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Electronic Supplementary Information

Two novel 3d-4f heterometallic coordination polymers with infinite $[Ln_4(OH)_4]_n^{8n+}$ chains involving *in situ* decarboxylation

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Materials and methods

All commercially available chemicals are of analytical reagent grade and used as supplied without further purification. The C, H and N microanalyses were carried out with a Perkin-Elmer 240Q elemental analyzer. The IR spectra were recorded on a Varian 660-IR spectrometer photometer as KBr pellets in the 4000-400cm^{-1}. TGA were recorded with a Netzsch TG 209 apparatus under a nitrogen atmosphere. All of magnetic measurements were performed on a Quantum Design SQUIDMPMS VSM magnetometer.Diamagnetic corrections were made with Pascal's constants for all the sample holders and constituent atoms.

X-Ray crystallography

Single crystals appropriate for the X-ray diffraction analysis were elaborately selected under microscope. Single-crystal determinations were performed on SMART APEX CCD diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were collected using ω scans mode, and corrected for Lorentz and polarisation effects and absorption using SADABS software. The structures were solved by direct methods with SHELXS-97 software and difference Fourier techniques.[1] The non-hydrogen atoms were also solved by direct methods, and their coordinates and anisotropic thermal parameters were refined by full-matrix least-squares methods on F^2. The positions of hydrogen atoms were obtained by hydrogenation theoretically. All of the calculations were carried out with program SHELXS-97 and program SHELXL-97. The hydrogen bonding parameters are shown in Table S1-S2. CCDC-1027471 (**1**) and CCDC-1027472 (**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

Ref S1. M. Sheldrick, *ActaCryst.*, 2008, **A64**, 112–122.

Synthesis of $[Tb_4Co(QDA)_2(QA)_6(OH)_4(H_2O)_4]$ (1) : A mixture of Tb_4O_7 (0.100 g, 0.1 mmol), $Co(NO_3)_2·6H_2O$ (0.116 g, 0.4 mmol), H_2QDA (0.217 g, 1mmol) and 8 mL water was sealed in a 23 mL Teflon-lined bomb at 150 ℃ for 2 days, and then cooled to room temperature at the rate of 20 ℃ h^{-1}. Brown prismatic crystals for **1** were obtained (yield: 28% based on Tb_4O_7). Anal. Calc. for **1**, $CoTb_4C_{82}H_{58}N_8O_{28}$: C 42.82, H 2.52, N 4.87%. Found: C 42.52, H 2.91, N 4.74%. IR bands (cm^{-1}) for **1**: 3432(vs), 1617(vs), 1601(vs), 1579(vs), 1545(s), 1493(w), 1461(s), 1428(s), 1416(s), 1400(s), 1317(m), 1210(w), 1128(w), 1066(w), 964(w), 937(w), 799(s), 770(w), 748(m), 614(w), 590(m).

Synthesis of $[Dy_4Co(QDA)_2(QA)_6(OH)_4(H_2O)_4]$ (2) : A mixture of Dy_2O_3 (0.075 g, 0.2 mmol), $Co(NO_3)_2·6H_2O$ (0.116 g, 0.4 mmol), H_2QDA (0.217 g, 1 mmol) and 8 mL water was sealed in a 23 mL Teflon-lined bomb at 150 ℃for 2 days, and then cooled to room temperature at the rate of 20 ℃ h^{-1}. Brown prismatic crystals for **2** were obtained (yield: 23% based on Dy_2O_3). Anal. Calc. for **2**, $CoDy_4C_{82}H_{58}N_8O_{28}$: C 42.56, H 2.51, N 4.84%. Found: C 42.56, H 2.88, N 5.06%. IR bands (cm^{-1}) for **2**: 3444(vs), 1647(vs), 1620(vs), 1587(vs), 1543(s), 1508(w), 1496(w), 1465(s), 1433(s), 1409(s), 1323(m), 1209(w), 1109(w), 1055(w), 960(w), 927(w), 800(s), 773(w), 748(m), 615(w), 596(m).

Crystallographic data for compound 1: M_r = 2297.97, triclinic, $P\bar{1}$, a = 7.6995(15) Å, b = 13.461(3) Å, c = 19.040(4) Å, α = 109.24(3)°, β = 93.49(3)°, γ = 92.70(3)°, V = 1879.6(6) $Å^3$, Z = 1, D_c = 2.030 g cm^{-3}, μ = 4.025 mm^{-1}, $F(000)$ = 1117, GOF = 1.085, a total of 18022 reflections were collected, 8308 of which were unique (R_{int} = 0.0344). R_1 (wR_2) = 0.0330 (0.0866) for 556 parameters and 7096 reflections ($I > 2\sigma(I)$).

Crystallographic data for compound 2: M_r = 2312.29, triclinic, $P\bar{1}$, a = 7.6805(15) Å, b = 13.635(3) Å, c = 19.036(4) Å, α = 109.16(3)°, β = 93.43(3)°, γ = 92.75(3)°, V = 1875.0(6) $Å^3$, Z = 1, D_c = 2.048g cm^{-3}, μ = 4.248 mm^{-1}, $F(000)$ = 1121, GOF = 1.097, a total of 18364 reflections were collected, 8474 of which were unique (R_{int} = 0.0313). R_1 (wR_2) = 0.0299 (0.0715) for 556 parameters and 7444 reflections ($I > 2\sigma(I)$).

Table S1 SHAPE analysis of Dy^{III} cation in **2**.

Label	SHAPE	Symmetry	Distortion(Dy1/Dy2)
OP-8	Octagon	D_{8h}	32.502/28.377
HPY-8	Heptagonal pyramid	C_{7v}	23.691/25.238
HBPY-8	Hexagonal bipyramid	D_{6h}	14.004/11.824
CU-8	Cube	O_h	9.587/7.718
SAPR-8	Square antiprism	D_{4d}	2.773/2.745
TDD-8	Triangular dodecahedron	D_{2d}	1.316/3.003
JGBF-8	Johnson gyrobifastigium J26	D_{2d}	12.526/9.887
JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	26.762/26.250
JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	1.787/2.242
BTPR-8	Biaugmented trigonal prism	C_{2v}	1.682/1.881
JSD-8	Snub diphenoid J84	D_{2d}	3.798/4.007
TT-8	Triakis tetrahedron	T_d	10.313/8.345
ETBPY-8	Elongated trigonal bipyramid	D_{3h}	23.527/22.223

Table S2 Hydrogen bonds for compound **1**.

D-H...A/(°)	d(D-H)/(Å)	d(H...A)/(Å)	d(D...A)/(Å)	<(D-H-A)
O(11)-H(111)...O(6)#3	0.85	2.12	2.949(6)	164.3
O(12)-H(121)...O(10)#3	0.85	2.25	3.030(6)	152.5
O(13)-H(131)...O(9)#6	0.85	2.48	2.865(5)	108.7
O(13)-H(131)...O(8)#6	0.85	2.71	2.941(5)	97.3
O(14)-H(141)...N(3)	0.85	1.92	2.743(7)	161.7
O(14)-H(142)...O(6)#7	0.85	1.90	2.754(7)	177.3

Symmetry transformations used to generate equivalent atoms:

#3 -*x*+1, -*y*, -*z*; #6 -*x*, -*y*, -*z*; #7 -*x*+1, -*y*+1, -*z*

Table S3 Hydrogen bonds for compound **2**.

D-H...A/(°)	d(D-H)/(Å)	d(H...A)/(Å)	d(D...A)/(Å)	<(D-H-A)
O(11)-H(111)...O(6)#3	0.85	2.13	2.953(5)	163.9
O(12)-H(121)...O(10)#3	0.85	2.25	3.029(5)	152.4
O(13)-H(131)...O(9)#6	0.85	2.47	2.856(4)	108.6
O(13)-H(131)...O(8)#6	0.85	2.70	2.934(4)	97.3
O(14)-H(141)...N(3)	0.85	1.92	2.742(6)	161.7
O(14)-H(142)...O(6)#7	0.85	1.91	2.756(5)	177.0

Symmetry transformations used to generate equivalent atoms:

#3 -*x*+1, -*y*, -*z*; #6 -*x*, -*y*, -*z*; #7 -*x*+1, -*y*+1, -*z*

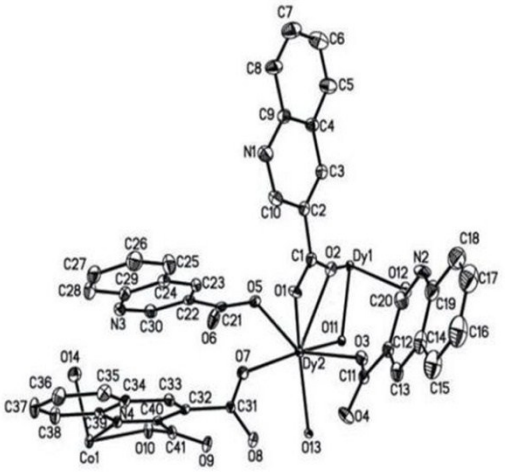

Fig. S1 The asymmetric unit of **2**.

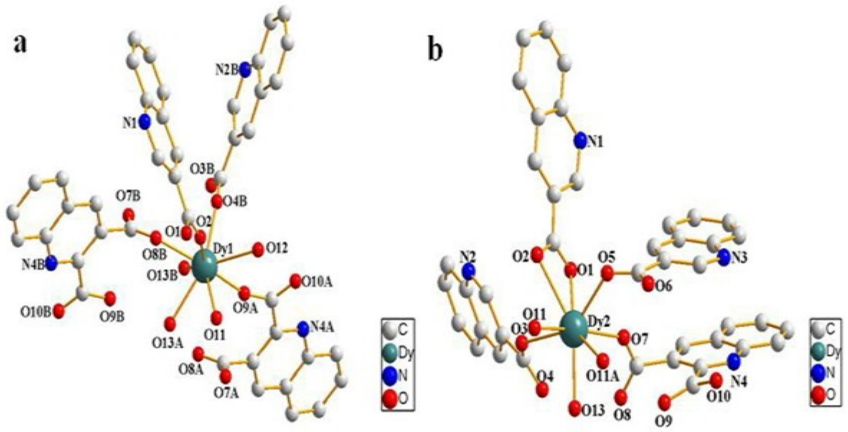

Fig. S2 Coordination environment of Dy1 (a) and Dy2 (b). Atoms with A, B in their labels are symmetry generated. Symmetry code: A: 1-*x*, -*y*, -*z*; B: 1+*x*, *y*, *z*.

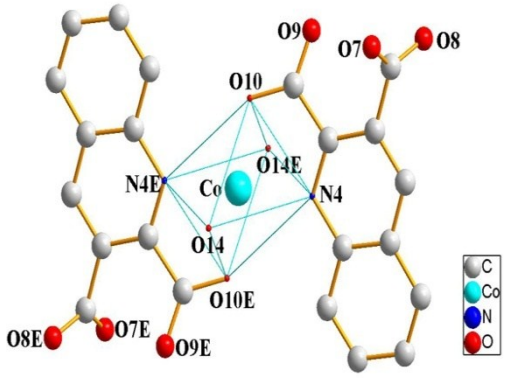

Fig. S3 Coordination environment of Co. Atoms with E in their labels are symmetry generated. Symmetry code: E: -*x*, 1-*y*, -*z*.

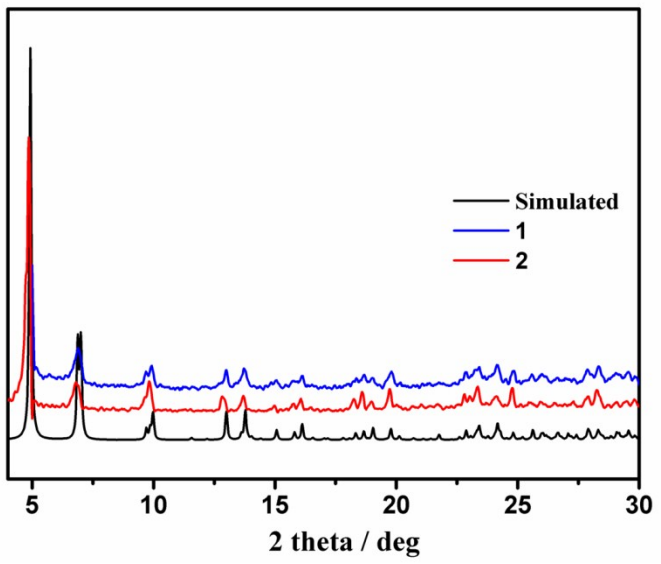

Fig. S4 PXRD patterns of **1** and **2**.

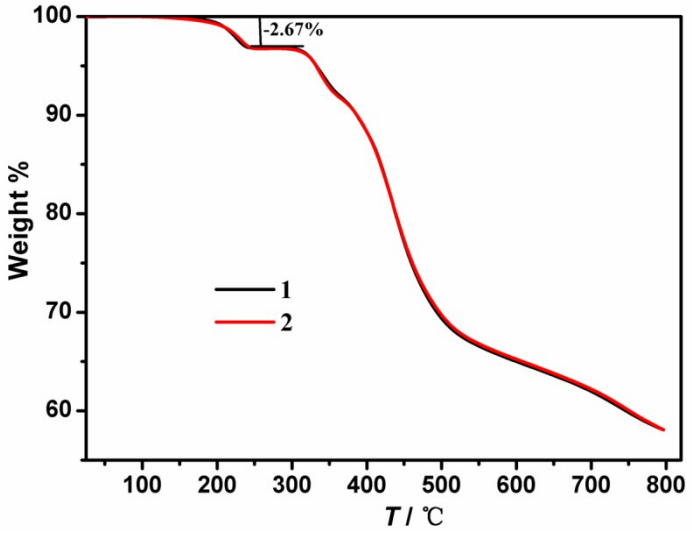

Fig. S5 The TG curves of **1** and **2**.

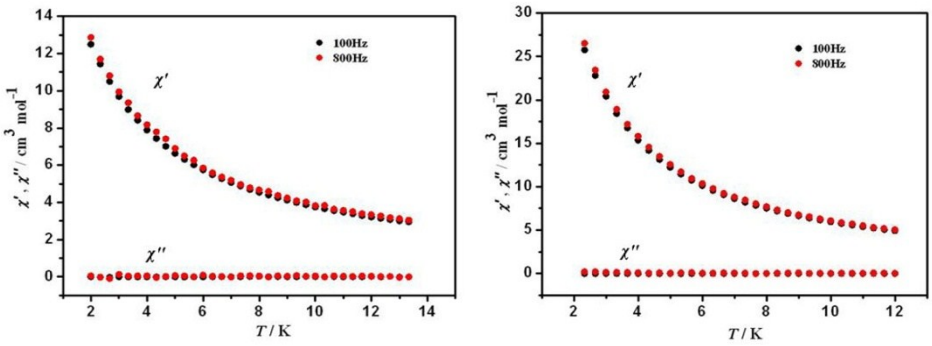

Fig. S6 Temperature dependence of ac susceptibilities under zero field for **1** (left) and **2** (right).