Supporting Information

A New Family of $\{Co_4Ln_8\}$ Metallacrowns with a Butterfly-Shaped Structure

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Table of contents

1: Syntheses.

Compound H_2pyzha[1] was prepared according to the literature procedures. All reagents were purchased from commercial sources and used without further purification.

[Dy(pyzic){Dy_3Co_2(pyzha)$_6$(*pyzha)$(NO_3)_2(H_2O)(MeOH)_2$}]$_2$·$(NO_3)_2$·10H_2O·8MeOH (**1**). H_2pyzha (60.8 mg, 0.4375 mmol), 2-Pyrazinecarboxylicacid (7.75 mg, 0.0625 mmol), $Co(NO_3)_2·6H_2O$ (145.5 mg, 0.5 mmol), and $Dy(NO_3)_3·6H_2O$ (45.6 mg, 0.1 mmol) were dissolved in MeOH (20 ml) together. The solution was stirred for 5 h and turned into brown. The dark brown crystal were crystallized upon slow evaporation of the solvent at room temperature for two months. Yield: 15%. Calcd for $C_{92}H_{122}Dy_8Co_4N_{52}O_{74}$: C, 23.63; H, 2.52; N, 15.58%. Found: C, 23.31; H, 2.53; N, 15.45%. FT-IR (KBr pellet, cm^{-1}): 3419 (br), 1583 (s), 1522 (w), 1470 (m), 1429 (m), 1384 (s), 1209 (w), 1165 (m), 1100 (s), 1050 (m), 949 (m), 839 (w), 767 (w), 751 (m), 553 (w), 506 (m), 450 (m).

[Ho(pyzic){Ho_3Co_2(pyzha)$_6$(*pyzha)$(NO_3)_2(H_2O)(MeOH)_2$}]$_2$·$(NO_3)_2$·10H_2O·8MeOH (**2**). Complex **2** were generated by adopting the procedures similar to those used for 1 except that $Dy(NO_3)_3·6H_2O$ was replaced by $Ho(NO_3)_3·6H_2O$ (45.8 mg, 0.1 mmol). Yield: 18%. Calcd for $C_{94}H_{126}Ho_8Co_4N_{52}O_{74}$: C, 23.88; H, 2.67; N, 15.41%. Found: C, 23.27; H, 2.57; N, 15.52%. FT-IR (KBr pellet, cm^{-1}): 3415 (br), 1630 (m), 1583 (s), 1522 (w), 1471 (m), 1429 (m), 1384 (s), 1210 (w), 1166 (m), 1101 (s), 1050 (m), 950 (m), 839 (w), 767 (w), 752 (m), 733 (w), 676 (w), 554 (w), 506 (m), 451 (m).

[Tm(pyzic){Tm_3Co_2(pyzha)$_6$(*pyzha)$(NO_3)_2(H_2O)_2(MeOH)$}]$_2$·$(NO_3)_2$·14H_2O·8MeOH (**3**). Complex **3** were generated by adopting the procedures similar to those used for 1 except that $Dy(NO_3)_3·6H_2O$ was replaced by $Tm(NO_3)_3·6H_2O$ (44.5 mg, 0.1 mmol). Yield: 61%. Calcd for $C_{90}H_{128}Tm_8Co_4N_{52}O_{78}$: C, 22.61; H, 2.68; N, 15.24%. Found: C, 22.11; H, 2.55; N, 15.41%. FT-IR (KBr pellet, cm^{-1}): 3419 (br), 1633 (m), 1584 (s), 1522 (w), 1471 (m), 1429 (m), 1384 (s), 1210 (w), 1166 (w), 1103 (s), 1049 (w), 951 (m), 834 (w), 767 (w), 752 (m), 734 (w), 556 (w), 506 (m), 455 (m).

2: Crystal Data and Structure.

X-ray Crystallography. Single-crystal X-ray diffraction data for compounds **1-3** were collected on a Bruker Smart CCD area-detector diffractometer with Cu Kα radiation (λ = 1.54184 Å) by ω-scan mode operating at 128(3) K. The program SAINT was used for integration of the diffraction profiles, and semiempirical absorption corrections were applied using SADABS.[2,3] All of the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[4]

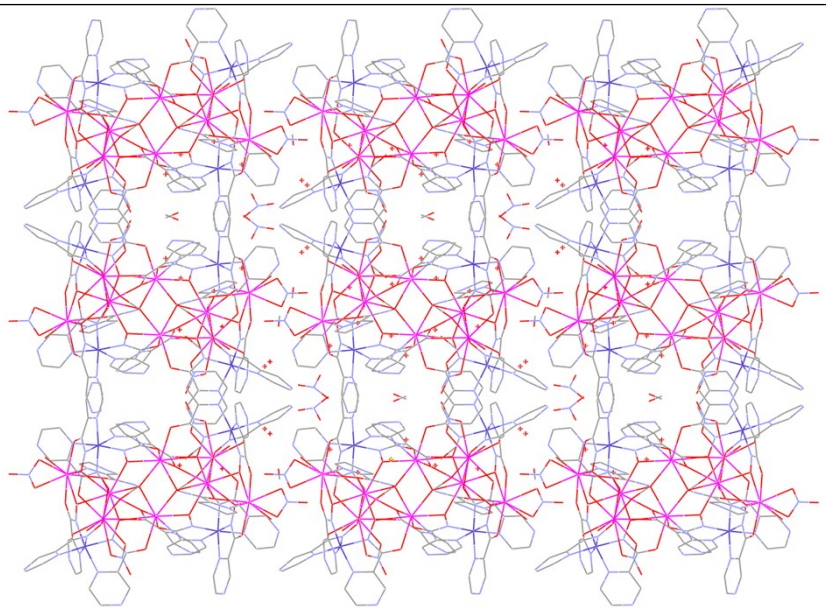

Figure S1. Packing arrangement of complexes along the b-axis. (H atoms are omitted for clarity)

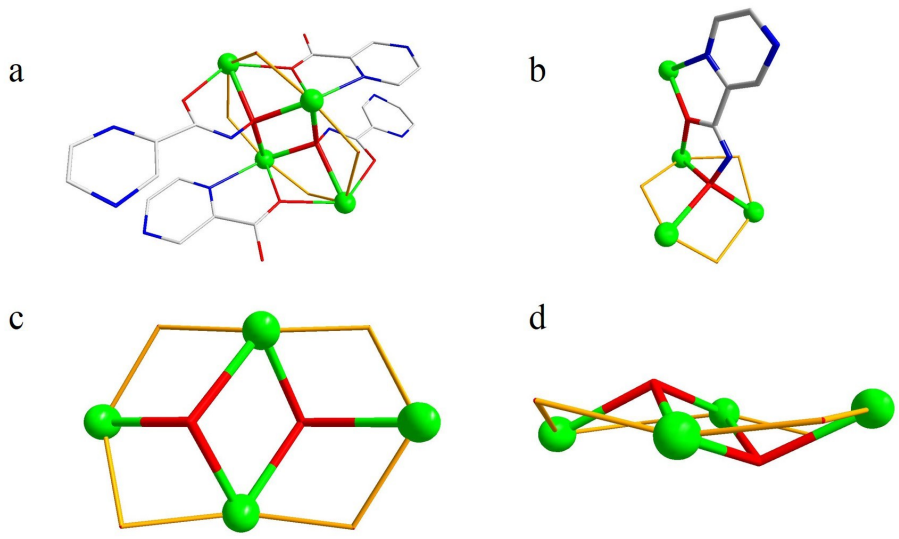

Figure S2. The central frame is constructed by the coordination of *pyzha^{2-} and pyzic^{-} (a), The four-coordinate oxygen ion (oxime) from the *pyzha^{2-} form a triangular structure (b), The triangular structure top view (c), side view (d).

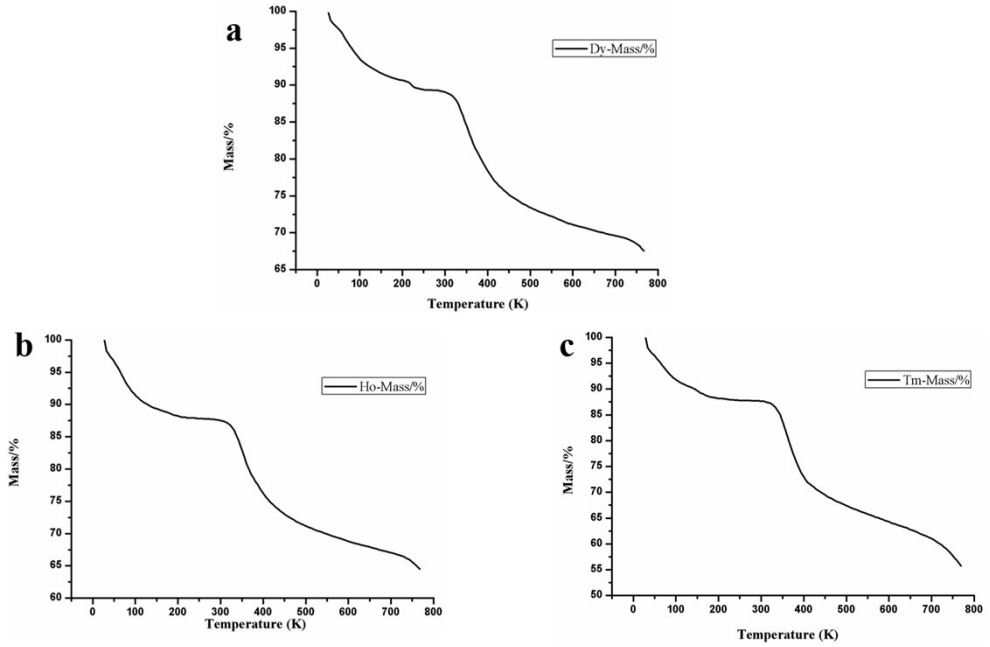

Figure S3. Thermogravimetric analysis of complexes: {Co$^{\text{III}}_4$Dy$_8$}-**1** (a), {Co$^{\text{III}}_4$Ho$_8$}-**2** (b), {Co$^{\text{III}}_4$Tm$_8$}-**3** (c).

Table S1. Crystal data and structure refinement for **1-3**.

complex	**1**	**2**	**3**
Chemical formula	C92 H122 Co4 Dy8 N52 O74	C94 H126 Co4 Ho8 N52 O74	C90 H128 Co4 Tm8 N52 O78
CCDC number	1843821	1904669	1900536
M, g mol $^{-1}$	4672.1	4723.63	4773.61
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
a /Å	23.688(3)	24.0051(9)	24.1637(9)

b/Å	17.7123(17)	17.2920(6)	17.1973(9)
c/Å	33.552(3)	33.5961(8)	33.5830(12)
Unit cell volume/Å^3	14077(3)	13945.6(8)	13955.4(10)
Temperature/K	128(3)	128(3)	128(3)
Space group	Pbca	Pbca	Pbca
Z	4	4	4
Absorption coefficient, μ/mm^{-1}	26.733	12.529	13.570
Rint	0.1390	0.0661	0.0574
R1 a (I > 2σ(I))	0.0979	0.0787	0.0850
wR2 b (all data)	0.2322	0.2185	0.2230
Goodness of fit on F 2	1.086	1.084	1.027
Largest diff. peak and hole / e.Å^{-3}	1.450 and -1875	1.303 and -1.563	3.061 and -3.343

$^aR_1 = \sum||F_o| - |Fc||/\sum|F_o|$, $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2. Selected bond distances (Å) and angles (deg) for **1**.

Dy(1)-O(15) 2.330(16)	Dy(2)-O(12) 2.398(15)	Dy(4)-O(3) 2.407(15)	Dy(2)-O(4) 2.335(17)	Dy(3)-O(17) 2.401(18)
Dy(1)-O(10) 2.345(17)	Dy(2)-O(1) 2.450(11)	Dy(4)-O(27) 2.478(18)	Dy(2)-O(2) 2.342(18)	Dy(3)-O(19) 2.429(18)
Dy(1)-O(3) 2.380(16)	Dy(2)-O(16) 2.498(17)	Dy(4)-O(28) 2.498(17)	Dy(2)-O(5) 2.357(13)	Dy(3)-O(22) 2.51(2)
Dy(1)-O(7) 2.398(16)	Dy(2)-N(21) 2.52(2)	Dy(4)-N(18) 2.76(2)	Dy(3)-O(20) 2.616(19)	Dy(4)-O(6) 2.33(2)
Dy(1)-O(13) 2.441(14)	Dy(2)-N(20) 2.92(2)	Co(1)-N(17) 1.840(2)	Dy(4)-O(15) 2.303(13)	Dy(4)-O(18) 2.346(17)
Dy(1)-O(1) 2.453(16)	Dy(3)-O(8) 2.303(18)	Co(1)-N(14) 1.864(2)	Dy(4)-O(13) 2.32(2)	Dy(4)-O(14) 2.38(2)
Dy(1)-O(5) 2.456(17)	Dy(3)-O(10) 2.320(16)	Co(1)-N(3) 1.898(16)	Dy(2)-O(4) 2.335(17)	Dy(3)-O(17) 2.401(18)
Dy(1)-O(12) 2.486(15)	Dy(3)-O(7) 2.349(18)	Co(1)-N(15) 1.913(2)	Dy(2)-O(2) 2.342(18)	Dy(3)-O(19) 2.429(18)
Dy(1)-O(16) 2.521(13)	Dy(3)-O(11) 2.373(14)	Co(1)-N(1) 1.934(2)	Dy(2)-O(5) 2.357(13)	Dy(3)-O(22) 2.51(2)
Dy(2)-O(16) 2.245(18)	Dy(3)-O(9) 2.383(15)	Co(1)-N(13) 1.953(18)	Dy(3)-O(20) 2.616(19)	Dy(4)-O(6) 2.33(2)
O(15)-Dy(1)-O(10) 141.8(5)	O(15)-Dy(1)-O(3) 68.6(5)	O(10)-Dy(1)-O(3) 106.2(5)	O(3)-Dy(1)-O(1) 134.1(5)	O(7)-Dy(1)-O(1) 137.8(6)
O(15)-Dy(1)-O(7) 142.8(6)	O(10)-Dy(1)-O(7) 64.4(6)	O(3)-Dy(1)-O(7) 79.2(5)	O(15)-Dy(1)-O(5) 79.1(6)	O(10)-Dy(1)-O(5) 138.6(5)
O(15)-Dy(1)-O(13) 68.1(6)	O(10-Dy(1)-O(13) 76.8(6)	O(3)-Dy(1)-O(13) 59.6(6)	O(7)-Dy(1)-O(5) 77.1(5)	O(13)-Dy(1)-O(5) 134.2(6)
O(7)-Dy(1)-O(13) 111.1(5)	O(15)-Dy(1)-O(1) 79.3(6)	O(10)-Dy(1)-O(1) 79.4(6)	O(15)-Dy(1)-O(12) 128.1(5)	O(10)-Dy(1)-O(12) 70.8(5)
O(7)-Dy(1)-O(5) 77.1(5)	O(13)-Dy(1)-O(5) 134.2(6)	O(7)-Dy(1)-O(5) 77.1(5)	O(3)-Dy(1)-O(1) 134.1(5)	O(7)-Dy(1)-O(1) 137.8(6)
N(3)-Co(1)-N(15) 94.5(8)	N(17)-Co(1)-N(1) 172.5(8)	N(14)-Co(1)-N(1) 89.8(10)	O(15)-Dy(1)-O(5) 79.1(6)	O(10)-Dy(1)-O(5) 138.6(5)

Table S3. Selected bond distances (Å) and angles (deg) for **2**.

Ho(1)-O(11) 2.299(9)	Ho(1)-O(1) 2.307(10)	Ho(2)-O(2) 2.382(9)	Ho(2)-O(10) 2.427(9)	Ho(3)-O(12) 2.442(9)
Ho(1)-O(9) 2.339(11)	Ho(1)-O(21) 2.344(12)	Ho(2)-O(3) 2.393(9)	Ho(2)-O(13) 2.429(9)	Ho(4)-O(4) 2.330(10)
Ho(1)-O(10) 2.377(10)	Ho(1)-O(2) 2.378(9)	Ho(2)-O(38) 2.407(9)	Ho(2)-O(12) 2.518(8)	Ho(4)-O(38) 2.343(9)

Ho(1)-O(40) 2.389(14)	Ho(1)-O(39) 2.639(15)	Ho(2)-O(7) 2.416(9)	Ho(3)-O(5) 2.326(9)	Ho(4)-O(14) 2.354(9)
Ho(1)-N(20) 2.752(15)	Ho(2)-O(11) 2.357(10)	Ho(2)-O(37 2.422(9)	Ho(3)-O(37) 2.335(8)	Ho(4)-O(15) 2.364(10)
Ho(4)-O(22) 2.372(12)	Ho(4)-O(3) 2.392(9)	Ho(4)-O(23) 2.424(11)	Ho(4)-O(18) 2.487(13)	Ho(4)-O(19) 2.628(13)
Co(2)-N(17) 1.963(13)	Co(2)-N(14) 1.960(13)	Co(2)-N(11) 1.941(11)	Co(1)-N(8) 1.958(11)	Co(1)-N(3) 1.968(12)
Co(2)-N(16) 1.880(12)	Co(2)-N(10) 1.891(12)	Co(2)-N(16) 1.880(12)	Co(1)-N(4) 1.882(13)	Co(1)-N(1) 1.900(12)
O(11)-Ho(1)-O(1) 84.0(3)	O(11)-Ho(1)-O(9) 87.5(4)	O(1)-Ho(1)-O(9) 155.4(4)	O(11)-Ho(1)-O(21) 130.4(4)	O(1)-Ho(1)-O(21) 78.4(4)
O(9)-Ho(1)-O(21) 89.9(4)	O(11)-Ho(1)-O(10) 70.9(3)	O(1)-Ho(1)-O(10) 129.7(3)	O(9)-Ho(1)-O(10) 67.8(4)	O(21)-Ho(1)-O(10) 149.9(4)
O(11)-Ho(1)-O(2) 69.3(3)	O(1)-Ho(1)-O(2) 69.5(3)	O(9)-Ho(1)-O(2) 128.3(4)	O(21)-Ho(1)-O(2) 140.4(4)	O(10)-Ho(1)-O(2) 61.2(3)
O(11)-Ho(1)-O(40) 149.2(4)	O(1)-Ho(1)-O(40) 119.5(4)	O(9)-Ho(1)-O(40) 77.8(4)	O(21)-Ho(1)-O(40) 77.1(5)	O(10)-Ho(1)-O(40) 78.5(4)
O(2)-Ho(1)-O(40) 98.9(4)	O(11)-Ho(1)-O(39) 138.6(4)	O(1)-Ho(1)-O(39) 69.9(4)	O(9)-Ho(1)-O(39) 128.5(4)	O(21)-Ho(1)-O(39) 76.1(5)
O(10)-Ho(1)-O(39) 101.5(4)	O(2)-Ho(1)-O(39) 71.6(4)	O(40)-Ho(1)-O(39) 50.8(4)	O(11)-Ho(1)-N(20) 60.3(4)	O(1)-Ho(1)-N(20) 87.2(4)
O(9)-Ho(1)-N(20) 68.6(4)	O(21)-Ho(1)-N(20) 72.8(5)	O(10)-Ho(1)-N(20) 114.1(4)	O(2)-Ho(1)-N(20) 126.2(3)	O(40)-Ho(1)-N(20) 134.2(5)
O(39)-Ho(1)-N(20) 144.4(5)	N(7)-Co(1)-N(4) 90.5(5)	N(7)-Co(1)-N(1) 91.6(5)	N(7)-Co(1)-N(5) 171.8(5)	N(1)-Co(1)-N(8) 170.6(5)

Table S4. Selected bond distances (Å) and angles (deg) for **3**.

Tm(1)-O(3) 2.264(11)	Tm(1)-O(18) 2.273(15)	Tm(1)-O(17) 2.283(14)	Tm(1)-O(6) 2.288(13)	Tm(1)-O(2) 2.297(13)
Tm(1)-O(5) 2.340(13)	Tm(1)-O(1) 2.359(12)	Tm(1)-N(4) 2.699(17)	Tm(1)-O(19) 2.718(15)	Tm(4)-O(22) 2.712(16)
Tm(2)-O(4) 2.232(11)	Tm(2)-O(8) 2.294(11)	Tm(2)-O(7) 2.299(10)	Tm(2)-O(16)#1 2.30(11)	Tm(2)-O(12)#1 2.370(12)
Tm(2)-O(4)#1 2.419(11)	Tm(2)-O(15)#1 2.43(10)	Tm(2)-N(10)#1 2.467(14)	Tm(4)-O(10) 2.326(12)	Tm(4)-O(24) 2.436(15)
Tm(3)-O(3)#1 2.313(12)	Tm(3)-O(1)#1 2.372(11)	Tm(3)-O(9) 2.380(12)	Tm(3)-O(14) 2.385(12)	Tm(3)-O(15) 2.401(11)
Tm(3)-O(5)#1 2.405(12)	Tm(3)-O(12) 2.419(11)	Tm(3)-O(7) 2.428(11)	Tm(3)-O(4)#1 2.518(11)	Tm(4)-O(21) 2.343(14)
Co(2)-N(23) 1.904(12)	Tm(4)-O(11) 2.315(11)	Tm(4)-O(14) 2.318(13)	Co(1)-N(15) 1.956(13)	Tm(4)-O(13) 2.339(13)
Co(2)-N(20) 1.878(14)	Tm(4)-O(25) 2.361(14)	Tm(4)-O(9) 2.377(12)	Co(2)-N(7)#1 1.967(16)	Co(2)-N(18) 1.959(14)
Co(1)-N(17) 1.893(14)	Co(1)-N(3)#1 1.893(13)	Co(1)-N(14) 1.897(12)	Co(1)-N(12) 1.943(13)	Co(1)-N(1)#1 1.951(14)
O(3)-Tm(1)-O(18) 149.0(5)	O(3)-Tm(1)-O(17) 133.7(5)	O(18)-Tm(1)-O(17) 76.0(6)	O(3)-Tm(1)-O(6) 89.9(4)	O(18)-Tm(1)-O(6) 80.3(5)
O(17)-Tm(1)-O(6) 89.3(5)	O(3)-Tm(1)-O(2) 85.6(4)	O(18)-Tm(1)-O(2) 114.6(4)	O(17)-Tm(1)-O(2) 77.0(5)	O(6)-Tm(1)-O(2) 155.9(5)
O(3)-Tm(1)-O(5) 70.7(4)	O(18)-Tm(1)-O(5) 78.3(5)	O(17)-Tm(1)-O(5) 149.1(5)	O(6)-Tm(1)-O(5) 69.6(5)	O(2)-Tm(1)-O(5) 130.1(4)
O(3)-Tm(1)-O(1) 69.0(4)	O(18)-Tm(1)-O(1) 95.2(5)	O(17)-Tm(1)-O(1) 137.8(5)	O(6)-Tm(1)-O(1) 130.4(5)	O(2)-Tm(1)-O(1) 69.5(4)
O(5)-Tm(1)-O(1) 61.2(4)	O(3)-Tm(1)-N(4) 62.9(5)	O(18)-Tm(1)-N(4) 136.4(5)	O(17)-Tm(1)-N(4) 74.0(5)	O(6)-Tm(1)-N(4) 68.5(5)
O(2)-Tm(1)-N(4) 88.4(5)	O(5)-Tm(1)-N(4) 115.7(5)	O(1)-Tm(1)-N(4) 128.2(4)	O(3)-Tm(1)-O(19) 137.7(4)	O(18)-Tm(1)-O(19) 46.3(3)
O(17)-Tm(1)-O(19) 74.3(6)	O(6)-Tm(1)-O(19) 126.2(4)	O(2)-Tm(1)-O(19) 69.4(4)	O(5)-Tm(1)-O(19) 99.7(5)	O(1)-Tm(1)-O(19) 70.5(4)

2: Magnetic Measurements.

The magnetic susceptibility was measured on polycrystalline samples with the Quantum Design SQUID magnetometer SQUID-VSM in the temperature range 1.8-300 K under an applied field of 1.0 KOe. AC susceptibility measurements were carried out in a zero applied dc field and 1000 Oe dc field for complexes.

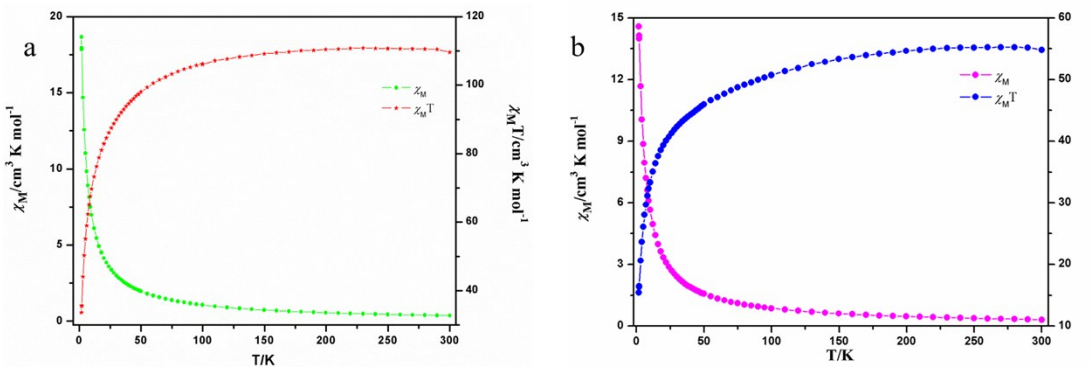

Figure S4. Temperature dependent magnetic susceptibility of complexes (a){$Co^{III}_4Ho_8$} (**2**), (b){$Co^{III}_4Tm_8$} (**3**) (1000 Oe; 2−300 K)

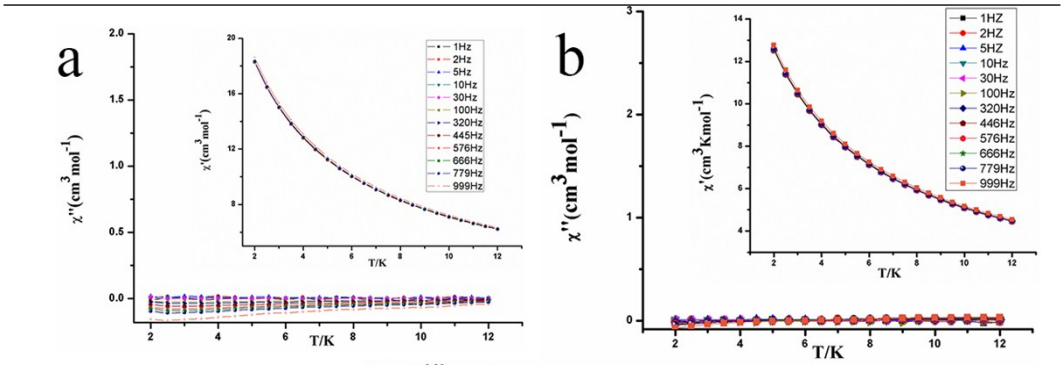

Figure S5. Plots of the out-phase (χ''M) and in-phase (χ'M) ac magnetic susceptibility vs. T for {$Co^{III}_4Ho_8$} (**2**) (a), {$Co^{III}_4Tm_8$} (**3**) (b), under zero-applied dc field between 1 and 1000 Hz and between 2.0 and 12 K.

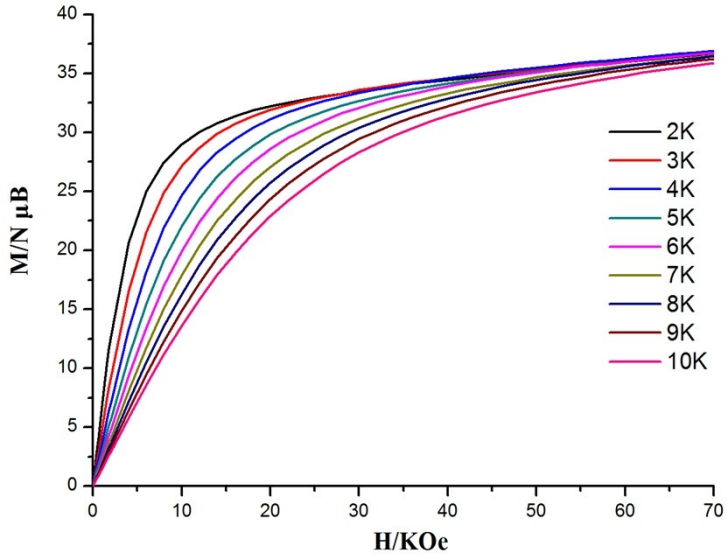

Figure S6. Field dependent magnetization of {$Co^{III}_4Dy_8$} (**1**).

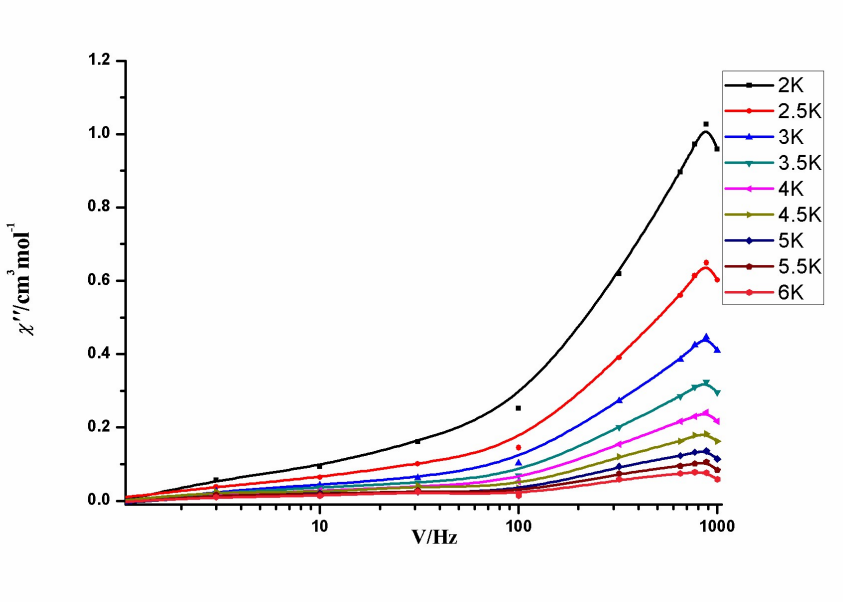

Figure S7. χ"M vs. frequency for {$Co^{III}_4Dy_8$} (**1**) below 6.0 K under zero-dc field.

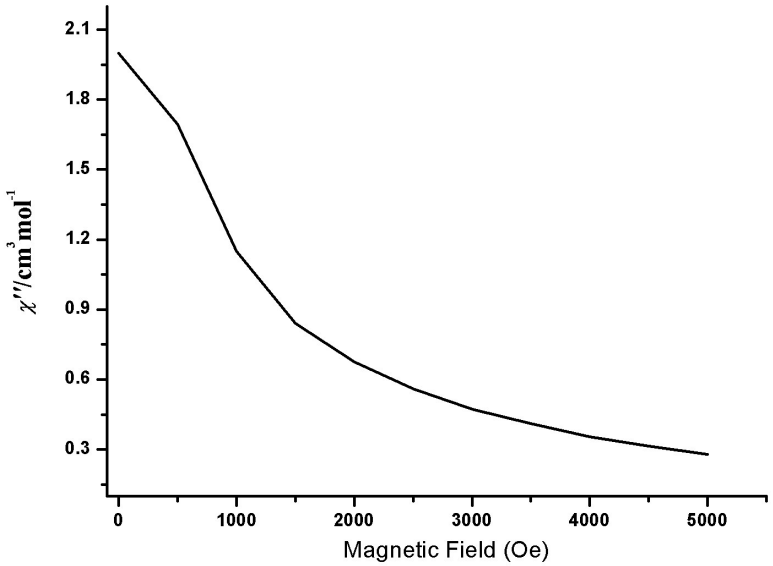

Figure S8. Ac-scanfield data of {$Co^{III}_4Dy_8$} (**1**) at 999 Hz and 2.0 K.

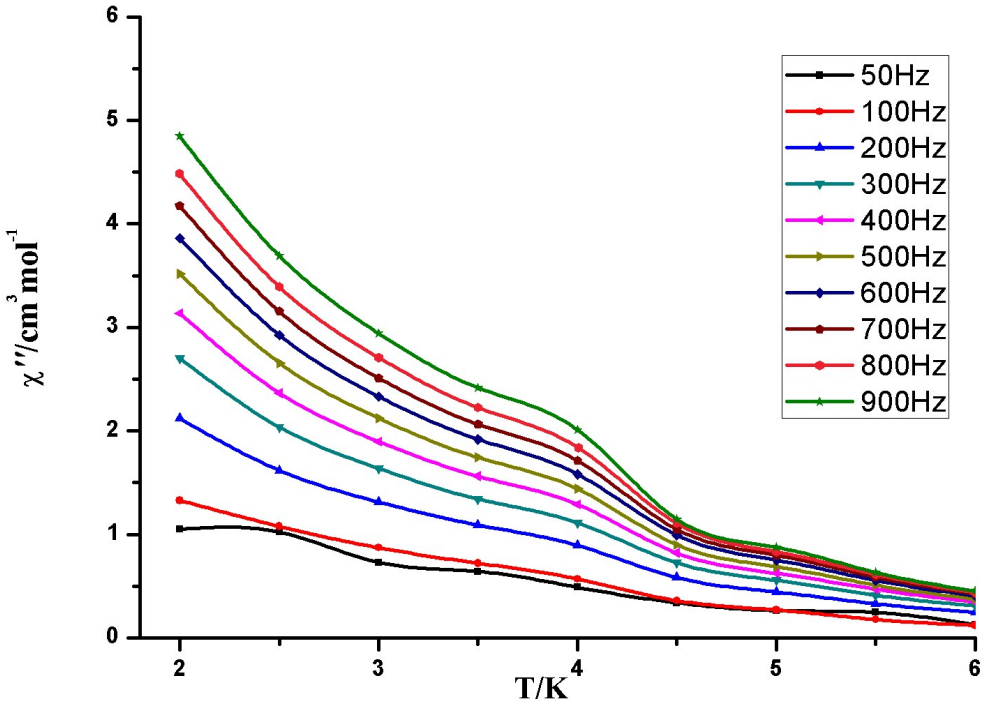

Figure S9. Plots of the out-phase (χ''_M) of $\{Co^{III}_4Dy_8\}$ (**1**) between 2 K and 6 K under 1000-dc field.

References

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