Supporting Information for

A unique example of 3-D framework based on the binuclear dysprosium(III) azobenzene -3,5,4'-tricarboxylate with three, six-connected topology showing ferromagnetic properties

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1. Reagents, general procedures and physical measurements.

All reagents used in the syntheses were of obtained from commercial sources, and starting materials and reagents were analytical grade. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000 ~ 400 cm^{-1}) were recorded by using KBr pellet on an AvatarTM 360 E. S. P. IR spectrometer. The elemental microanalysis was performed by the North-West University of China, Department of Chemistry, Microanalytical Laboratory using an Exeter Analytical CE440. Fourier transform infrared (FT-IR) spectra were measured on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellet samples. Absorptions are described as very strong (vs), strong (s), medium (m), weak (w), shoulder (sh), and broad (br) and stretches (st) are labeled symmetric (s) or asymmetric (as). Chemical shift of ^{1}H were referenced to internal deuteriated dimethyl sulphoxide solvents and

then recalculated to SiMe$_4$ (δ= 0). Magnetic measurements were performed in the temperature range 2-300 K, using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 0.2 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

Synthesis of sodium azobenzene -3,5,4'-tricarboxylate:

T shape ligand, azobenzene -3,5,4'-tricarboxylic acid was prepared from 4-nitrobenzenamine and dimethyl isophthalate as starting materials through nitrification, esterification, reduction, diazotization, coupling reaction, oxidation processes, and was purified through the filtering, re-crystallization, respectively. The light yellow solid was collected by filtration, dried in vacuum. IR (KBr): 3723 s, 3369m, 2607s, 1512m, 1054w, 823s, 719vs, 573s, 448vs. Anal for $C_{15}H_{10}N_2O_6$. Calc. C, 57.33; H, 3.20; N, 8.91 % , Found C, 57. 62; H, 3.28; N, 8.86 %. The synthesis Procedure and method for the ligands is similar to or is little modified routines from Ref 1.

Preparation of sodium azobenzene -3,5,4'-tricarboxylate

A mixture suspension of azobenzene -3,5,4'-tricarboxylic acid, (4.31 g, 13.7 mmol) and toluene (Acros, 9.8%, 30 mL) was refluxed in ethanol solution for one hour, then 10 ml methanol solution of sodium hydroxide (0.60 g, 15 mmol) was added dropwise to above solution slowly. The mixture was stirred at 50 ^{o}C under argon over night. After cooling to room temperature, the red-yellow solid was collected by removal of the solvents by rotary evaporators consequently, dried in vacuum, yield 68%.

Spectroscopic Methods

Absorption spectra were recorded on a Perkin-Elmer Lambda 9 Spectrometer coupled with a personal computer using software supplied by Perkin-Elmer. Emission and excitation spectra in the visible range were measured using a Varian Cary Eclipse Fluorescence Spectrophotometer coupled to a personal computer with software provided by Varian.

Photophysical analysis of H$_3$ABTA and [Dy(ABTA)]·2H$_2$O}$_n$

For analysis of the photophysical properties of H$_3$ABTA, a solution of this ligand about 5.0×10^{-4}

mol/L was prepared by dissolving 1.36 mg of the H_3ABTA ligand in 7.00 mL of methanol solvent. This stock solution was diluted for UV-visible absorbance measurements and fluorescence analysis. Complex **1** were collected as solid samples under methanolic soluation by dissolving 1.76 mg of the $\{[Dy(ABTA)]\cdot 2H_2O\}_n$ into 7.00 mL of methanol solvent.
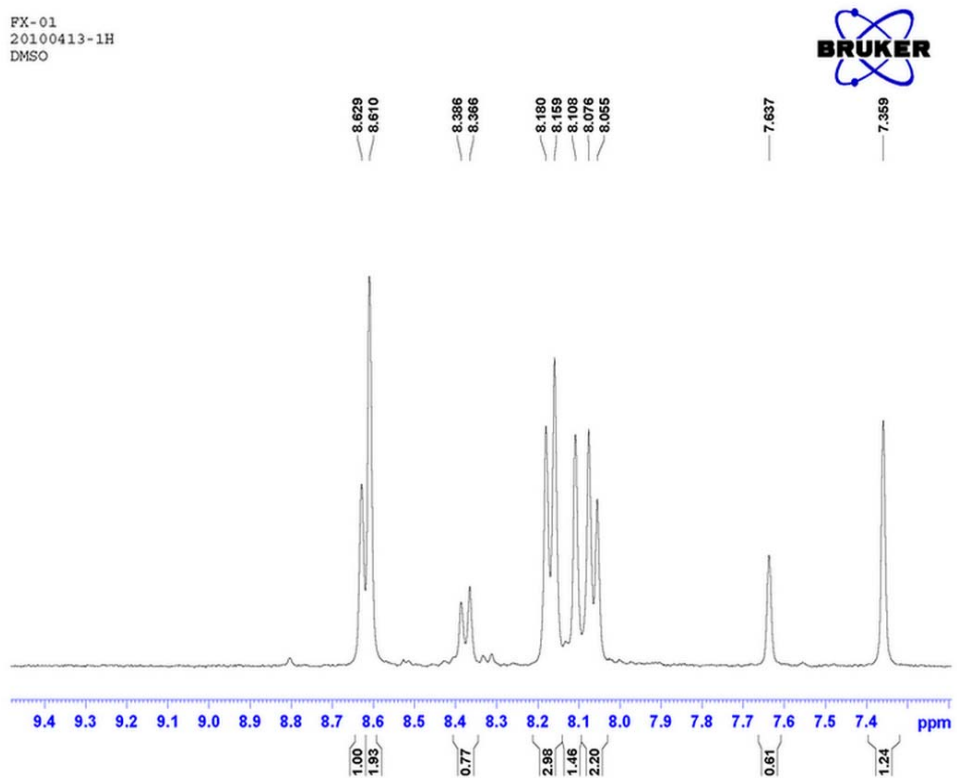
2   Additional figures

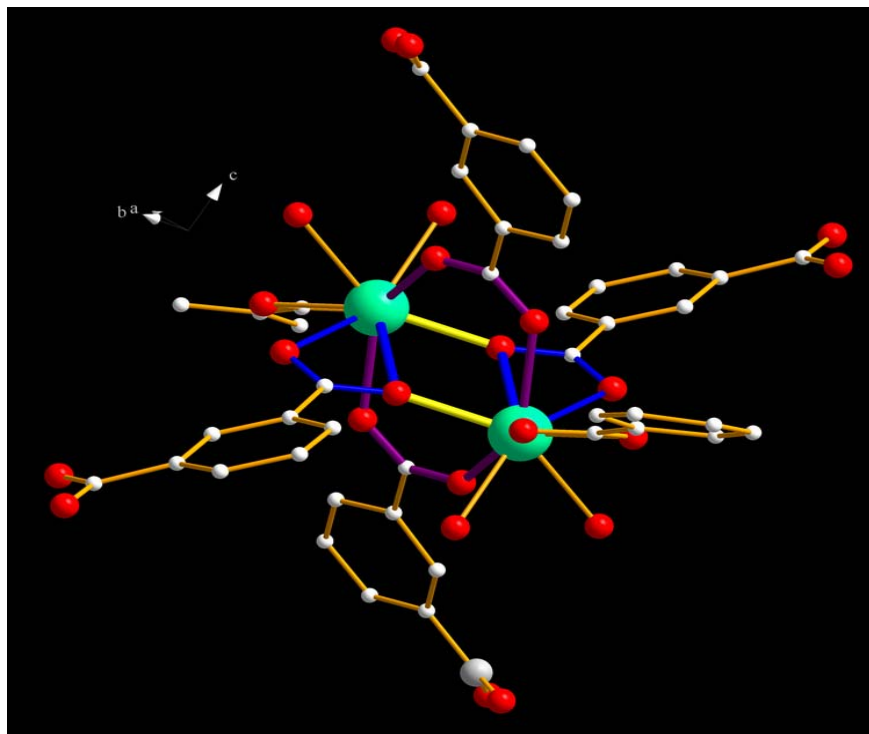**Figure S1.**   1H NMR of polymer **1** (DMSO, 300 MHz);

Figure S2 (a)   Illustration of two adjacent Dy(III) ions are bridged by the carboxylic group
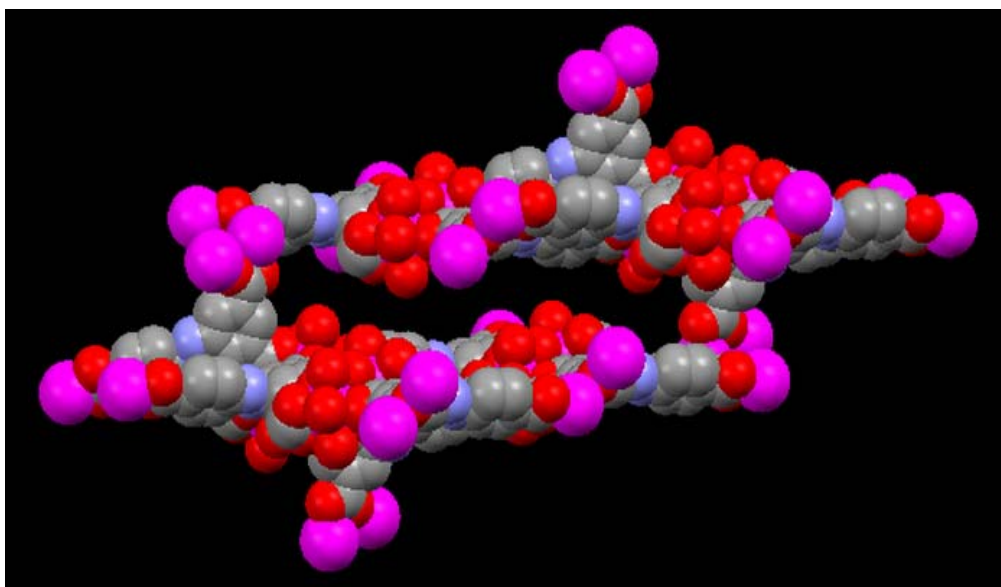and carboxylate oxygen atoms from the isophthalate fragments into the dinuclear unit.

Figure S2 (b) Space filling representation of the intersecting channel in the 3D framework along
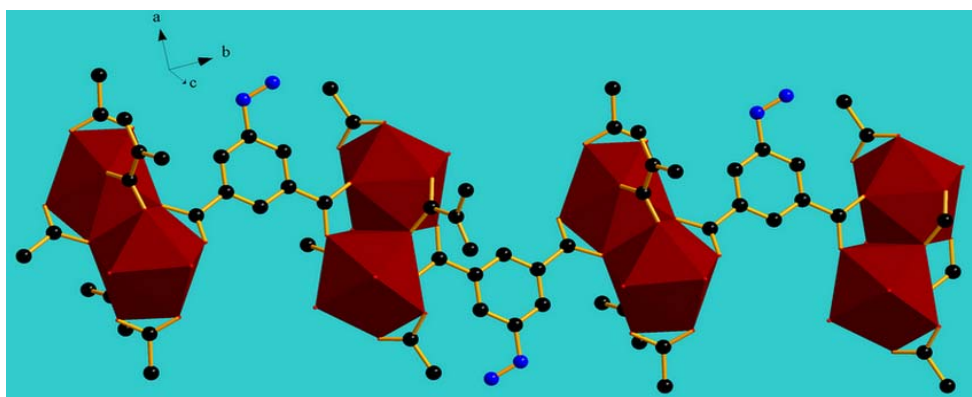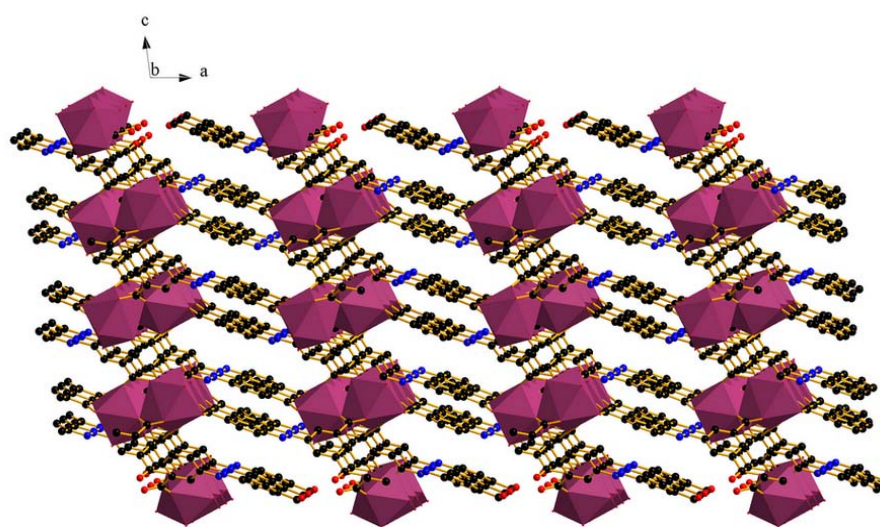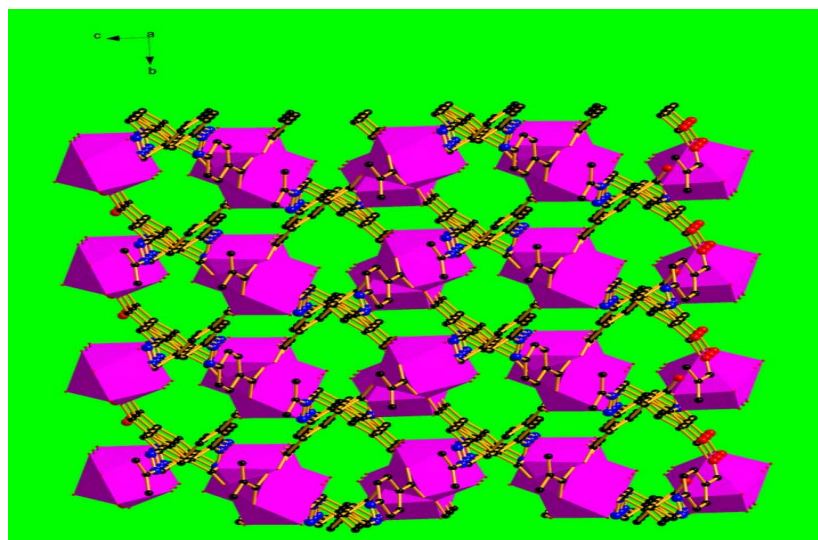
the *b c* plane.

Figure S3   Polyhedral view of the 1D alternating chain consisted of the bidysprosium SBUs
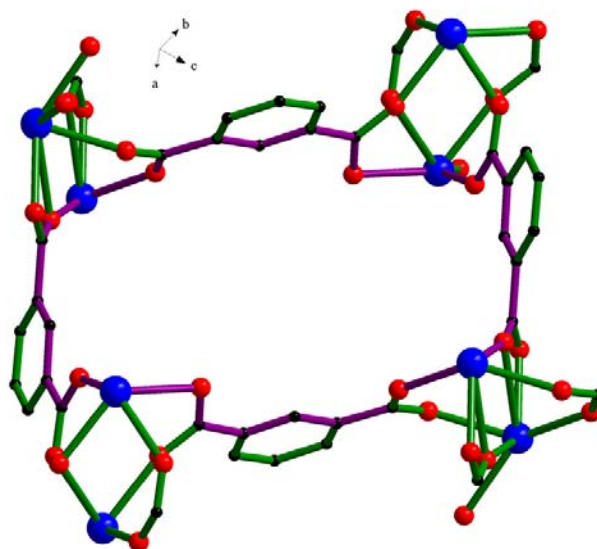linked by isophthalate ligand in **1**

(a)

(b)

Figure S4. Polyhedron representation of 3D framework parallel to the *ac* plane in **1**, viewed along the *a c* plane (**a**) *b c* plane (**b**). Color scheme: Dy atoms, purple polyhedron; C atoms, black; O atoms, red; N atoms, blue.
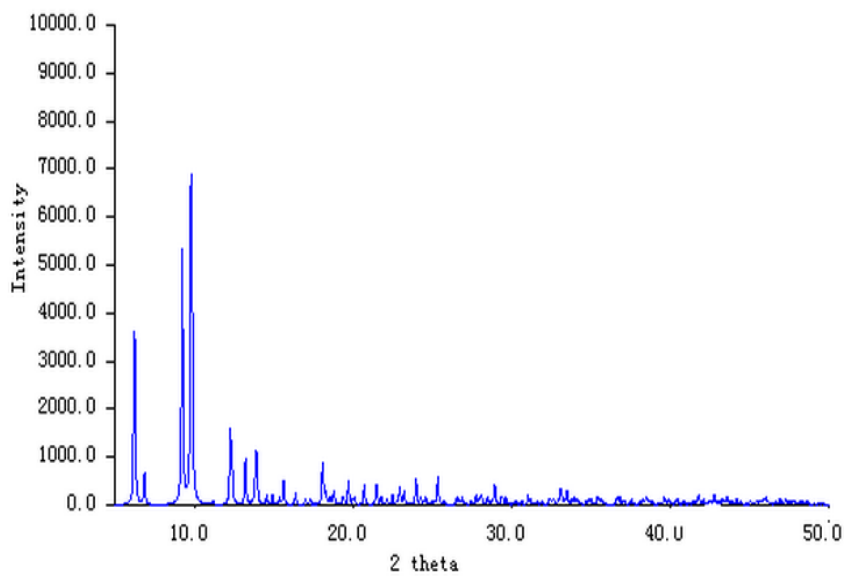

(a)

Figure S5. (a) Ball and- stick representation of the crown-shaped macro-cyclic ring based on four binuclear units along the approximately *ac* plane
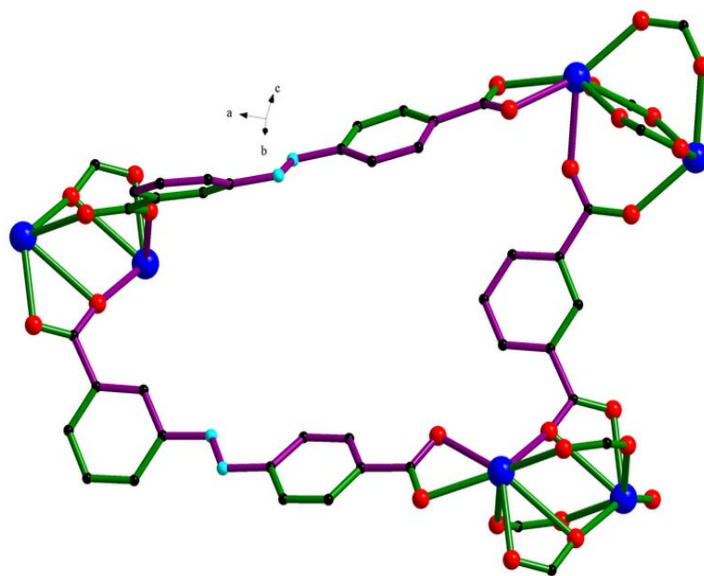
(b)

Figure S5. (b) Illustration of the 44 membered macrocyclic ring consisted of three binuclear units along the approximately *a c* plane
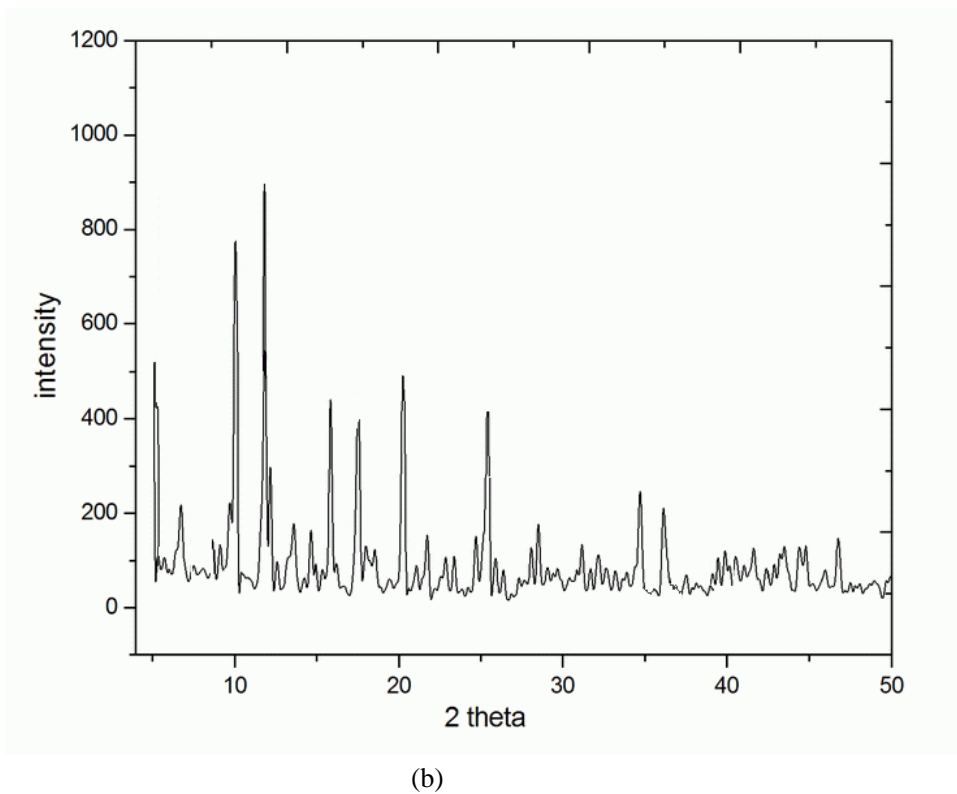

(a)

(b)

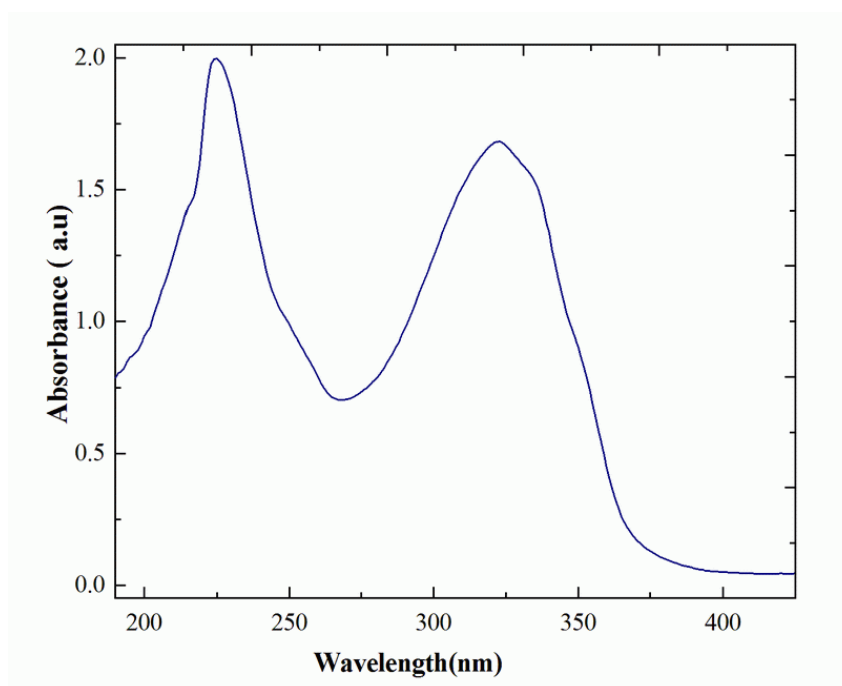**Figure S6**. The simulated (a) and experimental (b) powders XRD patterns of polymer **1**.

Figure S7   The UV-Vis absorbance spectra of the H_3ABTA ligand in methanol
suspension.

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3 Additional Table

Table S1   Selected bond distances (Å) and angles (degree) for polymer **1**

Dy(1)-O(4)#1	2.304(5)	O(5)-C(15)	1.241(10)	O(7)-Dy(1)-O(8)	74.9(3)
Dy(1)-O(1)#2	2.346(5)	O(5)-Dy(1)#7	2.473(6)	O(3)#3-Dy(1)-O(8)	75.0(2)
Dy(1)-O(2)	2.357(5)	O(6)-C(15)	1.224(11)	O(4)#1-Dy(1)-O(6)#4	134.42(19)
Dy(1)-O(7)	2.374(7)	O(6)-Dy(1)#7	2.425(5)	O(1)#2-Dy(1)-O(6)#4	77.8(2)
Dy(1)-O(3)#3	2.390(5)	O(3)#3-Dy(1)-O(4)#3	49.76(16)	O(2)-Dy(1)-O(6)#4	143.7(2)
Dy(1)-O(8)	2.406(6)	O(4)#1-Dy(1)-O(1)#2	74.48(19)	O(7)-Dy(1)-O(6)#4	98.2(2)
Dy(1)-O(6)#4	2.425(5)	O(4)#1-Dy(1)-O(2)	80.10(19)	O(3)#3-Dy(1)-O(6)#4	81.80(19)
Dy(1)-O(5)#4	2.473(6)	O(1)#2-Dy(1)-O(2)	131.7(2)	O(8)-Dy(1)-O(6)#4	71.0(2)
Dy(1)-O(4)#3	2.744(5)	O(4)#1-Dy(1)-O(7)	78.5(2)	O(4)#1-Dy(1)-O(5)#4	84.7(2)
Dy(1)-C(15)#4	2.778(7)	O(1)#2-Dy(1)-O(7)	136.0(3)	O(1)#2-Dy(1)-O(5)#4	73.1(2)
Dy(1)-C(7)#3	2.926(7)	O(2)-Dy(1)-O(7)	75.0(2)	O(2)-Dy(1)-O(5)#4	144.3(2)
O(1)-C(8)	1.242(10)	O(4)#1-Dy(1)-O(3)#3	123.94(19)	O(7)-Dy(1)-O(5)#4	70.4(3)
O(1)-Dy(1)#2	2.346(5)	O(1)#2-Dy(1)-O(3)#3	75.6(2)	O(3)#3-Dy(1)-O(5)#4	128.7(2)
O(2)-C(8)	1.261(8)	O(2)-Dy(1)-O(3)#3	86.11(19)	O(8)-Dy(1)-O(5)#4	105.6(3)
O(3)-C(7)	1.233(9)	O(7)-Dy(1)-O(3)#3	148.0(2)	O(6)#4-Dy(1)-O(5)#4	52.6(2)
O(3)-Dy(1)#5	2.390(5)	O(4)#1-Dy(1)-O(8)	145.9(2)	O(4)#1-Dy(1)-O(4)#3	75.19(18)
O(4)-C(7)	1.265(9)	O(1)#2-Dy(1)-O(8)	139.5(2)	O(1)#2-Dy(1)-O(4)#3	67.77(19)
O(4)-Dy(1)#6	2.304(5)	O(2)-Dy(1)-O(8)	72.7(2)	O(2)-Dy(1)-O(4)#3	66.30(18)
O(4)-Dy(1)#5	2.744(5)	O(5)#4-Dy(1)-O(4)#3	139.5(3)	O(7)-Dy(1)-O(4)#3	136.1(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2, y+1/2, -z+3/2; #2 -x+1/2, -y+3/2, -z+2;

#3 x, -y+1, z+1/2; #4 x-1/2, -y+3/2, z+1/2; #5 x, -y+1, z-1/2; #6 -x+1/2, y-1/2, -z+3/2; #7 x+1/2,-y+3/2, z-1/2.

References

1 Y. Zhang, S. J. Yu , L. Wang, C. Li, *Chin. Chem. Lett.*, 2009, **20**, 235–237.

2 H. Meng, W. L. Yu, W. Huang, *Macromolecules.,* 1999, **32,** 8841-8847.