Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Two organic-inorganic hybrid polyoxotungstogermanates containing organic ligand chelated Fe-Dy heterometallic clusters and frequency dependent magnetic properties

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Contents

1. Materials and Methods

Preparation of aqueous solutions of $Dy(ClO_4)_3$ (1.0 mol L^{-1}): Dy_2O_3 (0.125 mol, 46.63g), adding perchloric acid aqueous solution(70.0% -72.0%, 60.0 ml) at about 70 ℃. Aqueous solution of 1.0 mol L^{-1} Dy $(ClO_4)_3$ was obtained by diluting the concentrated solution to 250.00 ml with deionized water.

Preparation of aqueous solutions of $K_8Na_2[GeW_9O_{34}]$ $25H_2O$: 2.092 g germanium dioxide was dissolved in 40 mL of 1 M sodium hydroxide solution. An aqueous solution containing 72.6 g of sodium tungstate dihydrate in 120 mL of water was added to the solution. The mixture was stirred and heated. 80 mL of 4 M hydrochloric acid was added to the hot solution with vigorous stirring. The solution was boiled for about 1h and cooled to room temperature. A white salt was precipitated upon addition of 30g of solid potassium chloride. The salt was recrystallized from hot water, we can get $K_6Na_2[GeW_{11}O_{39}]$ $13H_2O$. 43.5 g (13.5 mmol) sample of $K_6Na_2[GeW_{11}O_{39}]$ $13H_2O$ was dissolved in 400 mL of water with stirring. Then 22.5 g (162.8 mmol) of K_2CO_3 was added. After stirring for about 30 min. (pH=9.5), a white precipitate appeared slowly. After an additional 20 min of stirring, the white solid product was collected, Stirring was continued for 20 minutes, suction filtered, and washed with saturated KCl solution (20 mL), and airdried. The yield is about 34.8 g and the yield is about 80%.

2. Additional Figure

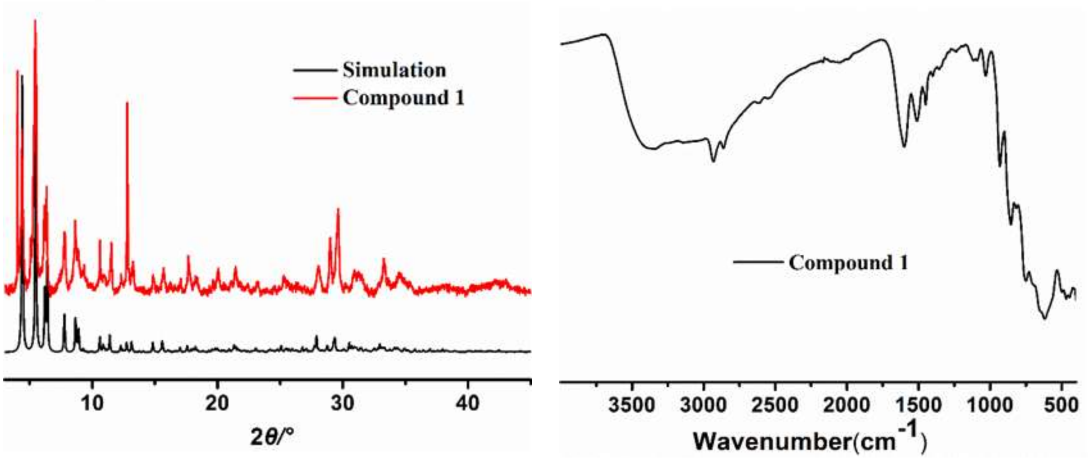

Fig. S1 Left: the simulated and experimental PXRD patterns; Right: IR spectrum of the compound **1.**

The absorption peak of compound **1** at 3367 cm $^{-1}$ is attributed to the stretching vibration peak of the O-H group of the water and the O–H of the coordinating hydroxyl group. The absorption peak of 1600 cm $^{-1}$ corresponds to the H–O–H bending vibration of crystal waters. The absorption peaks at 2862 cm $^{-1}$ and 2932 cm^{-1} are attributed to the stretching vibration peak of C–H group and N–H of *trans*-1,2-diaminocyclohexane. The absorption peak of 1448 cm $^{-1}$ is attributed to the bending vibration of C–H bending vibration, and the peaks at 1105 cm^{-1} and 1034 cm^{-1} are attributed to N–H bending vibrations. Characteristic absorption peaks in the range of 600 - 1000 cm $^{-1}$ may be attributed to v_{as} (W–O$_c$ –W) , v_{as} (W–O$_b$–W), v_{as} (Ge–O$_a$), v_{as} (W –O$_t$) stretching vibration peaks. The characteristic absorption peaks at 459 cm $^{-1}$ belong to the stretching vibration peak of v_{as} (Fe-O) and v_{as} (Dy-O) .

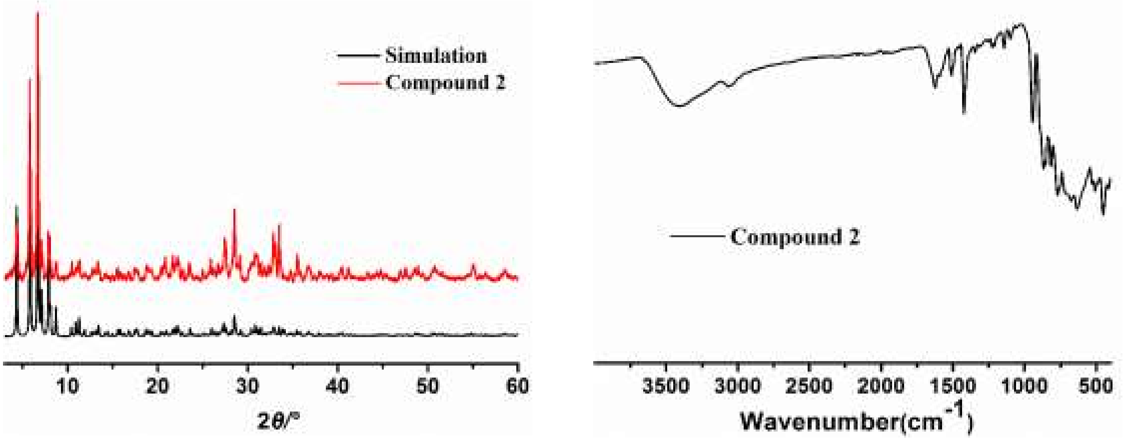

Fig. S2 Left: the simulated and experimental PXRD patterns; Right: IR spectrum of the compound **2.**

The absorption peak of compound **2** at 3412 cm $^{-1}$ is attributed to the stretching vibration peak of the O-H group of the water and the O–H of the coordinating hydroxyl group. The absorption peak of 1629 cm $^{-1}$ corresponds to the H–O–H bending vibration of crystal waters. The absorption peaks at 3064 cm^{-1} are attributed to the stretching vibration of Ar-H group of 1,10-phen. The absorption peaks of 1513 cm^{-1} and 1422 cm $^{-1}$ are attributed to the ring vibration of benzene ring, and the peaks at 1215 cm^{-1} and 1145 cm^{-1} are attributed to C-C and C-N stretching vibrations. Characteristic absorption peaks in the range of 600 - 1000 cm $^{-1}$ may be attributed to ν_{as} (W–O$_c$ –W) , ν_{as} (W–O$_b$–W), ν_{as} (Ge–O$_a$), ν_{as} (W –O$_t$) stretching vibration peaks. The characteristic absorption peaks at 508 cm^{-1} and 459 cm $^{-1}$ belong to the stretching vibration peaks of ν_{as} (Fe-O) and ν_{as} (Dy-O) .

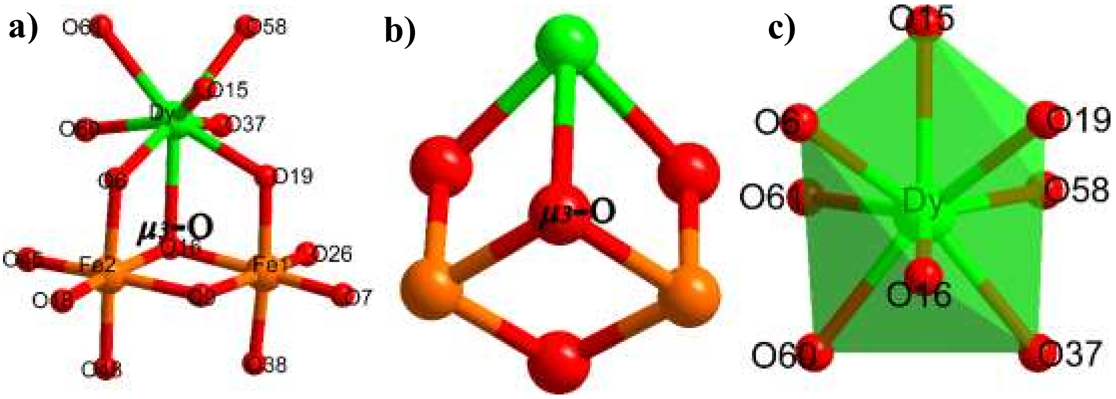

Fig. S3 (a) {Fe_2DyO_3} six-member ring *via* vertex-sharing in **1**; (b) The μ_3-O atom is capped on the {Fe_2DyO_3} six-member ring in **1**; (c) The coordination environment of Dy^{3+} in {Fe_2DyO_4} cluster in **1**.

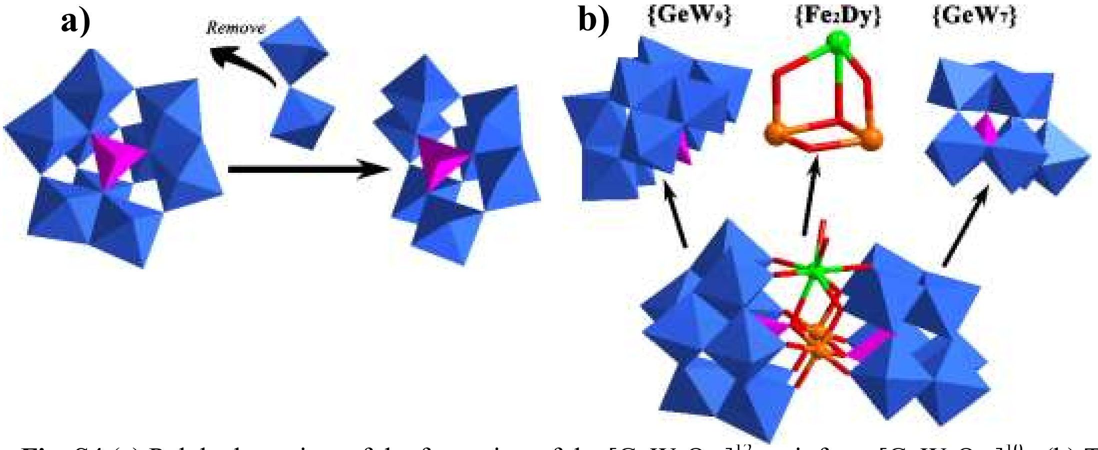

Fig. S4 (a) Polyhedron view of the formation of the $[GeW_7O_{29}]^{12-}$ unit from $[GeW_9O_{34}]^{10-}$; (b) The tungstogermanate dimer in compound **1**.

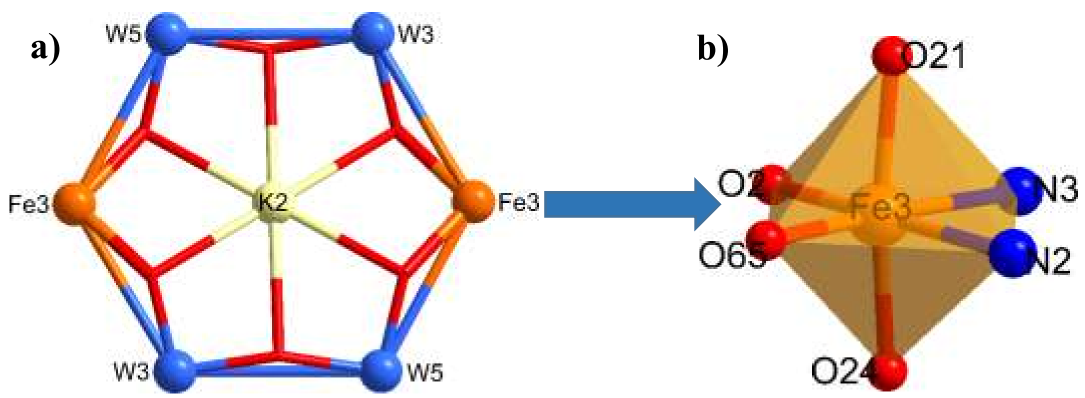

Fig. S5 (a) View of the hexagonal [$Fe_2W_4O_6$] ring in the middle layer of compound **1**; (b) The coordination environment of Fe(3) in the middle layer of compound **1**.

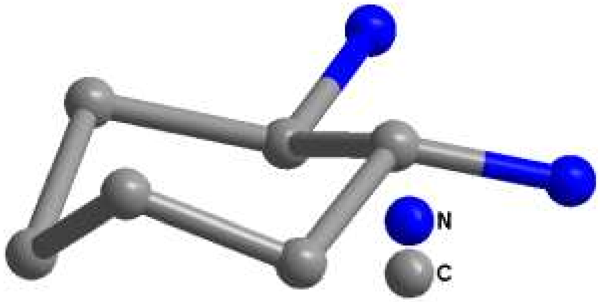

Fig. S6 The chair-configuration of the *trans*-1,2-cyclohexanediamine ligand in compound **1**.

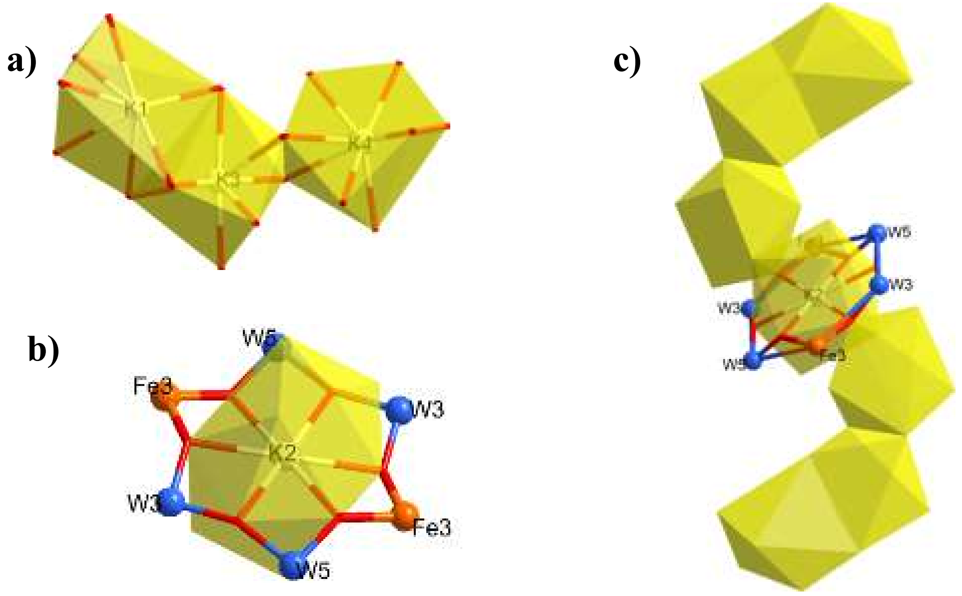

Fig. S7 (a) A "V"-shaped trinuclear [K_3O_5] cluster subunit in **1**; (b) The K(2) atom is embedded in the center of the regular hexagonal [$Fe_2W_4O_6$] ring and coordinated with six O atoms of the [$Fe_2W_4O_6$] ring in **1**; (c) "S"-shaped [K_7O_{14}] cluster-chain fragment passes through the middle layer of tetrameric tungstogermanate in **1**.

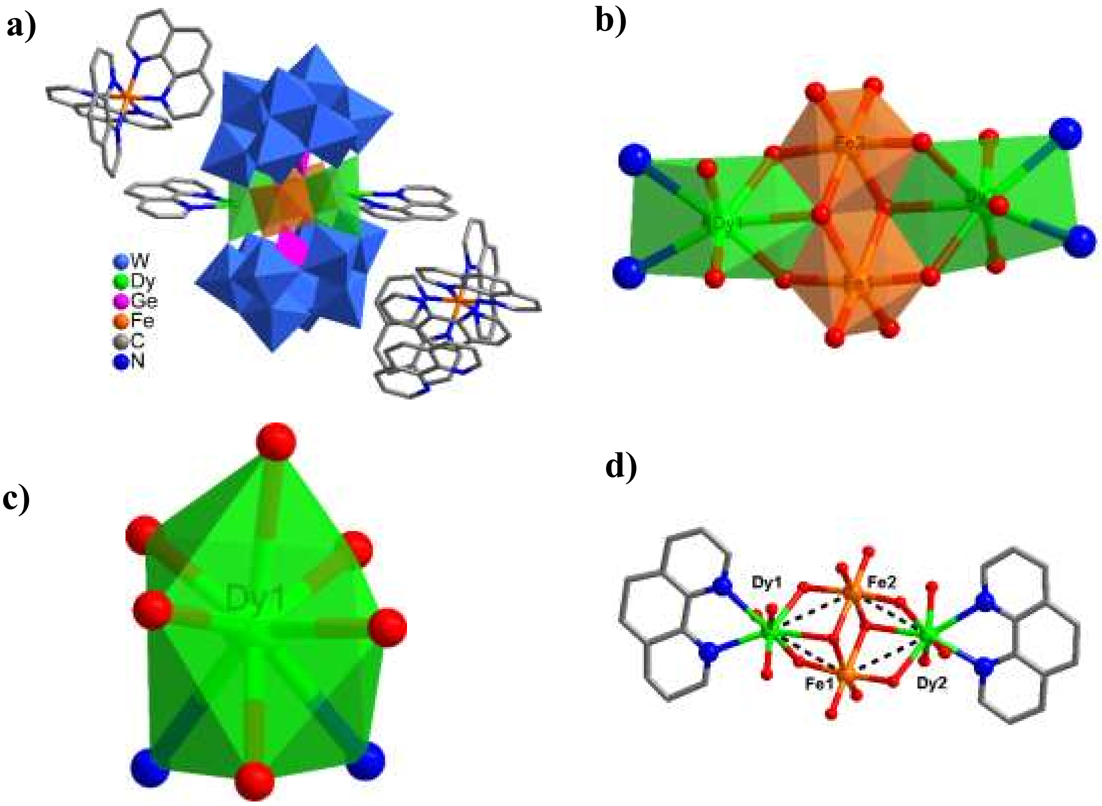

Fig. S8 (a) The asymmetric unit of **2** containing a dimer $[Dy_2(phen)_2Fe_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$ polyanion, two $[Fe(phen)_3]^{3+}$ cation, two $(H_2phen)^{2+}$; (b) The coordination environment of Fe^{3+} and Dy^{3+} in $\{(phen)_2Dy_2Fe_2O_6\}$ cluster unit of **2**; (c) The coordination geometry Dy^{3+} in $[(phen)_2Dy_2Fe_2O_6]$ cluster unit in **2**; (d) View of the $\{(phen)_2Dy_2Fe_2O_6\}$ cluster unit in **2**.

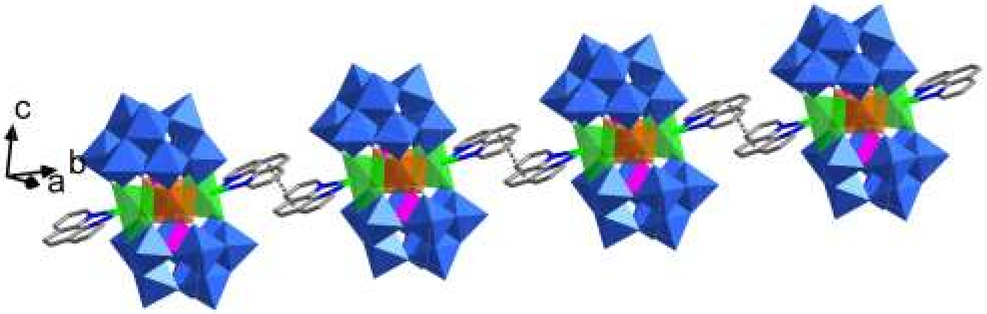

Fig. S9 View of 1D supramolecular linear chain structure running along *b* axis in compound **2**.

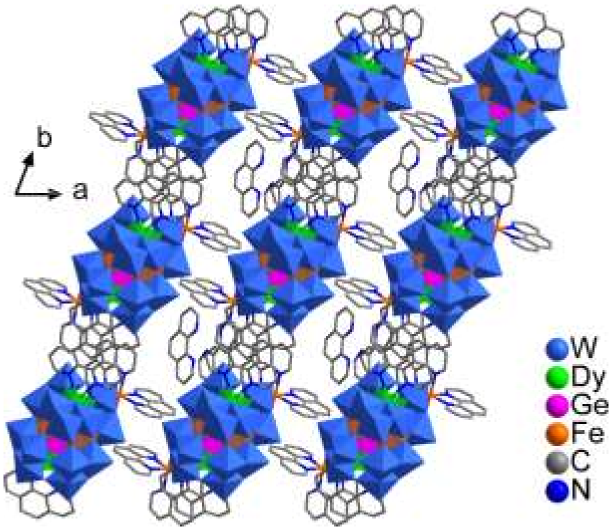

Fig. S10 3-D supramolecular network of compound **2** viewed along *c* axis.

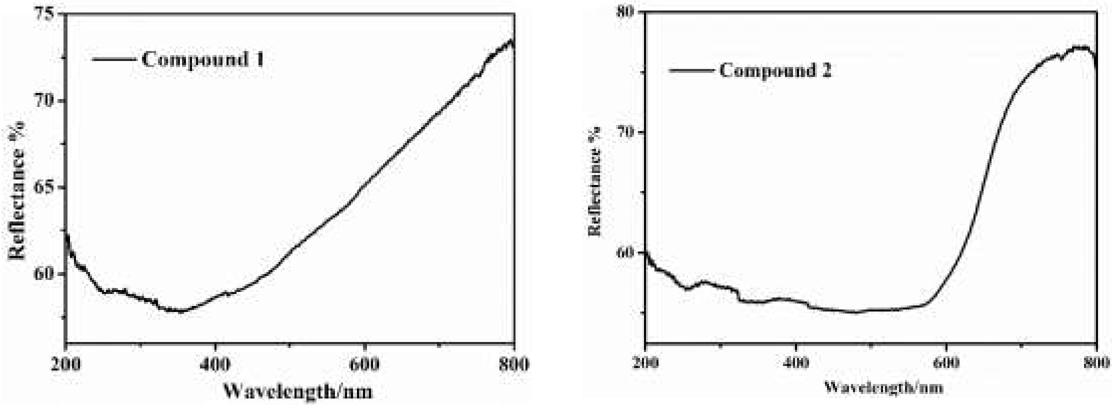

Fig. S11 The UV spectra of compound **1** (L) patterns and The UV spectra of compound **2** (R).

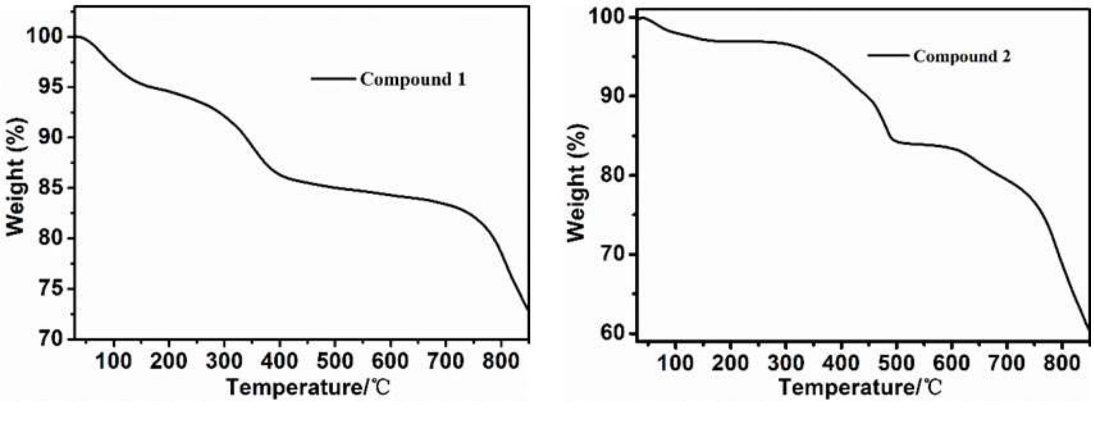

Fig. S12 (Left): The TG curve of compound **1;** (Right) TG curve of compound **2**.

Thermal gravimetric analyses (TGA) of **1**, **2** were performed under nitrogen atmosphere in the range 35–850 °C to determine their thermal stabilities. There are three-step weight loss for **1**, the first weight loss of 5.61% for **1** from 150 to 280 °C corresponding to the release of the 6 free trans-1, 2-Diaminocyclohexane molecules (calcd 6.68% for **1**). The second weight loss of 10.21% for **1** from 280 to 420 °C corresponding to the water molecules and the coordinated t*rans*-1, 2-diaminocyclohexane molecules in the structure. There are three-step weight loss for **2**, the first weight loss of 2.96% for **2** from 30 to 150 °C corresponding to the release of the 2 free 1,10-phen ligands. The second weight loss of 13.12% for **2** from 310 to 500 °C corresponding to the eight coordinated phen ligands in the structure.

3. Bond Valence Sum (BVS) Calculations

Table S1. The bond valence sum calculations of the Ge W Dy and Fe atoms for compound 1.

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
Dy1	3.75347	3	W2	6.22127	6	W10	6.25480	6
Fe1	3.09779	3	W3	6.04513	6	W11	5.83076	6
Fe2	3.07315	3	W4	5.83814	6	W12	6.18255	6
Fe3	3.04974	3	W5	6.16814	6	W13	6.10144	6
Ge1	3.93667	4	W6	6.12364	6	W14	6.07601	6
Ge2	3.98346	4	W7	6.29844	6	W15	6.25071	6
Ge3	3.77117	4	W8	6.18100	6	W16	5.93751	6
W1	5.88324	6	W9	6.14300	6			

Table S2. The bond valence sum calculations of the Ge W Dy and Fe atoms for compound 2.

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
Dy1	3.15111	3	W2	6.14833	6	W11	5.77785	6
DY2	2.96308	3	W3	6.34293	6	W12	6.46779	6
Fe1	3.14620	3	W4	5.95656	6	W13	5.91292	6
Fe2	2.78834	3	W5	5.68375	6	W14	6.46918	6
FE3	3.31863	4	W6	5.66712	6	W15	6.10364	6
FE4	3.30177	4	W7	6.88496	6	W16	6.61215	6
Ge1	4.23211	4	W8	6.54537	6	W17	5.83844	6
Ge2	3.98321	4	W9	6.48976	6	W18	5.59251	6
W1	6.22157	6	W10	5.97417	6			