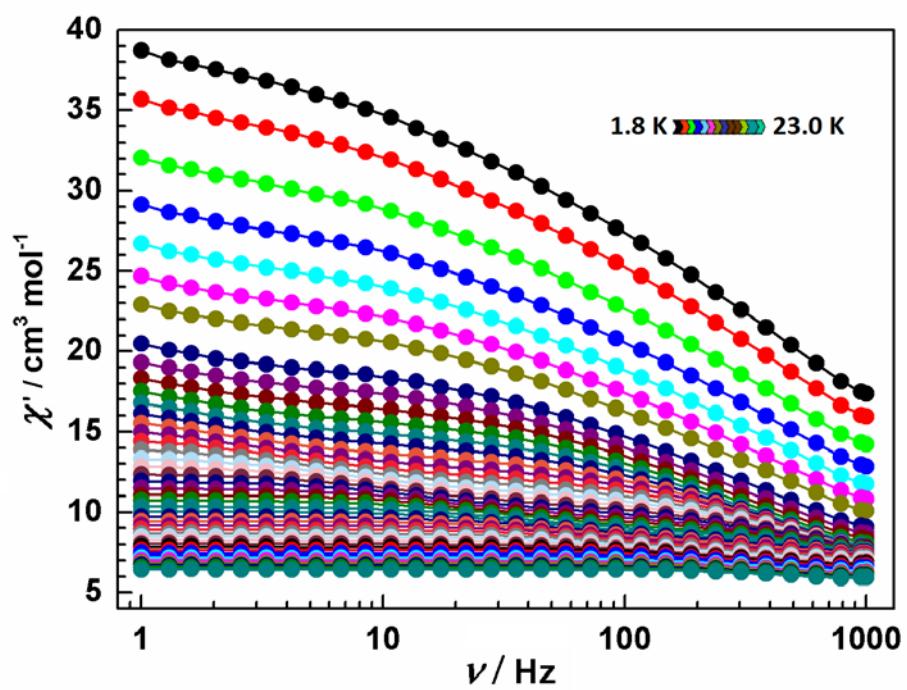
Figure S16. Frequency dependence of the χ' and χ'' products, *ac* susceptibility under zero-dc field for compound **1**.
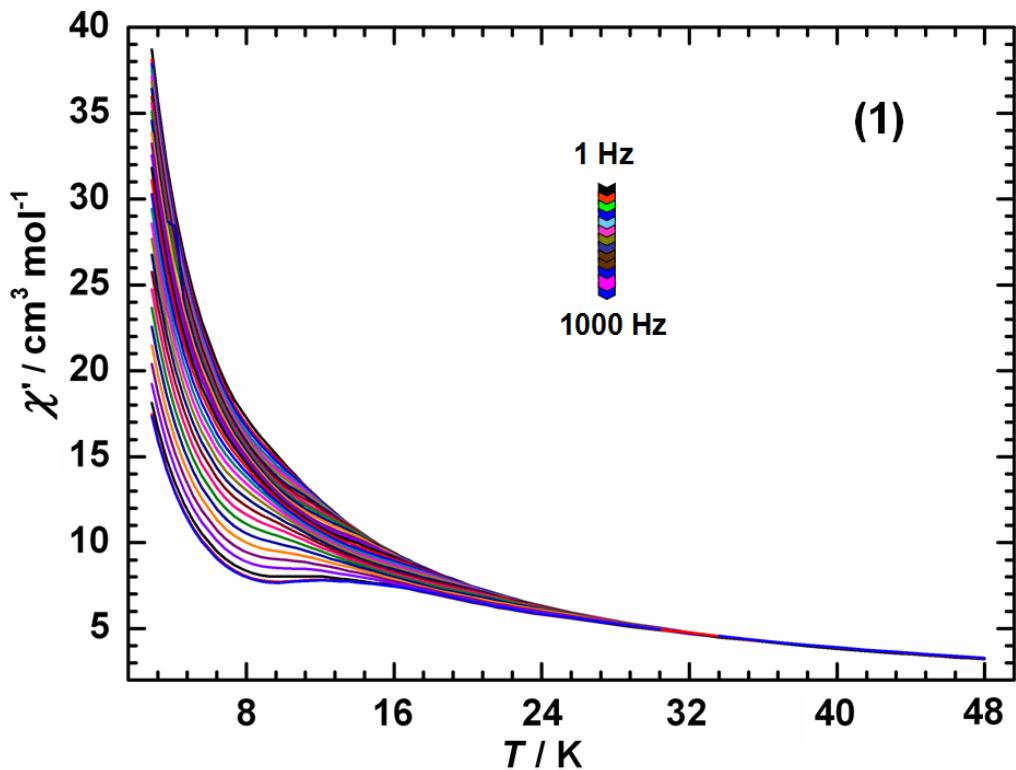
Figure S17. Temperature dependence of the χ' product, *ac* susceptibility under zero-dc field for compound **1**.
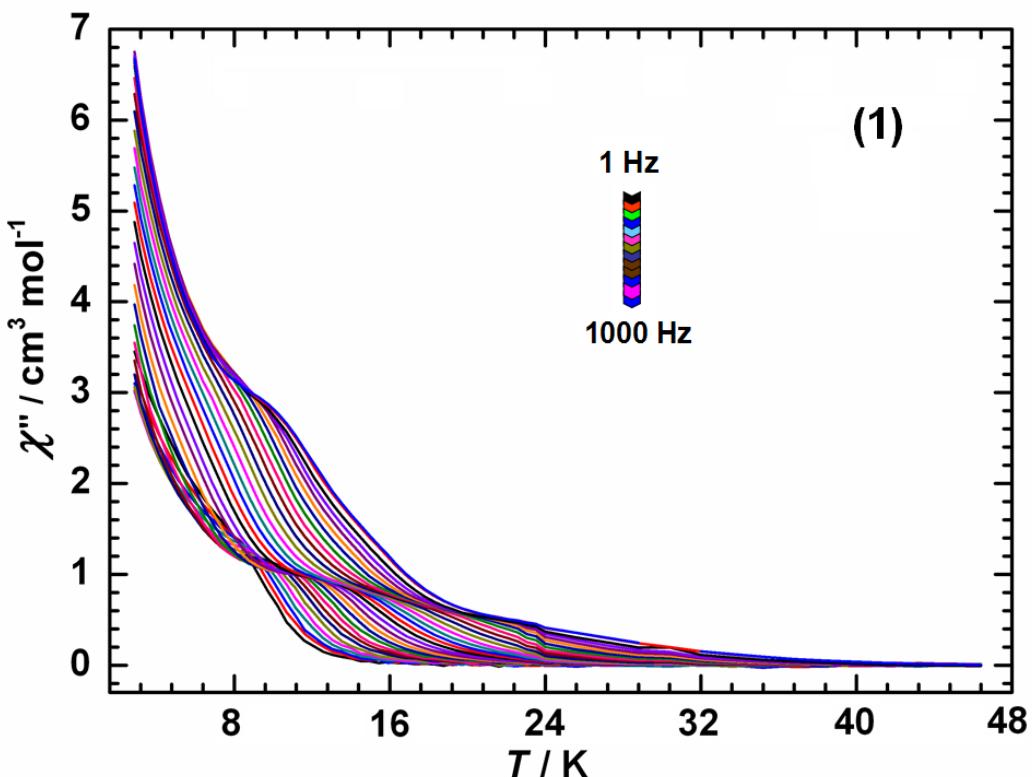

Figure S18. Temperature dependence of the χ'' product, *ac* susceptibility under zero-dc field for compound **1**.
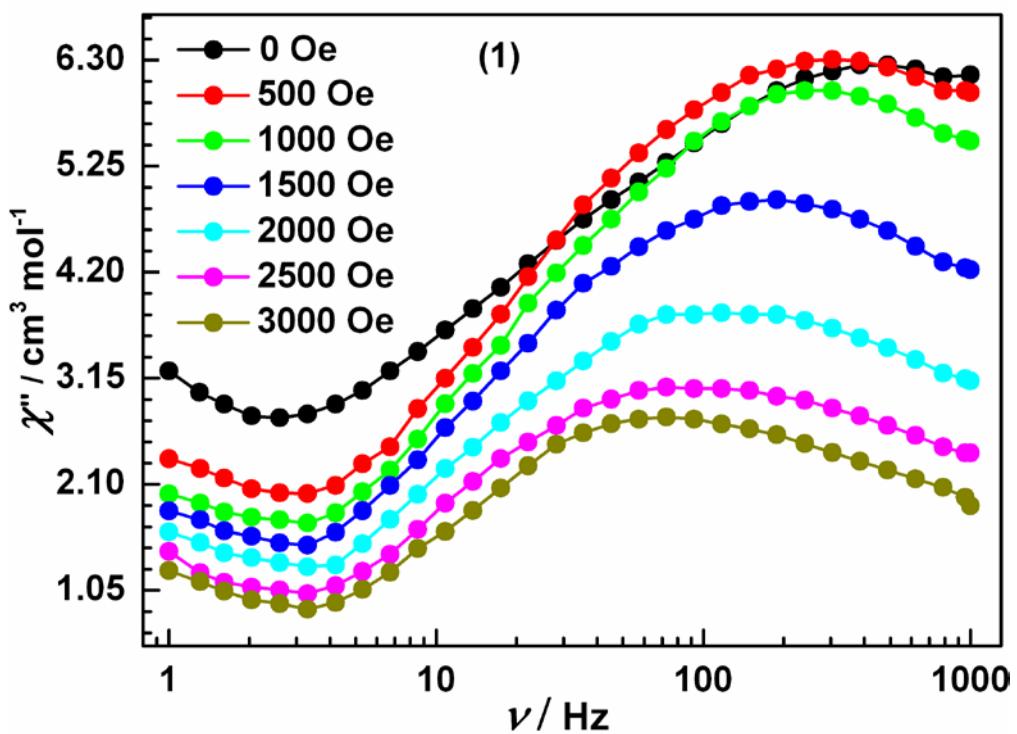
Figure S19. The out-of-phase (χ'') ac susceptibility as a function of the dc applied field measured at 2.0 K for compound **1**.
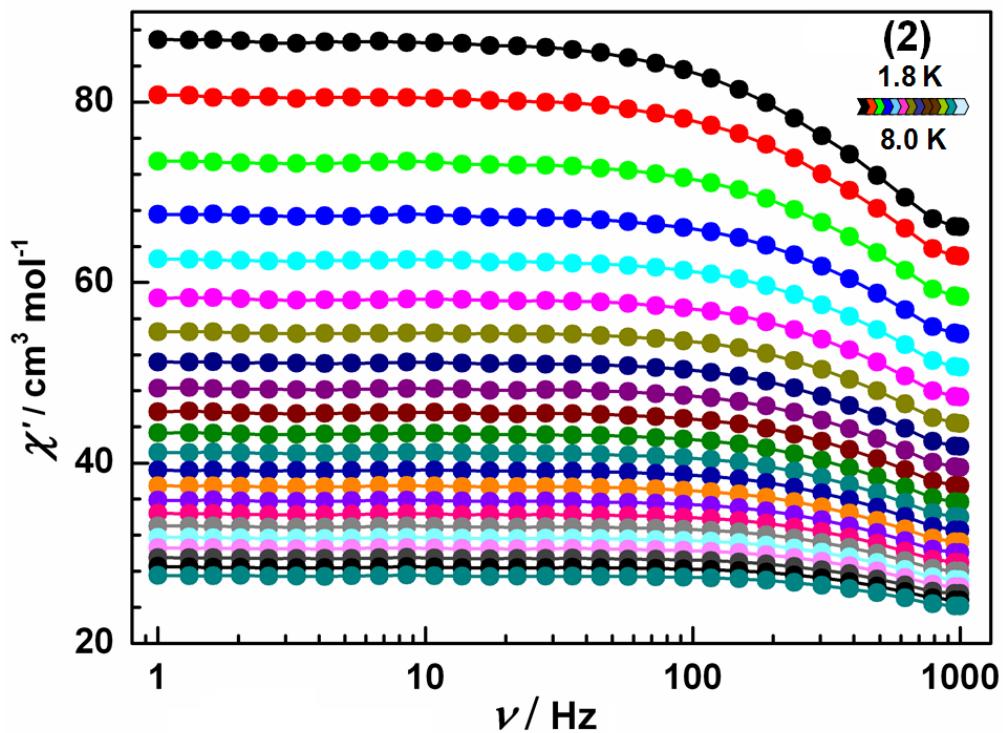

Figure S20. Frequency dependence of the χ' product, *ac* susceptibility under zero-dc field for compound **2**.
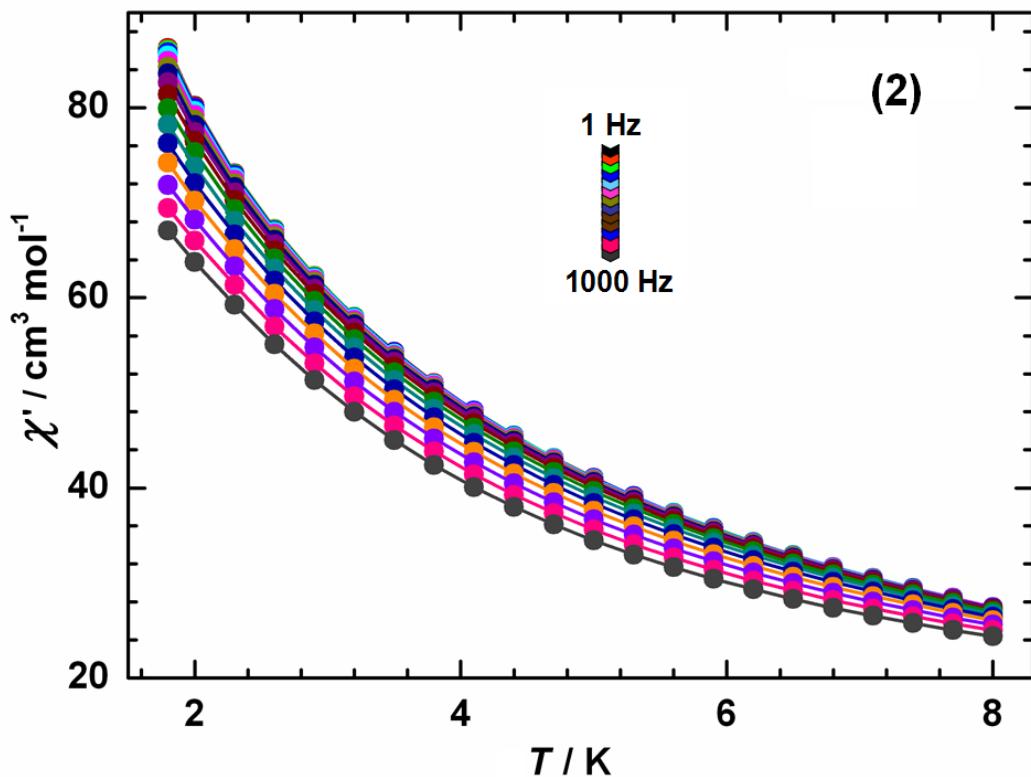
Figure S21. Temperature dependence of the χ' product, *ac* susceptibility under zero-dc field for compound **2**.
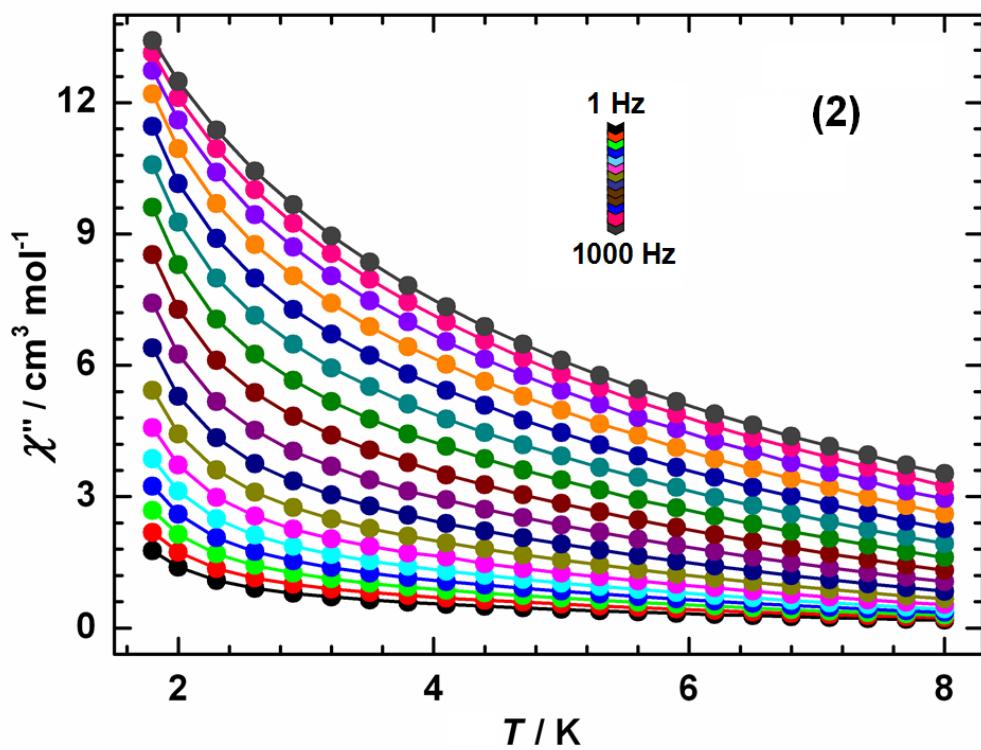
Figure S22. Temperature dependence of the χ'' product, *ac* susceptibility under zero-dc field for compound **2**.
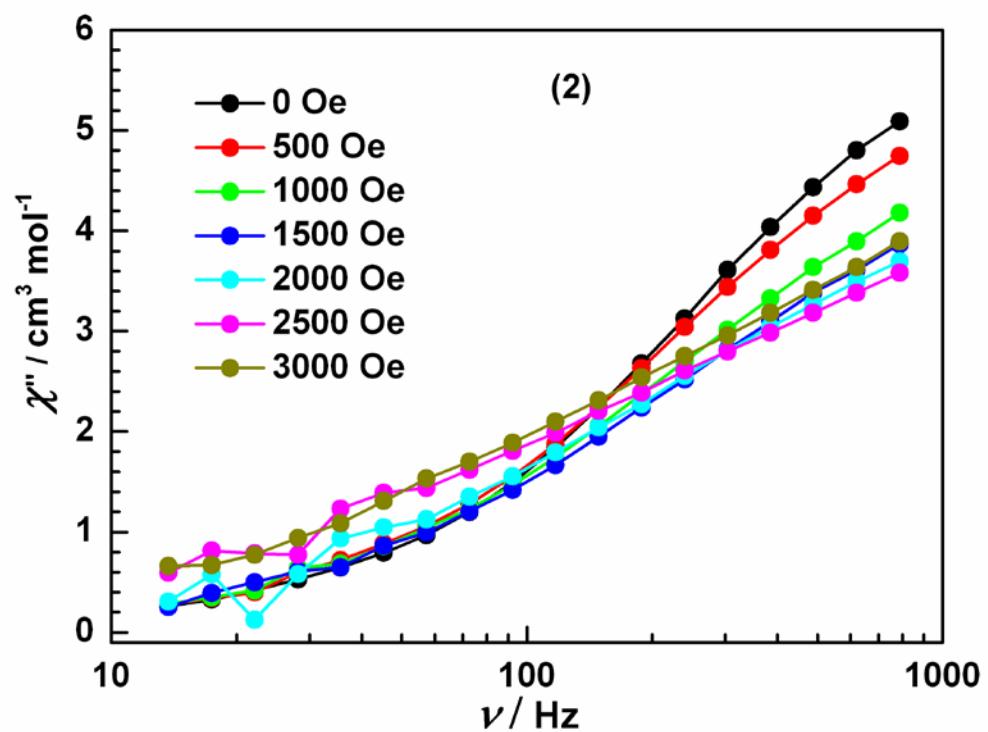
Figure S23. The out-of-phase (χ'') ac susceptibility as a function of the dc applied field measured at 2.0 K for compound **2**.