Electronic Supplementary Information (ESI)

An Octanuclear $Mn^{III}_4Dy^{III}_4$ Cluster Connected via Two μ_5-NO_3^- Bridges with Slow Relaxation of Magnetization

Feng Wang[ab], Hua Peng[b], Yu Ding*[a]

[a] College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan 432000, China

[b] Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, China

*Corresponding authors.

E-mail address: dy9802@126.com (Y. Ding)

Experiment Section

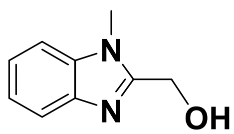
All chemicals and solvents used in the syntheses were commercially available A.R. grade and used as received without further purification.

Synthesis of $[Mn^{III}_4Dy^{III}_4(mbm)_{14}(\mu_5\text{-}NO_3)_2(\mu\text{-}NO_3)_2(MeOH)_2](NO_3)_6\cdot 12H_2O$ (1): $Mn(ClO_4)_2\cdot 6H_2O$ (0.50 mmol, 0.181 g), $Dy(NO_3)_3\cdot 6H_2O$ (0.10 mmol, 0.035 g) and Hmbm (0.857 mmol, 0.137 g) were dissolved in 30 mL MeCN/MeOH (v/v = 2:1), then triethylamine (0.75 mmol, 0.11 mL) was added to this solution with stirring. The resulted dark brown solution was stirred for another hour, filtrated, and the filtrate left undisturbed at ambient temperature. Large dark-brown crystals were collected by filtration after two weeks. Yield: 35％. Anal. Calcd for $C_{128}H_{158}Dy_4Mn_4N_{38}O_{58}$: C, 38.11; H, 3.95; N, 13.20%. Found: C, 38.02; H, 4.05; N, 13.47%. FT-IR data (kBr): 3381(w), 3023(w), 2910(w), 2829(w), 1581(s), 1469(w), 1447(m), 1388(s), 1245(w), 1015(w), 809(w), 725(s), 642(w), 506(w).

Crystal Structure Determination: Suitable single crystals of compounds were selected and mounted onto thin glass fibers. Diffraction data for compounds were collected on a Siemens SMART CCD diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Data reductions and absorption corrections were performed with the Bruker SAINT package. The structures were solved by direct methods and refine on F^2 by full-matrix least-squares using SHELXTL 2000 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were carried out using the SHELXTL 2000 program package.

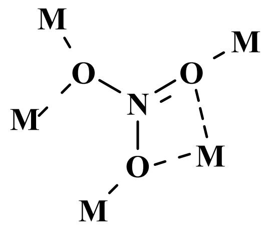
Crystallographic data for the compound has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-849069.

Physical measurements: The FT-IR spectra were obtained (KBr disks) on a Bruker Vector spectrometer. Elemental analyses were performed on a Perkin Elmer 240 elemental analyzer. Variable temperature direct current (*dc*) magnetic susceptibility data down to 1.8 K on microcrystalline samples were carried out on a Quantum Design MPMP-XL7 SQUID magnetometer. The alternating current (*ac*) susceptibility data down to 1.8 K were also performed on a Quantum Design MPMP-XL7 magnetometer in a zero dc field and a 5 Oe field oscillating at frequencies in the 1-1488 Hz range. Diamagnetic corrections were made for all compounds the sample holder as the background and the compounds estimated from Pascal's constants.

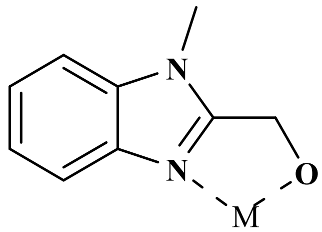


Hmbm

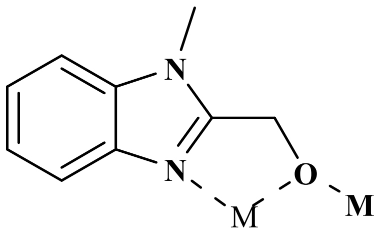
Scheme S1 The structures of Hmbm



μ_5-NO_3^- chelating mode



η^1:η^1:μ_1 chelating mode



η^1:η^2:μ_2 chelating mode

Scheme S2 The coordination modes of the nitrato and mbm⁻ ligands

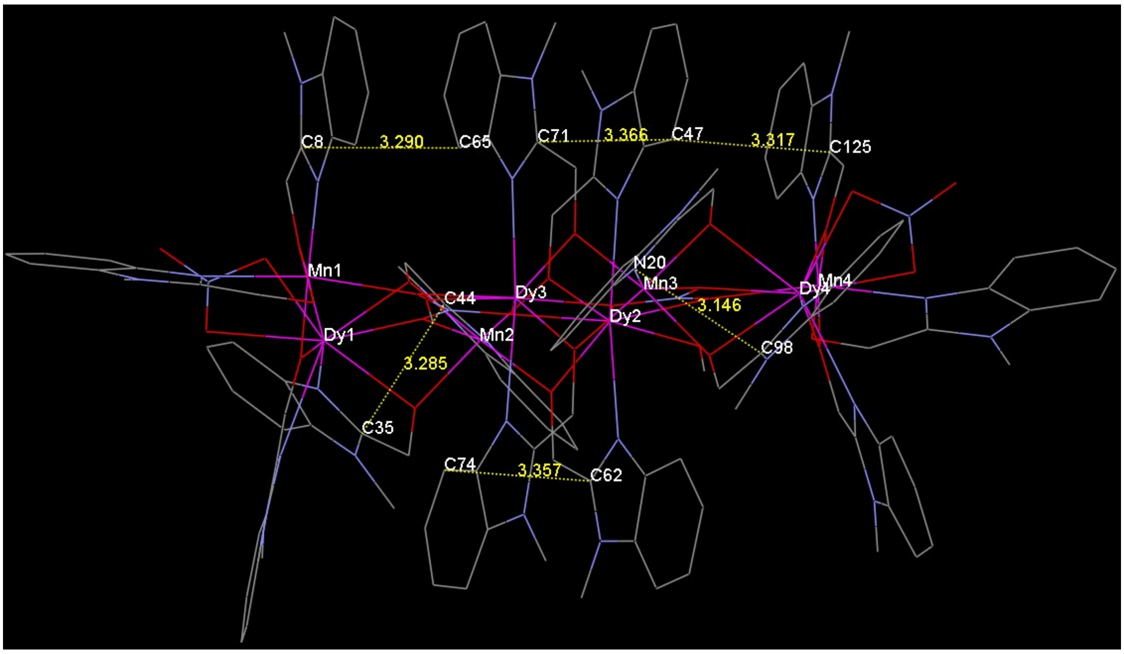


Fig. S1 The crystal structure showing the intracluster π-π stacking of complex **1**. The numbers indicate the shortest atom···atom distances between the adjacent benzimidazole rings, unit Å.

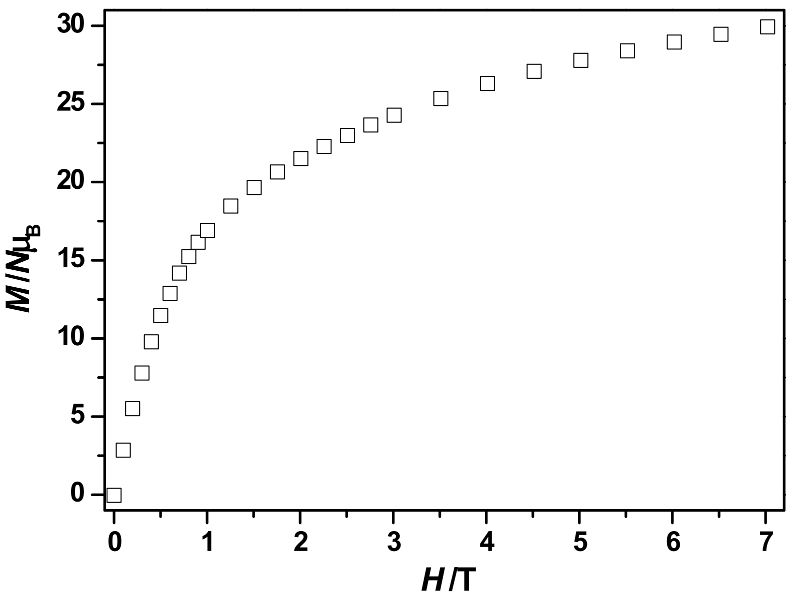


Fig. S2 Plot of M versus H for **1** at 1.8 K.

Table S1 Selected interatomic distances (Å) for **1**

Dy(1)-O(3)	2.336(3)	Dy(4)-O(14)	2.412(3)
Dy(1)-O(18)	2.360(4)	Dy(4)-O(11)	2.425(4)
Dy(1)-O(4)	2.404(4)	Dy(4)-O(25)	2.433(4)
Dy(1)-O(1)	2.426(3)	Dy(4)-O(10)	2.483(3)
Dy(1)-O(16)	2.449(4)	Dy(4)-O(24)	2.489(4)
Dy(1)-O(5)	2.461(3)	Dy(4)-N(24)	2.550(4)
Dy(1)-O(15)	2.461(3)	Dy(4)-N(22)	2.582(4)
Dy(1)-N(6)	2.589(4)	Dy(4)-N(32)	2.823(5)
Dy(1)-N(8)	2.605(4)	Mn(1)-O(2)	1.885(3)
Dy(1)-N(29)	2.843(4)	Mn(1)-O(1)	1.901(3)
Dy(2)-O(20)	2.309(4)	Mn(1)-O(3)	1.932(4)
Dy(2)-O(28)	2.320(4)	Mn(1)-N(2)	1.992(4)
Dy(2)-O(6)	2.327(3)	Mn(1)-N(4)	2.267(5)
Dy(2)-O(7)	2.336(4)	Mn(1)-O(19)	2.272(4)
Dy(2)-O(21)	2.337(3)	Mn(2)-O(6)	1.917(4)
Dy(2)-O(22)	2.491(4)	Mn(2)-O(7)	1.945(4)
Dy(2)-N(12)	2.524(4)	Mn(2)-O(5)	1.955(4)
Dy(2)-N(14)	2.546(4)	Mn(2)-O(4)	1.958(4)
Dy(2)-N(31)	2.849(4)	Mn(2)-N(10)	2.180(4)
Dy(2)-Mn(2)	3.3965(11)	Mn(2)-O(18)	2.263(3)
Dy(3)-O(21)	2.290(3)	Mn(3)-O(10)	1.919(4)
Dy(3)-O(27)	2.311(3)	Mn(3)-O(8)	1.937(4)
Dy(3)-O(8)	2.312(4)	Mn(3)-O(11)	1.939(4)
Dy(3)-O(20)	2.339(3)	Mn(3)-O(9)	1.940(4)
Dy(3)-O(9)	2.355(3)	Mn(3)-N(20)	2.212(4)
Dy(3)-O(19)	2.472(4)	Mn(3)-O(23)	2.255(3)
Dy(3)-N(16)	2.539(4)	Mn(4)-O(13)	1.877(4)
Dy(3)-N(18)	2.551(4)	Mn(4)-O(14)	1.916(4)
Dy(3)-N(30)	2.846(4)	Mn(4)-O(12)	1.935(4)
Dy(4)-O(12)	2.338(3)	Mn(4)-N(28)	2.034(4)
Dy(4)-O(23)	2.372(4)	Mn(4)-O(22)	2.255(4)
		Mn(4)-N(26)	2.284(4)

Table S2 Selected interatomic angle (°) for **1**

O(3)-Dy(1)-O(18)	75.27(13)	O(28)-Dy(2)-N(31)	97.56(9)	O(12)-Dy(4)-N(32)	108.32(13)
O(3)-Dy(1)-O(4)	107.78(13)	O(6)-Dy(2)-N(31)	147.57(12)	O(23)-Dy(4)-N(32)	139.70(9)
O(18)-Dy(1)-O(4)	63.90(12)	O(7)-Dy(2)-N(31)	148.76(12)	O(14)-Dy(4)-N(32)	70.83(12)
O(3)-Dy(1)-O(1)	61.76(12)	O(21)-Dy(2)-N(31)	27.68(9)	O(11)-Dy(4)-N(32)	146.07(12)
O(18)-Dy(1)-O(1)	75.80(12)	O(22)-Dy(2)-N(31)	26.87(9)	O(25)-Dy(4)-N(32)	24.93(9)
O(4)-Dy(1)-O(1)	139.61(12)	N(12)-Dy(2)-N(31)	81.55(13)	O(10)-Dy(4)-N(32)	101.14(12)
O(3)-Dy(1)-O(16)	85.75(12)	N(14)-Dy(2)-N(31)	82.89(13)	O(24)-Dy(4)-N(32)	27.08(9)
O(18)-Dy(1)-O(16)	153.09(11)	O(21)-Dy(3)-O(27)	170.06(12)	N(24)-Dy(4)-N(32)	97.42(14)
O(4)-Dy(1)-O(16)	141.77(12)	O(21)-Dy(3)-O(8)	83.06(9)	N(22)-Dy(4)-N(32)	80.13(13)
O(1)-Dy(1)-O(16)	78.47(12)	O(27)-Dy(3)-O(8)	92.72(9)	O(2)-Mn(1)-O(1)	177.51(15)
O(3)-Dy(1)-O(5)	134.65(12)	O(21)-Dy(3)-O(20)	62.90(9)	O(2)-Mn(1)-O(3)	102.42(14)
O(18)-Dy(1)-O(5)	61.96(12)	O(27)-Dy(3)-O(20)	124.89(9)	O(1)-Mn(1)-O(3)	79.27(14)
O(4)-Dy(1)-O(5)	67.21(12)	O(8)-Dy(3)-O(20)	136.05(13)	O(2)-Mn(1)-N(2)	96.34(16)
O(1)-Dy(1)-O(5)	92.28(11)	O(21)-Dy(3)-O(9)	82.42(9)	O(1)-Mn(1)-N(2)	82.08(17)
O(16)-Dy(1)-O(5)	127.29(12)	O(27)-Dy(3)-O(9)	87.65(9)	O(3)-Mn(1)-N(2)	161.05(16)
O(3)-Dy(1)-O(15)	121.30(12)	O(8)-Dy(3)-O(9)	62.23(12)	O(2)-Mn(1)-N(4)	78.22(16)
O(18)-Dy(1)-O(15)	122.65(12)	O(20)-Dy(3)-O(9)	132.14(11)	O(1)-Mn(1)-N(4)	99.90(16)
O(4)-Dy(1)-O(15)	130.71(11)	O(21)-Dy(3)-O(19)	116.53(9)	O(3)-Mn(1)-N(4)	93.62(16)
O(1)-Dy(1)-O(15)	69.66(11)	O(27)-Dy(3)-O(19)	72.24(9)	N(2)-Mn(1)-N(4)	92.82(17)
O(16)-Dy(1)-O(15)	52.95(12)	O(8)-Dy(3)-O(19)	140.43(12)	O(2)-Mn(1)-O(19)	80.35(14)
O(5)-Dy(1)-O(15)	75.02(12)	O(20)-Dy(3)-O(19)	54.11(12)	O(1)-Mn(1)-O(19)	101.60(14)
O(3)-Dy(1)-N(6)	64.61(12)	O(9)-Dy(3)-O(19)	148.41(12)	O(3)-Mn(1)-O(19)	88.06(15)
O(18)-Dy(1)-N(6)	111.36(13)	O(21)-Dy(3)-N(16)	88.31(10)	N(2)-Mn(1)-O(19)	92.46(17)
O(4)-Dy(1)-N(6)	78.16(13)	O(27)-Dy(3)-N(16)	98.39(10)	N(4)-Mn(1)-O(19)	158.37(14)
O(1)-Dy(1)-N(6)	121.47(12)	O(8)-Dy(3)-N(16)	67.22(13)	O(6)-Mn(2)-O(7)	75.99(15)
O(16)-Dy(1)-N(6)	75.95(13)	O(20)-Dy(3)-N(16)	83.91(12)	O(6)-Mn(2)-O(5)	100.45(15)
O(5)-Dy(1)-N(6)	144.03(12)	O(9)-Dy(3)-N(16)	129.32(13)	O(7)-Mn(2)-O(5)	172.05(14)
O(15)-Dy(1)-N(6)	125.53(14)	O(19)-Dy(3)-N(16)	78.78(13)	O(6)-Mn(2)-O(4)	164.78(15)
O(3)-Dy(1)-N(8)	145.43(13)	O(21)-Dy(3)-N(18)	89.23(10)	O(7)-Mn(2)-O(4)	94.91(16)
O(18)-Dy(1)-N(8)	123.61(13)	O(27)-Dy(3)-N(18)	86.37(9)	O(5)-Mn(2)-O(4)	86.97(15)
O(4)-Dy(1)-N(8)	65.86(13)	O(8)-Dy(3)-N(18)	128.56(13)	O(6)-Mn(2)-N(10)	97.67(15)
O(1)-Dy(1)-N(8)	145.15(12)	O(20)-Dy(3)-N(18)	80.49(12)	O(7)-Mn(2)-N(10)	107.07(15)
O(16)-Dy(1)-N(8)	82.60(13)	O(9)-Dy(3)-N(18)	66.34(13)	O(5)-Mn(2)-N(10)	80.32(15)
O(5)-Dy(1)-N(8)	76.38(12)	O(19)-Dy(3)-N(18)	87.80(13)	O(4)-Mn(2)-N(10)	96.67(16)
O(15)-Dy(1)-N(8)	75.56(12)	N(16)-Dy(3)-N(18)	163.54(13)	O(6)-Mn(2)-O(18)	96.62(14)
N(6)-Dy(1)-N(8)	80.99(13)	O(21)-Dy(3)-N(30)	89.58(9)	O(7)-Mn(2)-O(18)	101.44(13)
O(20)-Dy(2)-O(28)	102.96(13)	O(27)-Dy(3)-N(30)	98.60(9)	O(5)-Mn(2)-O(18)	71.70(13)
O(20)-Dy(2)-O(6)	142.99(12)	O(8)-Dy(3)-N(30)	148.25(12)	O(4)-Mn(2)-O(18)	72.94(14)
O(28)-Dy(2)-O(6)	144.65(12)	O(20)-Dy(3)-N(30)	26.77(12)	N(10)-Mn(2)-O(18)	150.43(15)
O(20)-Dy(2)-O(7)	71.39(11)	O(9)-Dy(3)-N(30)	147.27(11)	O(10)-Mn(3)-O(8)	97.78(16)
O(28)-Dy(2)-O(7)	25.44(12)	O(19)-Dy(3)-N(30)	27.41(11)	O(10)-Mn(3)-O(11)	89.55(16)
O(6)-Dy(2)-O(7)	102.38(13)	N(16)-Dy(3)-N(30)	81.77(12)	O(8)-Mn(3)-O(11)	164.54(15)
O(20)-Dy(2)-O(21)	27.54(12)	N(18)-Dy(3)-N(30)	81.94(12)	O(10)-Mn(3)-O(9)	172.09(15)

O(28)-Dy(2)-O(21)	100.24(14)	O(12)-Dy(4)-O(23)	74.57(9)	O(8)-Mn(3)-O(9)	76.95(15)
O(6)-Dy(2)-O(21)	78.95(12)	O(12)-Dy(4)-O(14)	63.20(12)	O(11)-Mn(3)-O(9)	94.22(16)
O(7)-Dy(2)-O(21)	168.64(10)	O(23)-Dy(4)-O(14)	75.78(9)	O(10)-Mn(3)-N(20)	81.56(16)
O(20)-Dy(2)-O(22)	81.91(12)	O(12)-Dy(4)-O(11)	101.20(12)	O(8)-Mn(3)-N(20)	99.21(15)
O(28)-Dy(2)-O(22)	95.62(9)	O(23)-Dy(4)-O(11)	64.25(9)	O(11)-Mn(3)-N(20)	95.31(16)
O(6)-Dy(2)-O(22)	82.17(12)	O(14)-Dy(4)-O(11)	139.89(13)	O(9)-Mn(3)-N(20)	104.97(16)
O(7)-Dy(2)-O(22)	86.92(10)	O(12)-Dy(4)-O(25)	91.04(9)	O(10)-Mn(3)-O(23)	71.87(10)
O(21)-Dy(2)-O(22)	61.31(12)	O(23)-Dy(4)-O(25)	152.47(11)	O(8)-Mn(3)-O(23)	94.76(10)
O(20)-Dy(2)-N(12)	62.64(9)	O(14)-Dy(4)-O(25)	76.79(9)	O(11)-Mn(3)-O(23)	74.53(10)
O(28)-Dy(2)-N(12)	124.41(13)	O(11)-Dy(4)-O(25)	142.86(9)	O(9)-Mn(3)-O(23)	102.43(10)
O(6)-Dy(2)-N(12)	134.73(9)	O(12)-Dy(4)-O(10)	134.86(12)	N(20)-Mn(3)-O(23)	151.40(13)
O(7)-Dy(2)-N(12)	132.55(8)	O(23)-Dy(4)-O(10)	60.96(8)	O(13)-Mn(4)-O(14)	177.43(16)
O(21)-Dy(2)-N(12)	116.77(9)	O(14)-Dy(4)-O(10)	96.90(11)	O(13)-Mn(4)-O(12)	101.78(15)
O(22)-Dy(2)-N(12)	71.85(12)	O(11)-Dy(4)-O(10)	67.22(12)	O(14)-Mn(4)-O(12)	80.52(14)
O(20)-Dy(2)-N(14)	141.22(8)	O(25)-Dy(4)-O(10)	125.26(8)	O(13)-Mn(4)-N(28)	96.64(16)
O(28)-Dy(2)-N(14)	148.84(9)	O(12)-Dy(4)-O(24)	126.38(9)	O(14)-Mn(4)-N(28)	81.14(16)
O(6)-Dy(2)-N(14)	54.53(12)	O(23)-Dy(4)-O(24)	119.05(11)	O(12)-Mn(4)-N(28)	161.32(15)
O(7)-Dy(2)-N(14)	91.23(13)	O(14)-Dy(4)-O(24)	70.57(9)	O(13)-Mn(4)-O(22)	80.56(12)
O(21)-Dy(2)-N(14)	98.07(10)	O(11)-Dy(4)-O(24)	132.09(8)	O(14)-Mn(4)-O(22)	100.76(12)
O(22)-Dy(2)-N(14)	67.32(13)	O(25)-Dy(4)-O(24)	51.97(12)	O(12)-Mn(4)-O(22)	87.68(11)
N(12)-Dy(2)-N(14)	128.62(13)	O(10)-Dy(4)-O(24)	74.37(8)	N(28)-Mn(4)-O(22)	92.31(13)
O(20)-Dy(2)-N(31)	85.27(10)	O(12)-Dy(4)-N(24)	64.58(12)	O(13)-Mn(4)-N(26)	80.32(16)
O(10)-Dy(4)-N(24)	144.04(13)	O(23)-Dy(4)-N(24)	118.28(10)	O(14)-Mn(4)-N(26)	98.45(16)
O(24)-Dy(4)-N(24)	122.23(10)	O(14)-Dy(4)-N(24)	118.31(13)	O(12)-Mn(4)-N(26)	93.47(15)
O(12)-Dy(4)-N(22)	142.46(12)	O(11)-Dy(4)-N(24)	80.23(13)	N(28)-Mn(4)-N(26)	92.68(16)
O(23)-Dy(4)-N(22)	122.87(10)	O(25)-Dy(4)-N(24)	73.64(11)	O(22)-Mn(4)-N(26)	160.67(12)
O(14)-Dy(4)-N(22)	147.83(13)				