

Supporting Information

Enlarging the ring by incorporating phosphonate ligand: from the cyclic hexanuclear to octanuclear dysprosium clusters

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Experimental Section

Synthetic procedures

1-naphthyl phosphonic 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 (*N',N''E,N',N''E*)-*N',N''*-(ethane-1,2-diylidene)dipyrazine-2-carbohydrazide

Pyrazine-2-carbohydrazide (10 mmol, 1.382 g) was suspended together with glyoxal (5 mmol, 0.291 g) in methanol (50 mL), and the resulting mixture was stirred at the room temperature overnight. The pure white solid was collected by filtration (yield 1.45 g (87%). 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 the compound 1

A mixture of $Dy(OAc)_3 \cdot 4H_2O$ (61.8 mg, 0.15 mmol) and H_2EDDC (29.8 mg, 0.10 mmol) in 20 mL CH_3OH was stirred with triethylamine (0.30 mmol) for 24 h. Then the mixture was transferred to a 25 mL glass ware and sealed. The glass ware was kept in a vacuum drying oven and the reaction mixture was heated at 100 °C. Pale yellow single crystals, suitable for X-ray diffraction analysis, were formed after 16 h as single-phase product. Yield: 35 mg, (46%, based on Dy). Elemental analysis (%) calcd for $C_{52}H_{64}Dy_6N_{16}O_{34}$: C, 25.67, H, 2.65, N, 9.22: found C, 26.00, H, 2.94, N, 10.80. IR

(KBr, cm^{-1}): 3422(w), 2361(m), 1681(w), 1553(vs), 1455(s), 1355(w), 1159(w), 1108(m), 1056(m), 1020(w), 938(w), 861(m), 782(w), 678(s), 649(w), 613(w), 478(m), 425(m).

Synthesis of the compound 2

A mixture of $\text{Dy}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ (61.8 mg, 0.15 mmol) and H_2EDDC (29.8 mg, 0.10 mmol) in 20 mL CH_3OH was stirred with triethylamine (0.30 mmol). After 12 h, $\text{C}_{10}\text{H}_7\text{PO}_3\text{H}_2$ (20.8 mg, 0.10 mmol) was added to the solution. Then the mixture was stirred for another 12 h, and the resulting solution was transferred to a 25 mL glass ware and sealed. The glass ware was kept in a vacuum drying oven and the reaction mixture was heated at 100 °C. Dark yellow single crystals, suitable for X-ray diffraction analysis, were formed after 48 h as single-phase product. Yield: 27 mg (35% based on Dy). Elemental analysis (%) calcd for $\text{C}_{104}\text{H}_{124}\text{Dy}_8\text{N}_{32}\text{O}_{52}\text{P}_4$: C, 30.62, H, 3.07, N, 10.99: found C, 30.20, H, 3.28, N, 10.46. IR (KBr, cm^{-1}): 3419(m), 1601(w), 1553(vs), 1499(s), 1433(s), 1365(w), 1283(m), 1161(s), 1102(w), 1053(w), 1011(vs), 976(m), 932(m), 855(m), 785(w), 681(w), 643(w), 611(w), 550(w), 510(w), 421(w).

Single-Crystal Structure Determination

Single crystals of dimensions $0.25 \times 0.20 \times 0.21 \text{ mm}^3$ for **1** and $0.25 \times 0.27 \times 0.31 \text{ mm}^3$ for **2** were mounted on a glass rod. The crystal data were collected on a Bruker SMART APEX II diffractometer using monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 SHELXL.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.

Physical measurements

Elemental analyses for C, N and H were determined with a Perkin Elmer 240C elemental analyzer. Infrared spectra were recorded on a VECTOR 22 spectrometer with KBr pellets in the range of 400-4000 cm^{-1} . 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:

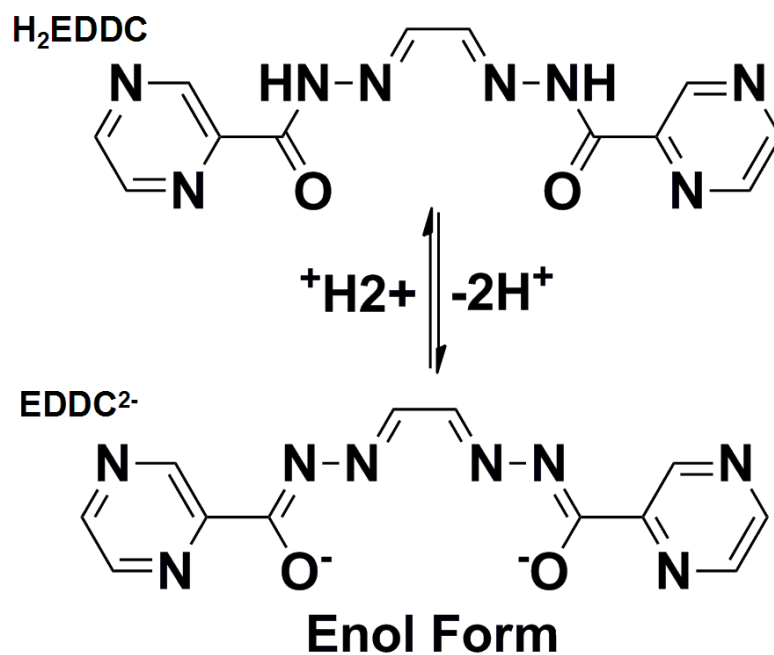
1. I. P. Beletskaya, M. A. Kazankova, *Russian J. Org. Chem.*, 2002, **38**, 1391.
2. SHELXTL (version 5.0), Reference Manual, Siemens Industrial Automation, Analytical Instruments Madison, WI, 1995.
3. Olivier Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.

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

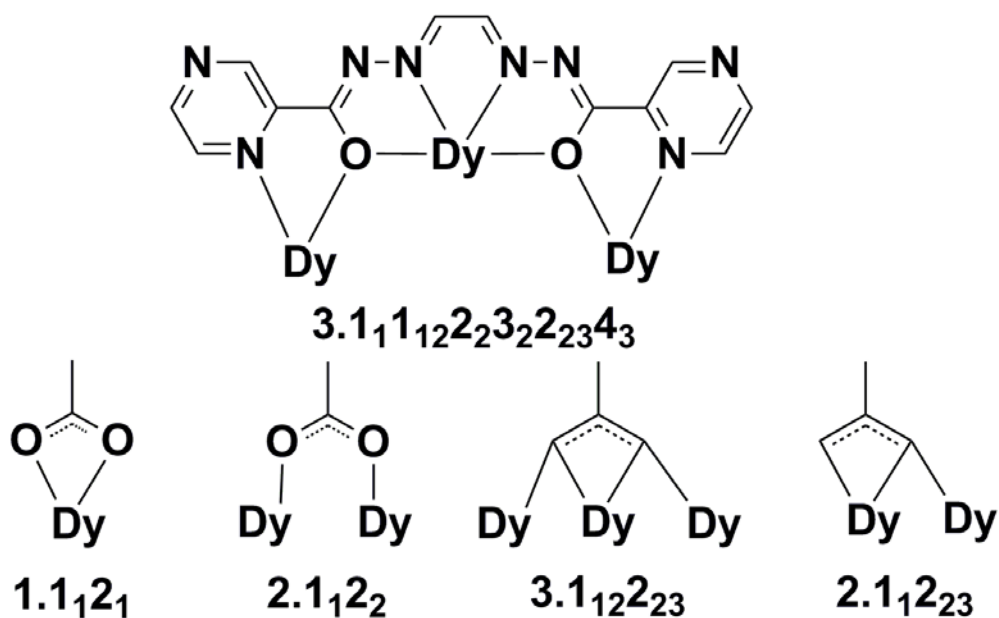
Complex	1	2
mol wt	2560.28	3917.23
<i>T</i> [K]	123 (2)	123(2)
λ [Å]	0.71073	0.71073
crystal syst	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
<i>a</i> [Å]	14.5013(16)	16.9559(18)
<i>b</i> [Å]	20.839(2)	17.1330(19)
<i>c</i> [Å]	14.9042(16)	24.352(3)
α [deg]	90	100.285(2)
β [deg]	118.255(1)	92.256(2)
γ [deg]	90	90.698(2)
<i>V</i> [Å ³]	3967.3(8)	6953.9(13)
<i>Z</i>	2	2
ρ [g cm ⁻³]	2.143	1.883
2θ [deg]	0.994 – 25.998	0.976 – 27.515
GOF	1.006	1.071
<i>R</i> 1	0.0424	0.0773
<i>wR</i> 2	0.0868	0.1453

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

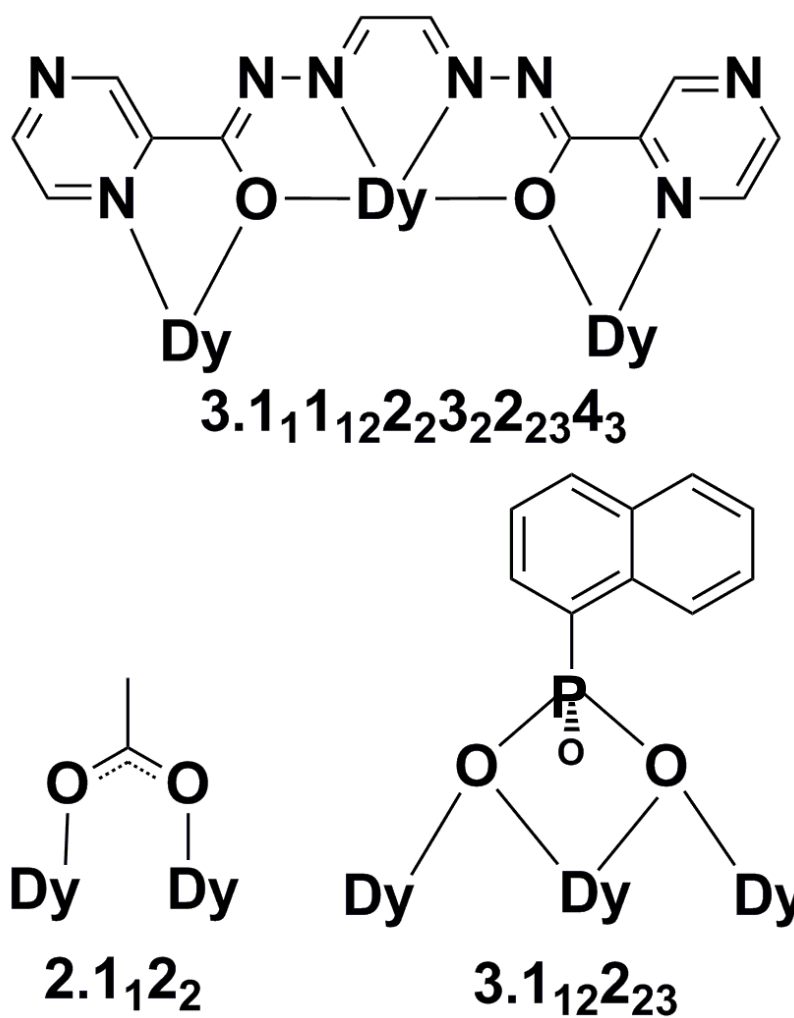
NO.	1	NO.	2	NO.	2	NO.	2
Dy1- O1	2.4430(2)	Dy1- O6	2.3240(2)	Dy5- O36	2.2716(2)	Dy1···Dy5	9.7673(10)
Dy1- O5	2.4045(2)	Dy1- O7	2.3453(2)	Dy5- N9	2.5644(2)	Dy1···Dy7	6.8976(5)
Dy1- O6	2.5573(2)	Dy1- O21	2.3494(2)	Dy5- N32	2.5899(2)	Dy1···Dy8	4.0502(3)
Dy1- O7	2.4721(2)	Dy1- O26	2.3692(2)	Dy6- O3	2.2607(2)	Dy2···Dy6	7.7703(6)
Dy1- O8	2.4036(2)	Dy1- O29	2.2712(2)	Dy6- O16	2.3207(2)	Dy3···Dy7	9.7793(10)
Dy1- O9	2.3643(2)	Dy1- O39	2.2428(2)	Dy6- O17	2.3085(2)	Dy4···Dy8	7.8299(6)
Dy1- O13	2.3591(2)	Dy1- N1	2.5708(2)	Dy6- O23	2.5850(2)	Dy1–O21–Dy2	108.777(6)
Dy1- O16a	2.2883(2)	Dy1- N17	2.5651(2)	Dy6- O24	2.6329(3)	Dy1–O29–Dy2	116.639(6)
Dy1- N1	2.5298(2)	Dy2- O1	2.2541(2)	Dy6- O36	2.4836(3)	Dy2–O22–Dy3	109.344(5)
Dy2- O2	2.4488(2)	Dy2- O8	2.3141(2)	Dy6- O37	2.4938(2)	Dy2–O30–Dy3	117.392(5)
Dy2- O6	2.3276(2)	Dy2- O9	2.3081(2)	Dy6- N12	2.5924(2)	Dy3–O27–Dy4	108.830(5)
Dy2- O10	2.3514(2)	Dy2- O21	2.6277(2)	Dy6- N13	2.5725(3)	Dy3–O33–Dy4	116.494(6)
Dy2- O11	2.4343(2)	Dy2- O22	2.6186(3)	Dy7- O18	2.3230(2)	Dy4–O28–Dy5	108.139(5)
Dy2- O12	2.4553(2)	Dy2- O29	2.4856(2)	Dy7- O19	2.3295(2)	Dy4–O34–Dy5	115.404(6)
Dy2- O13	2.6147(2)	Dy2- O30	2.5094(2)	Dy7- O24	2.3752(2)	Dy5–O23–Dy6	109.399(5)
Dy2- O14	2.3997(2)	Dy2- N4	2.6027(3)	Dy7- O25	2.3995(3)	Dy5–O36–Dy6	116.976(5)
Dy2- O15	2.2755(2)	Dy2- N5	2.5920(2)	Dy7- O37	2.2808(2)	Dy6–O24–Dy7	108.834(5)
Dy2- N8	2.5398(2)	Dy3- O10	2.3299(2)	Dy7- O40	2.2654(2)	Dy6–O37–Dy7	117.147(6)
Dy3- O1	2.4466(3)	Dy3- O11	2.3510(2)	Dy7- N15	2.5728(2)	Dy7–O25–Dy8	108.653(5)
Dy3- O2	2.4643(2)	Dy3- O22	2.3636(3)	Dy7- N23	2.5553(2)	Dy7–O40–Dy8	116.646(6)
Dy3- O3	2.3612(2)	Dy3- O27	2.3489(2)	Dy8- O4	2.2576(2)	Dy1–O26–Dy8	108.360(5)
Dy3- O4	2.3285(2)	Dy3- O30	2.2485(2)	Dy8- O5	2.2896(2)	Dy1–O39–Dy8	117.034(6)
Dy3- O9	2.5698(2)	Dy3- O33	2.2684(2)	Dy8- O20	2.6175(2)	Dy1–Dy2–Dy3	116.837(4)
Dy3- O10	2.5359(2)	Dy3- N7	2.6021(2)	Dy8- O25	2.5951(2)	Dy1–Dy3–Dy2	31.503(2)
Dy3- O1w	2.3325(2)	Dy3- N25	2.5564(2)	Dy8- O26	2.6224(3)	Dy2–Dy1–Dy3	31.569(2)
Dy3- N4	2.5361(2)	Dy4- O2	2.2682(2)	Dy8- O39	2.5039(2)	Dy3–Dy4–Dy5	117.456(4)
Dy3- N5	2.5528(2)	Dy4- O12	2.3041(2)	Dy8- O40	2.5027(2)	Dy3–Dy5–Dy4	31.229(2)
Dy1···Dy2	6.8718(7)	Dy4- O13	2.3083(2)	Dy8- N20	2.6175(3)	Dy4–Dy3–Dy5	31.315(2)
Dy1···Dy3	4.1770(5)	Dy4- O27	2.6206(2)	Dy8- N21	2.5955(2)	Dy5–Dy6–Dy7	116.383(4)
Dy2···Dy3	4.1714(3)	Dy4- O28	2.6299(3)	Dy1···Dy2	4.0495(3)	Dy5–Dy7–Dy6	31.714(2)
Dy1–Dy2–Dy3	34.627(2)	Dy4- O33	2.4861(2)	Dy2···Dy3	4.0675(3)	Dy6–Dy5–Dy7	31.902(2)
Dy1–Dy3–Dy2	110.799(3)	Dy4- O34	2.5032(2)	Dy1···Dy3	6.9149(5)	Dy1–Dy7–Dy8	31.685(2)
Dy2–Dy1–Dy3	34.574(2)	Dy4- N28	2.5780(2)	Dy3···Dy4	4.0445(3)	Dy7–Dy1–Dy8	31.761(2)
Dy1–O1–Dy3	117.358(5)	Dy4- N29	2.5552(2)	Dy4···Dy5	4.0545(3)	Dy1–Dy8–Dy7	116.554(4)
Dy1–O9–Dy3	115.615(5)	Dy5- O14	2.3087(2)	Dy3···Dy5	6.9223(7)	Dy4–Dy6–Dy8	68.891(2)
Dy1–O6–Dy2a	115.524(4)	Dy5- O15	2.3298(2)	Dy5···Dy6	4.0542(3)	Dy1–Dy3–Dy5	89.801(2)
Dy1–O13–Dy2a	108.540(4)	Dy5- O23	2.3805(2)	Dy6···Dy7	4.0757(3)	Dy3–Dy5–Dy7	89.990(2)
Dy2–O2–Dy3	116.212(4)	Dy5- O28	2.3739(2)	Dy5···Dy7	6.9089(5)	Dy1–Dy7–Dy5	90.055(2)
Dy2–O10–Dy3	117.144(4)	Dy5- O34	2.2916(2)	Dy7···Dy8	4.0589(3)	Dy3–Dy1–Dy7	90.145(2)



Scheme S1. Reversible deprotonation and base-assisted keto-enol tautomerism of H_2EDDC .



Scheme S2. Coordination modes of the EDDC^{2-} ligands (top) and the acetate groups (bottom) in compound **1**.



Scheme S3. Coordination modes of the EDTC²⁻ ligands (top), the acetate groups and 1-Naphthyl phosphonic acids (bottom) in compound **2**.

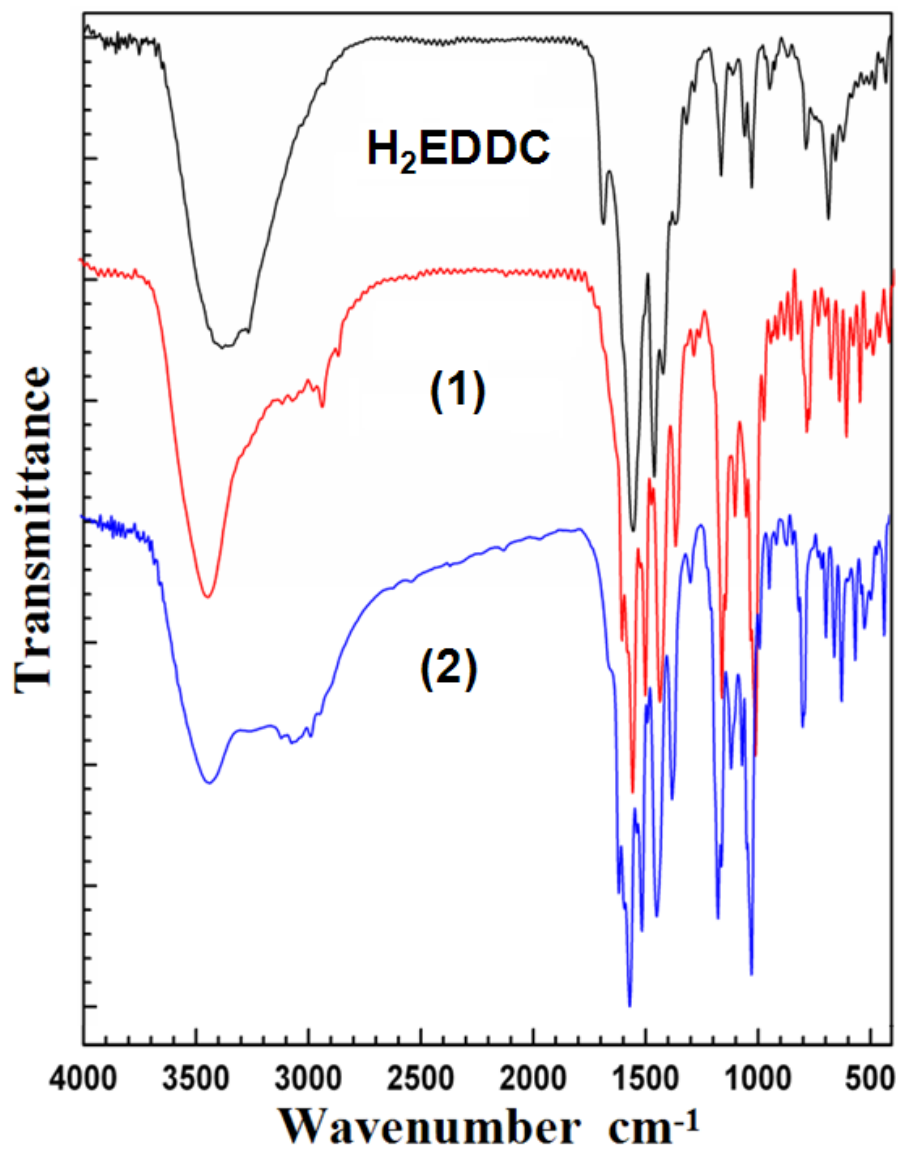


Figure S1. Infrared spectra of H_2EDDC , 1 and 2.

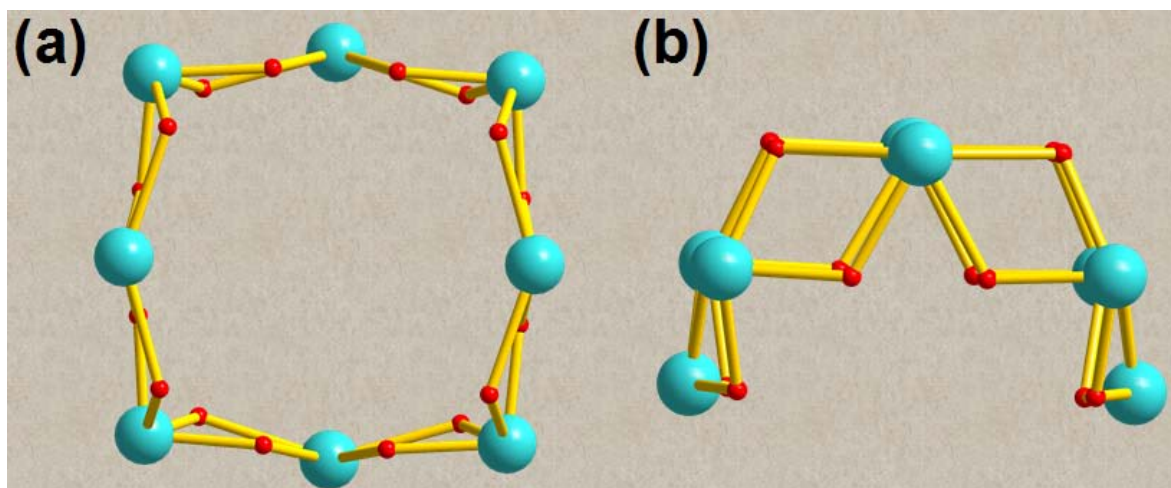


Figure S2. (a) Top-view and (b) side-view of the [Dy₈(μ₂-O)₁₆]²⁴⁺ core in compound 2.

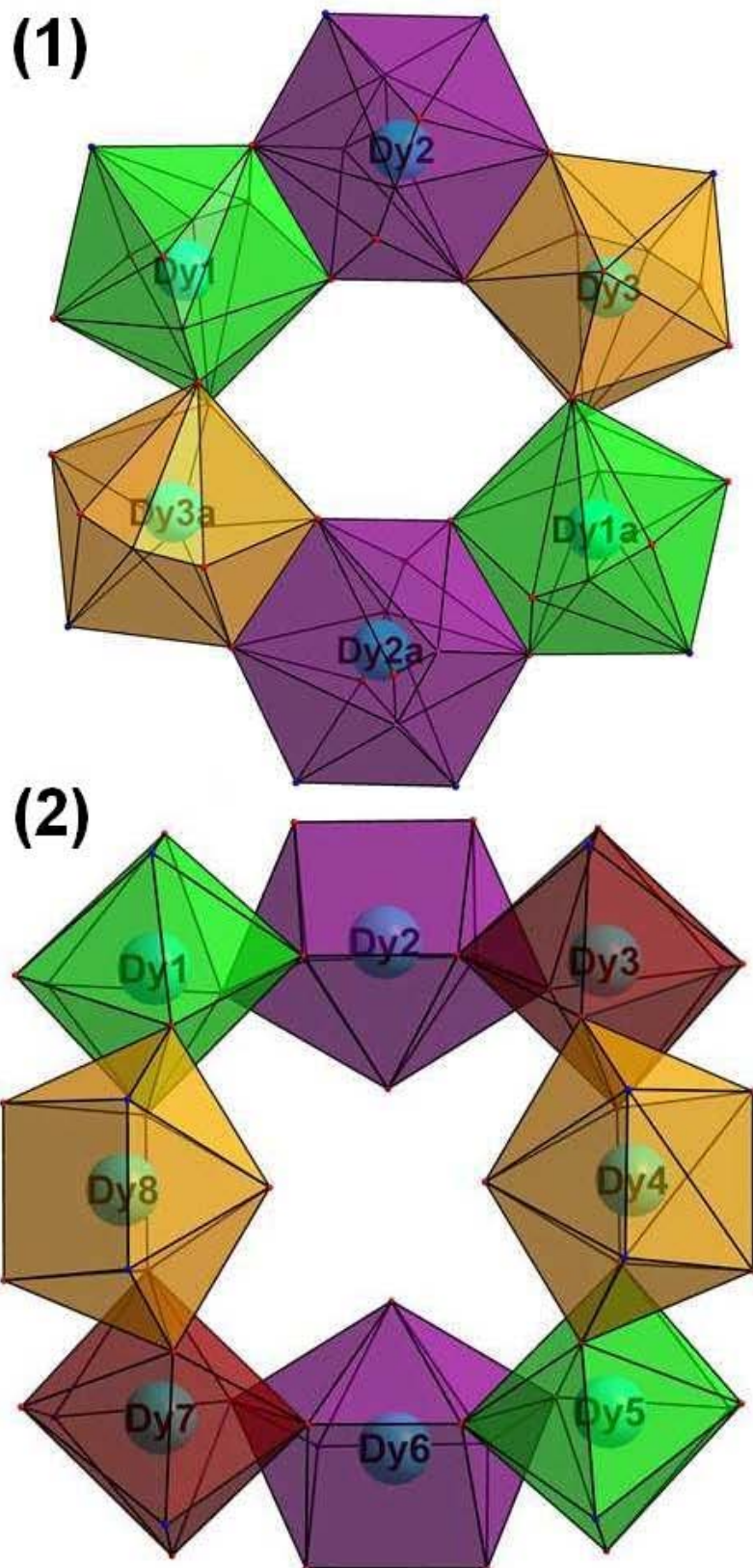


Figure S3. Coordination polyhedra observed for the metal centers in **1** (top) and **2** (bottom).

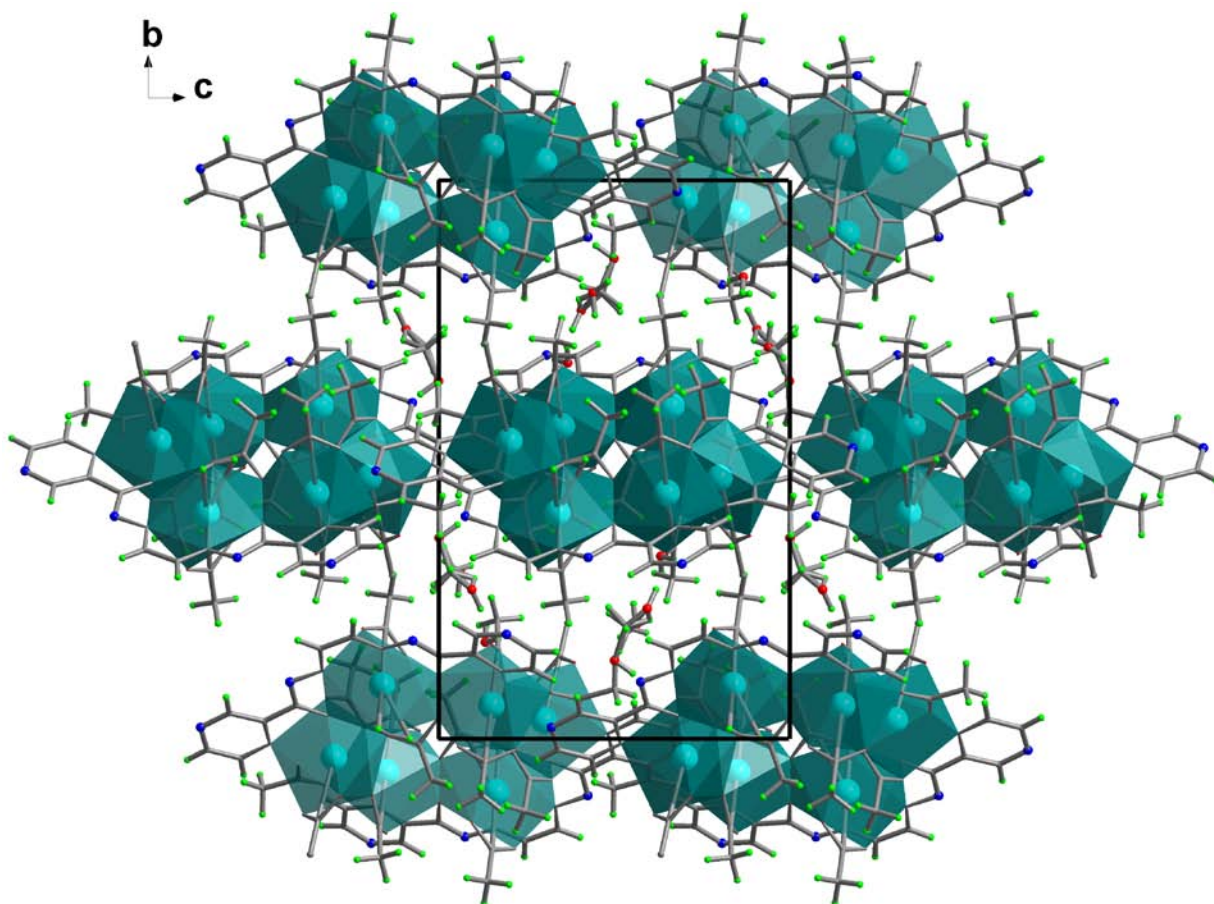


Figure S4. Packing arrangement of the molecules viewed along the *a*-axis in **1**. Turquoise Dy, Red O, Blue N.

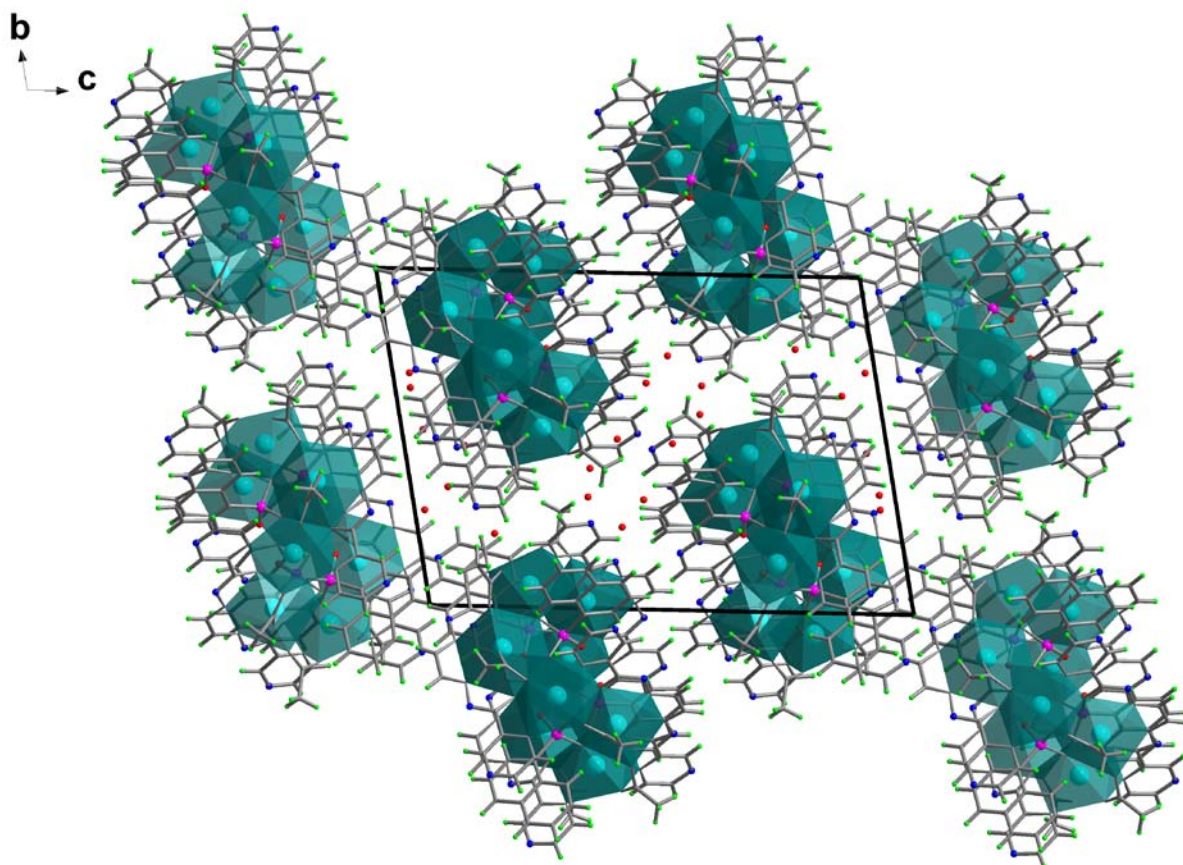


Figure S5. Packing arrangement of the molecules viewed along the *a*-axis in **2**. Turquoise Dy, Red O, Blue N.

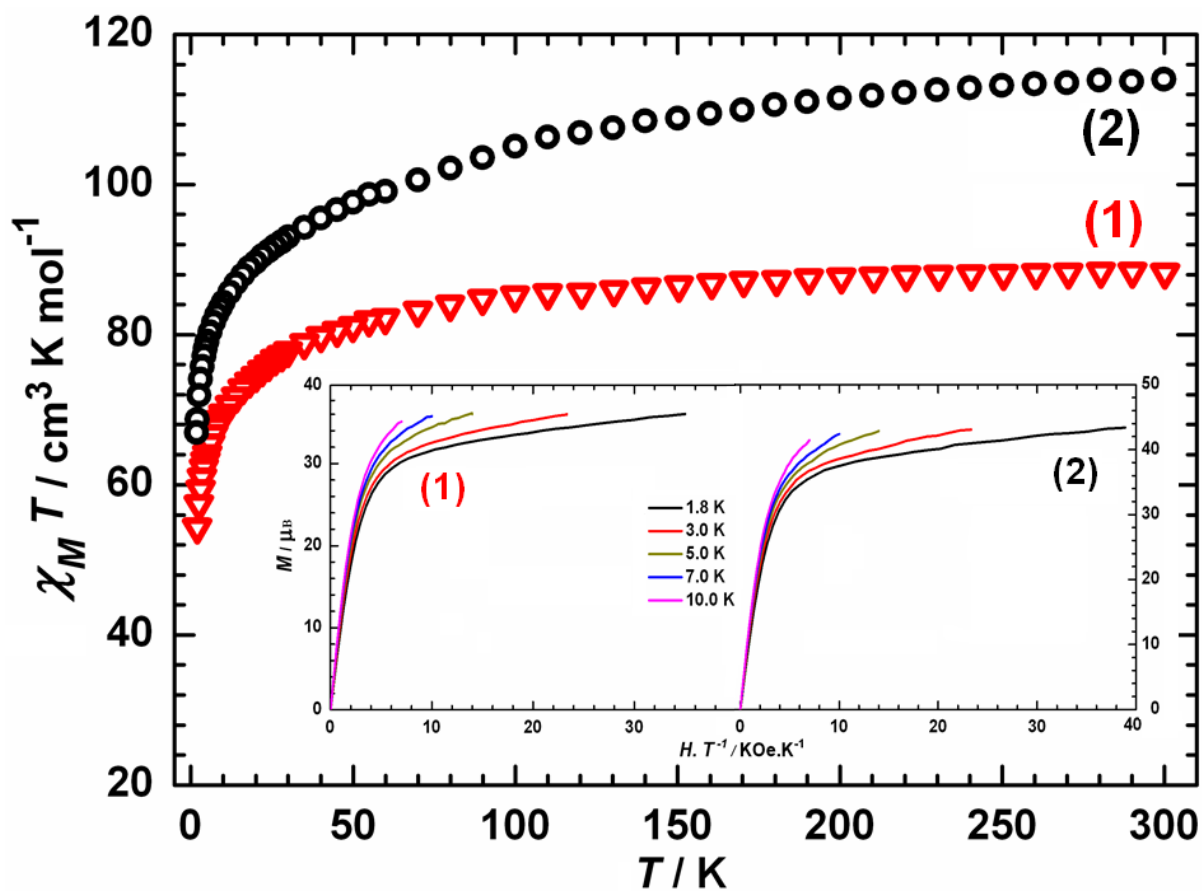


Figure S6. Temperature dependence of the $\chi_M T$ product at 1 kOe for **1** and **2**. Inset: M vs. H/T plots at different temperatures below 10.0 K.

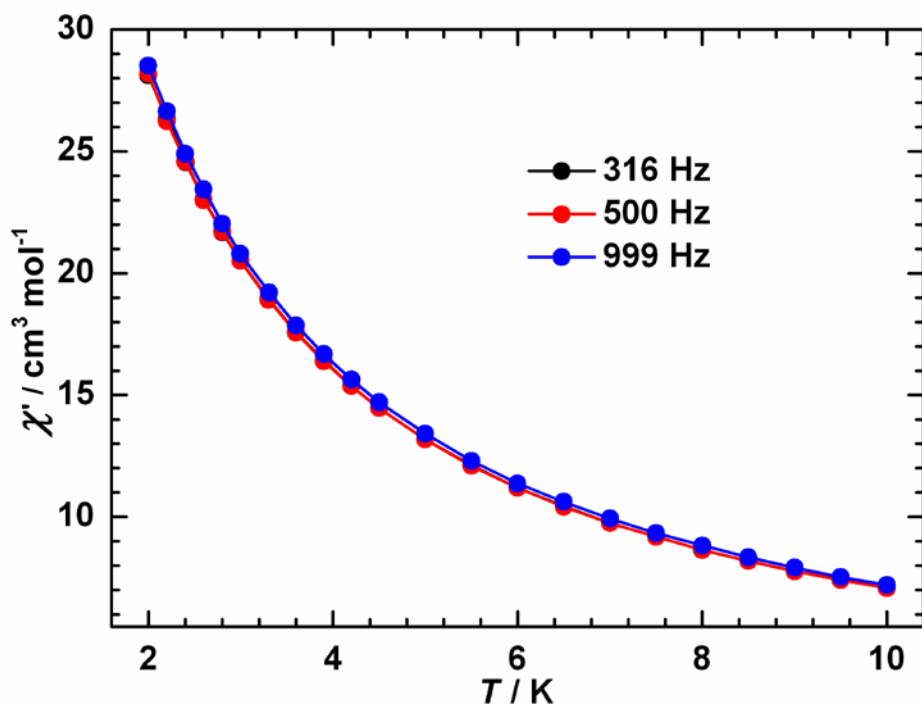


Figure S7. Temperature dependence of the χ' product, *ac* susceptibility under zero-dc field for compound **1**.

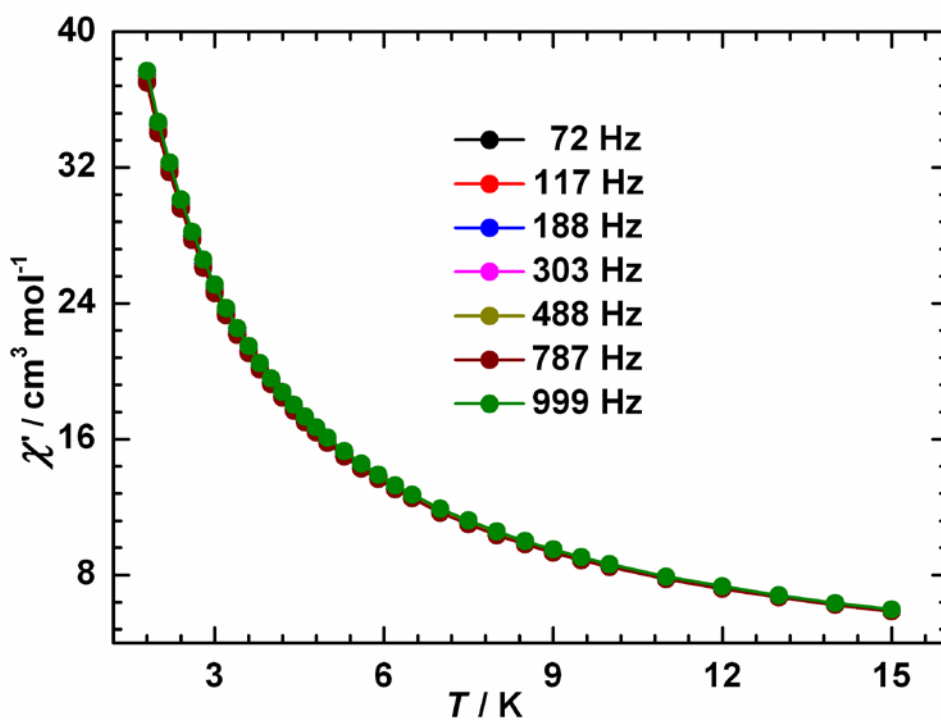


Figure S8. Temperature dependence of the χ' product, *ac* susceptibility under zero-dc field for compound **2**.

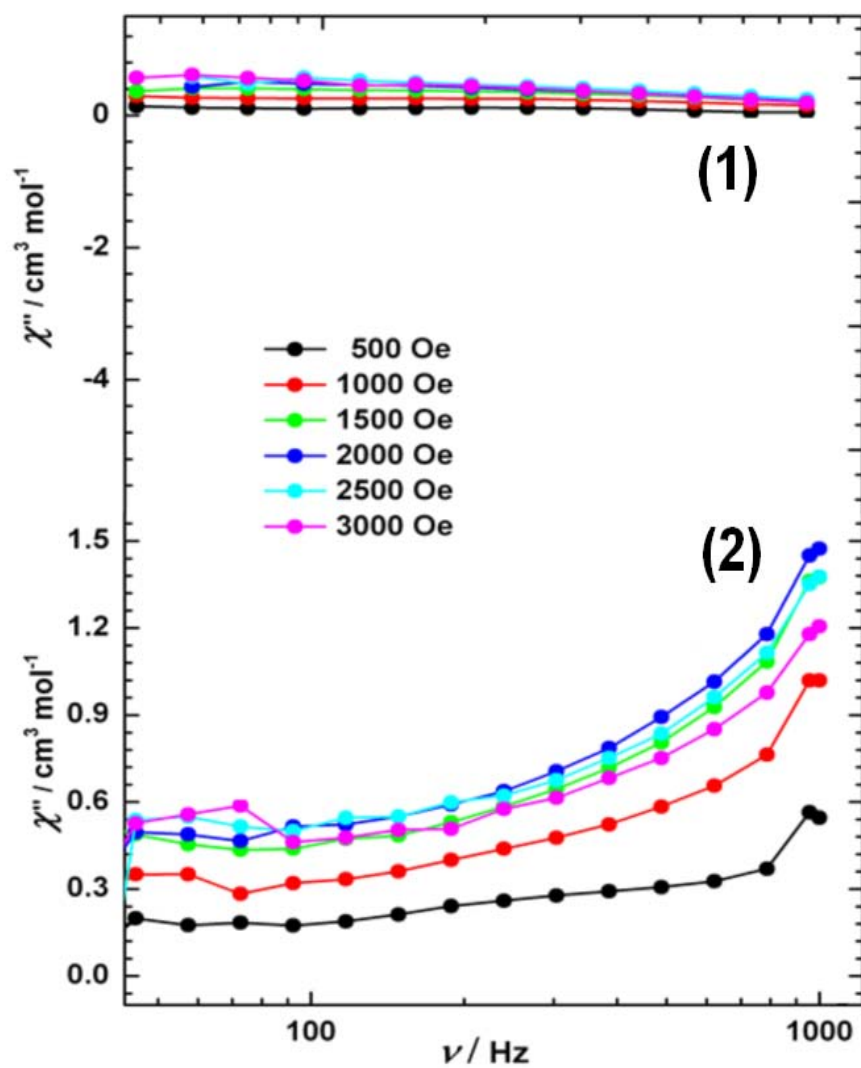


Figure S9. The out-phase (χ'') *ac* susceptibility as a function of the dc applied field measured at 2.0 K for compounds **1** (top) and **2** (bottom).