Electronic Supporting Information for Dalton. Trans.

Reticular three-dimensional 3d–4f frameworks constructed through substituted imidazole–dicarboxylate: syntheses, luminescence and magnetic properties study

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1. Additional experimental section

1.1. Synthesis of complexes 5 and 6

Cobalt nitrate hexahydrate (0.0292 g, 0.1 mmol) and 0.1 mmol of lanthanide (III) nitrate hexahydrate, $Tb(NO_3)_3{\cdot}6H_2O$ (0.042g), (**5**); $Dy(NO_3)_3{\cdot}6H_2O$, 0.046 g (**6**) were mixed in a ethanol-water solution (10 mL) of H_3mimda (0.3 mmol, 0.079 g). After stirring for 30 min in air, the aqueous mixture was placed into 25 mL Teflon-lined autoclave under autogenous pressure being heated at 165 °C for 90 h, and then the autoclave was cooled over a period of 24 h at a rate 5 °C/h. pale red crystals were obtained suitable for X-ray diffraction analysis. For (**5**), yield: yield: 0.0241 g (38%) based on Ln element. Elemental analysis (%): calcd for $C_{12}H_{16}CoN_4O_{12.5}Tb$: C 22.72, H 2.54, N 8.83, found: C 21.85, H 2.43, N 8.75. IR: 3352()s, 3030 ()br, 2859()s, 2150()m, 1716()s, 1613()s, 1572()vs, 1430(s), 1117(m), 1009(s), 789(s). For red crystals of (**6**), yield: 0.0325 g (51%). Elemental analysis (%): calcd for $C_{12}H_{15}CoDyN_4O_{12}$: C 22.92, H 2.41, N 8.91, found: C 22.85, H 2.43, N 8.79. IR: 3402(s), 3028(br), 2909 (s), 2100(m), 1711(s), 1621(s), 1495(vs), 1380(s), 1078(s), 822(s).

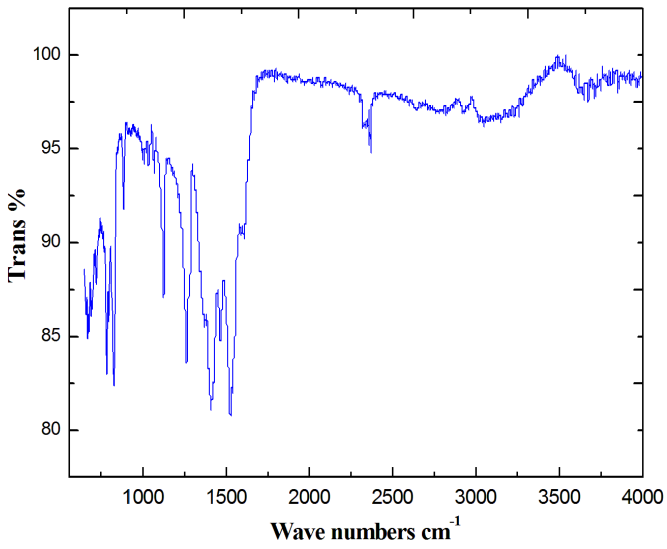
1.2. About fluorescence method

For fluorescence titrations, a stock solution of the sensor was prepared as the same as UV-vis luminescence spectra. The solutions of the guest cations using the 0.5mol/L $ZnCl_2$ salts in the order of 1 to 6 equates were prepared in deionized water. Solutions of $ZnCl_2$ salts were prepared separately in NH_3. H_2O/NH_4Cl buffer solution at pH = 7.3. The spectra of these solutions were recorded by means of fluorescence methods through microliter syringe adding the $ZnCl_2$ solution at 0.1 ml once time. The

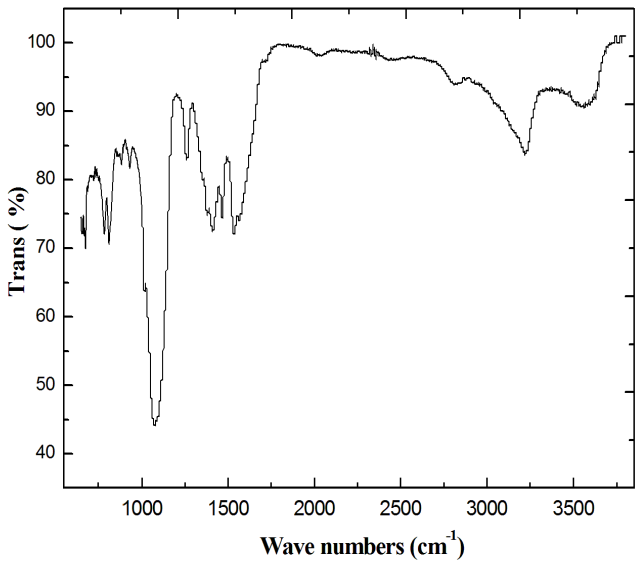
luminescence quantum yield measurements were obtained with a Fluorolog-3 Horiba Jobin Yvon equipped with a Hamamatsu R928P photomultiplier with a SPEX 1934 D phosphorimeter and a xenon lamp at room temperature, from 1 x 10^{-4} mol/L chloroform solutions at an excitation wavelength of *ca* 360 nm, with a slit width of 1.0 nm for the excitation, and 1.0 nm for the maximum emission, with a Horiba Quanta-Q F-3029 integrating sphere mounted in the sample.

2. Addition discussions and results

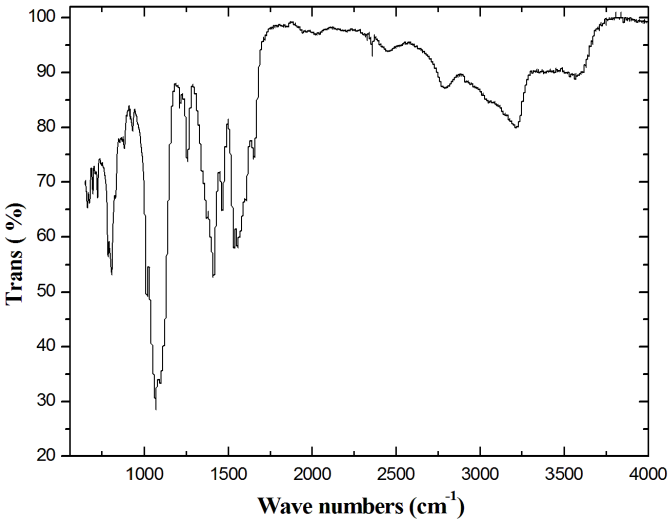
2. 1. IR spectra of complexes 1-6



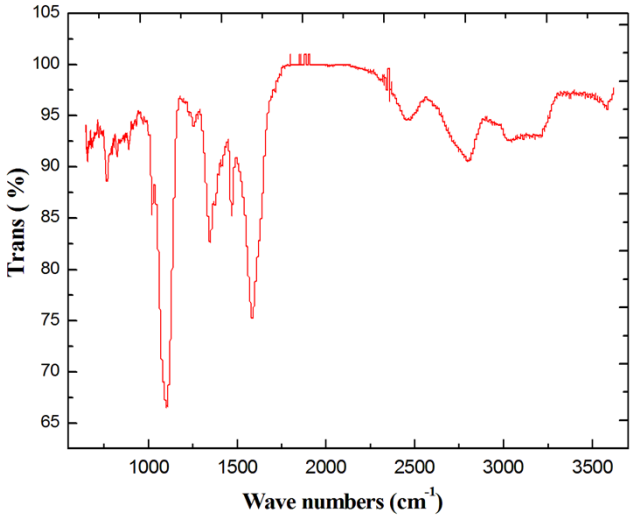
(a)



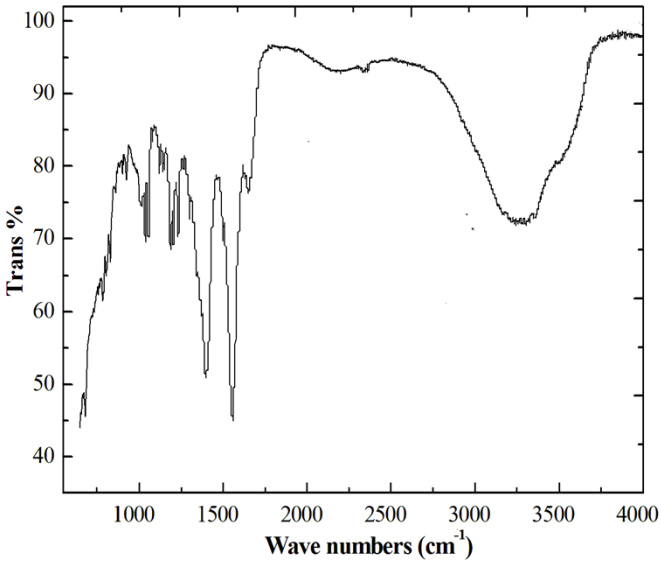
(b)


Trans (%)
Wave numbers (cm-1)

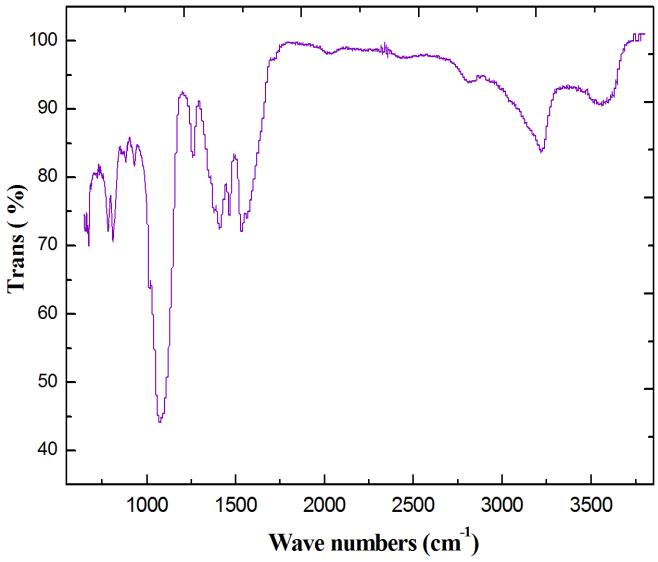
(c)


Trans (%)
Wave numbers (cm-1)

(d)


Trans %
Wave numbers (cm-1)

(e)



(f)

Fig. S 1. IR spectra for compounds **1**(a)**, 2**(b)**, 3**(c)**, 4**(d)**, 5** (e) and **6** (f)

2. 1. Comparison of the Structures of 1-6

The X-ray diffraction analysis (owing to the less optimum quality of data measurements, a number of restraints were used in the refinements) reveals that compounds **2 -6** are isostructural, even if compounds **5** and **6** feature different transition metals. They all crystallize in monoclinic system, with C2/*c* space group. The perspective view of **2** with atom labeling scheme is illustrated in Fig. S2. The asymmetry unit contains one Ho(III) ion, one zinc (II) ion, four Hmimda ligands, and two coordinated water molecules as well as two solvate water molecules. The octa-coordinated Ho(III) cation exhibits distorted dodecahedral prism geometry, being accomplished by an O_8 donor set, among which two oxygen atoms are from water molecules, and six are from imidazole carboxylate. As far as the Zn(II) ion is concerned, it exhibits a octahedron geometry, being coordinated by four oxygen atoms from two carboxylic groups and two nitrogen of imidazole ring from the next mimda ligand. It just demonstrates slightly different coordination environment being compared with the pure Zn(II) compound for the bond lengths and angles.[1,2] Two dicarboxylate ligands sharing the common Zn (II) ion adopt two types of bridging coordination modes, but all in chelating bridging bidentate fashions. The first category has been completed deprotonated for carboxyl group, but an H atom was added to imidazole N bearing one positive charge, and the imidazole N in the second category has been deprotonated. They are denoted as $mimda^{2-}$ and

Hmimda$^-$, respectively. The 5-carboxylic group adopts bidentate, monodentate and cheated modes. The Hmimda$^-$ ligand, while adopts a μ_3-*k*N, O: *k*O, O': *k*N', O' modes connecting two Zn(III) and one Ho(III) centers in bis-(bridging) and monodentate modes. In this structure, the shortest separation of Ho-Zn is 6.274 Å, as illustrated in Fig .S2.

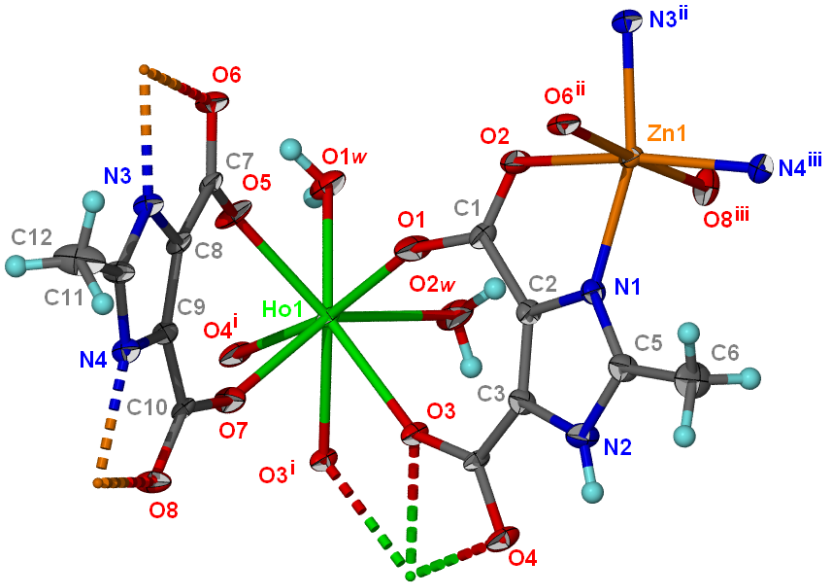


Fig. S2. (a) Coordination environments of the Ho(III) and Zn (II) cation with partial atomic labels in **2**

Two Ho(III) ions and four Zn(II) ions are combined by two μ_3- Hmimda ligands to produce a heterometallic hexanuclear [Ho_2Zn_4 (Hmimda)$_4$] as second building unit, rather than tetraunclear ring-like aggregate, as displayed in Fig S4. These hexanuclear clusters are grafted on to an infinite 1D double-stranded structure H_3mimda ligand acts as three- connected nodes connecting two Ho (III) and one Zn (II) ion, or connecting two Zn (II) ions and one Ho (III) ion. Both Ho (III) and Zn (II) are coordinated to three H_3mimda ligands, assuming both the metal cation and H_3mimda ligand act as three- connected nodes, as shown in Figure. S6. The TOPOS analysis of this network results in a zeolite-like topology with the point number of $(4.8^2)(8^2.12)$. Total Schlafli symbol is $\{3;4;5^2;6;7;\ 8^2;\ 11^2;12^4;13\}\ \{4^3;8;\ 10^2;\ 12^3;14^3;15;16;17\}$, which is similar to reported analogous hetero-metallic coordination polymers.[4]

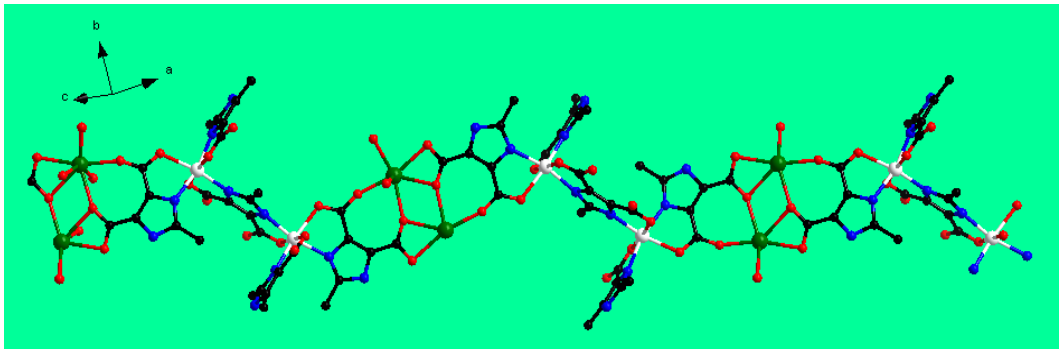


Fig. S3. 1D zig-zag chain assembled from alternate sub-units based upon Ho(III) (green) and Zn(II) (white) ions.

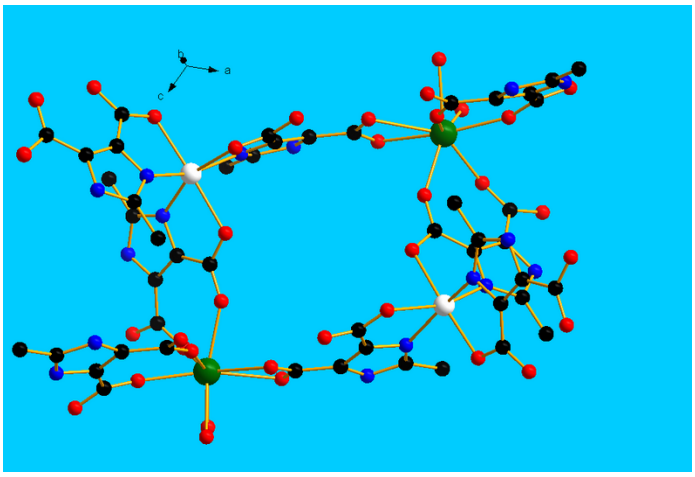


Fig. S4. Illustration of an individual Ho_2Zn_2 parallelogram fragment linked by Hmimda ligands viewed approximately down the *bc* plane in **2.** Color codes: Ho(III), green; Zn, white.

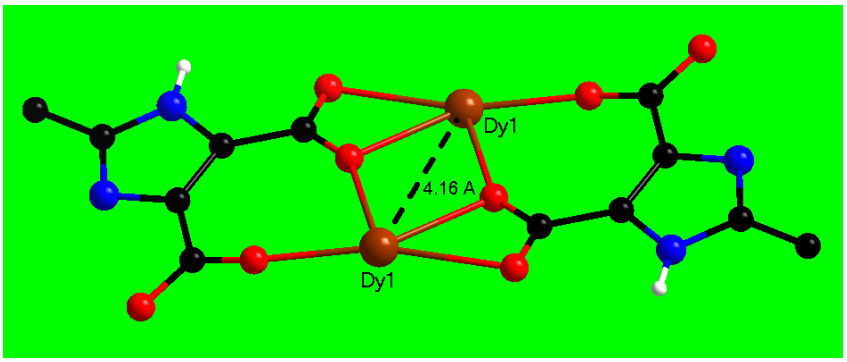


Fig. S5. Illustration of two adjacent Dy(III) ions doubly connected by 4-carboxylic group from Hmimda ligands viewed approximately down *ac* plane in **6**.

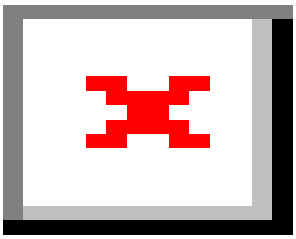


Fig. S6. Topology showing the connectivity between three linking nodes in **2**. Non-bridging atoms of ligands and hydrogen atoms have been omitted for clarity. Color codes, Co: green; Ho: purple; Hmimda ligand: gray.

1.3 Additional PXRD and thermal deposition property

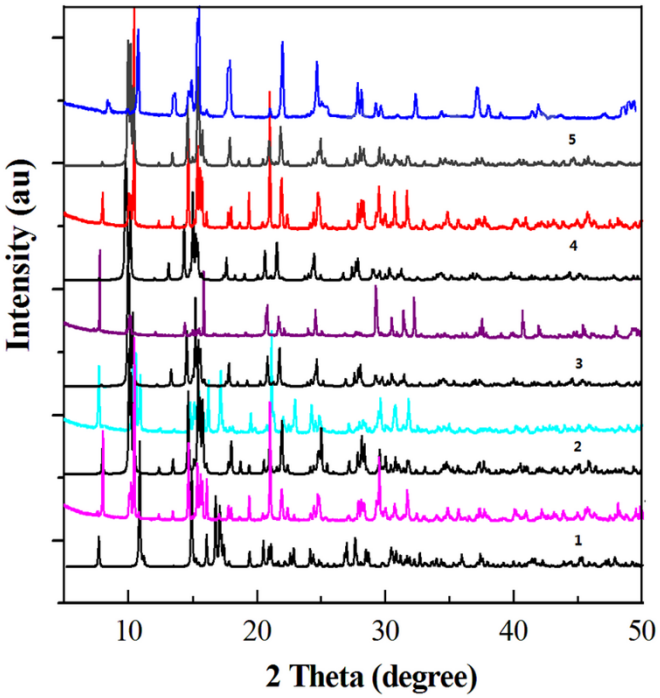


Fig. S7. Comparing the simulated XRD (all in black) and experimental PXRD patterns of compounds **1-5** (presented by pink, cyan, purple, red and blue pattern, respectively)

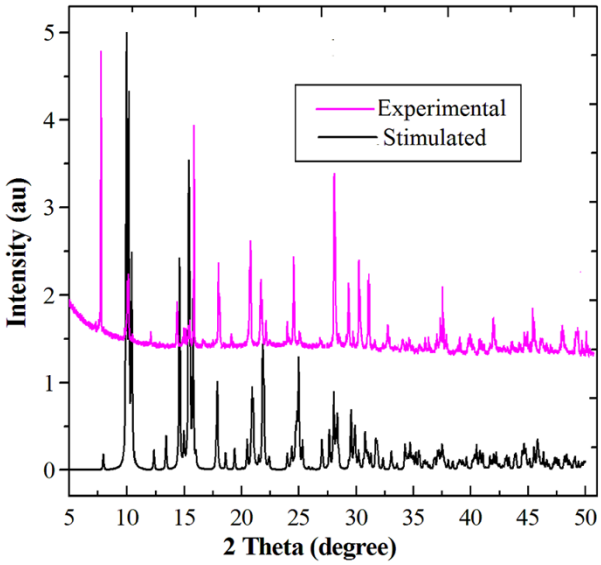


Fig. S8. Comparing the simulated PXRD and experimental PXRD of **6**

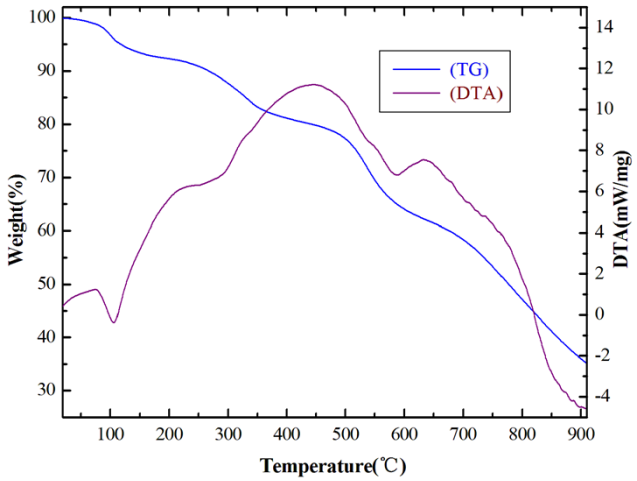


Fig. S9. The TGA curves for complex **1**

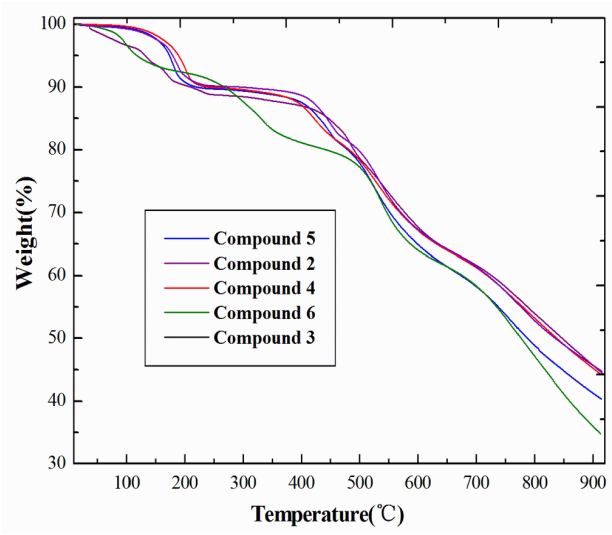


Fig. S10. The TG analysis curves for complexes **2- 6**.

Photoluminescence Property of Zn complex

The photoluminescence properties of [Zn(Hmimda)$_2$] in the methanol suspension samples (ca. 0.001 mol/L) were investigated at room temperature. As shown in Fig. S11, upon photo-excitation at 326 nm the emission spectra showed the intense emission bands ranging from 400 to 430 nm in purple regions with a maximum wavelength of 414 nm. In comparison with the emission of the free H_3mimda ligand (λmax = 372 nm) in a methanol solution at room temperature, the fluorescence of zinc compound has a red shift, which may be assigned to the metal ligand charge transfer (MLCT) [4]. The coordination of the ligand to the metal ion increases the rigidity of molecular edifice and shows intense fluorescence due to the presence of relatively rigid conjugated systems such as imidazole ring.

3. Additional Figures

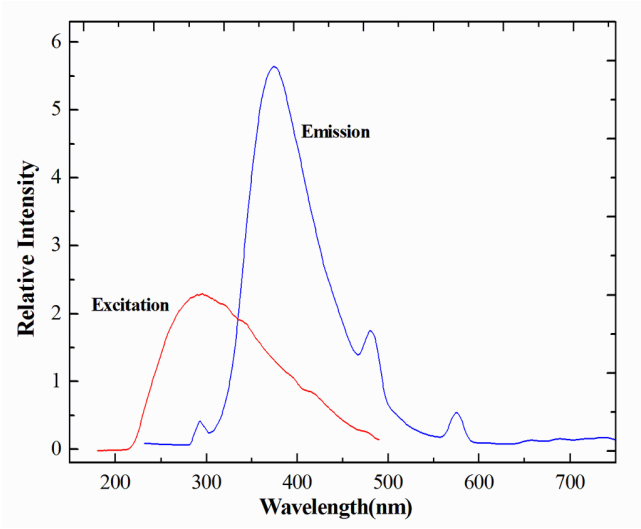


Fig. S11. PL excitation and emission spectra of Zn-Hmimda complex in the methanol suspension.

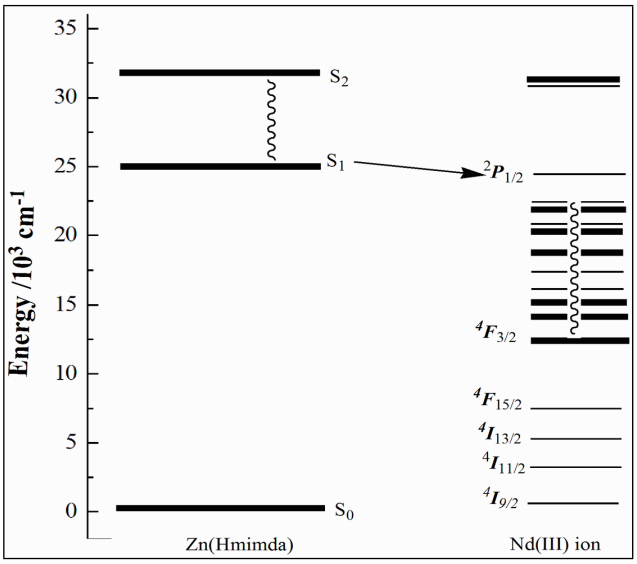


Fig. S12. Schematic representation of the energy flow paths during sensitization of Nd(III) ion luminescence via the [Zn-Hmimda] unit.

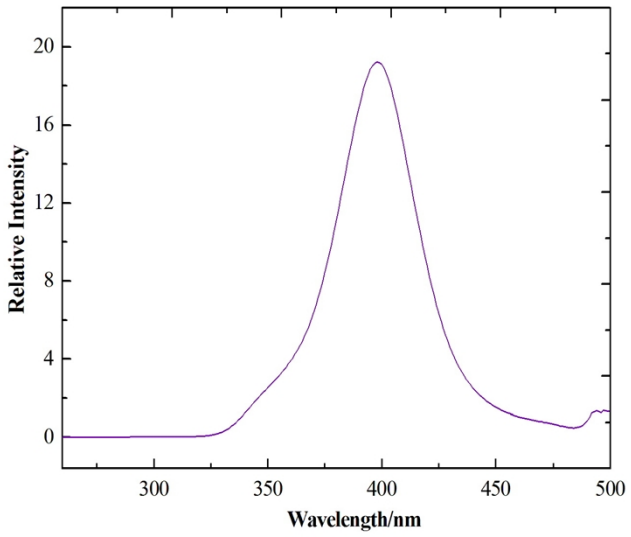


Fig. S13. The excitation spectrum of **4** normalized on emission at 900 nm.

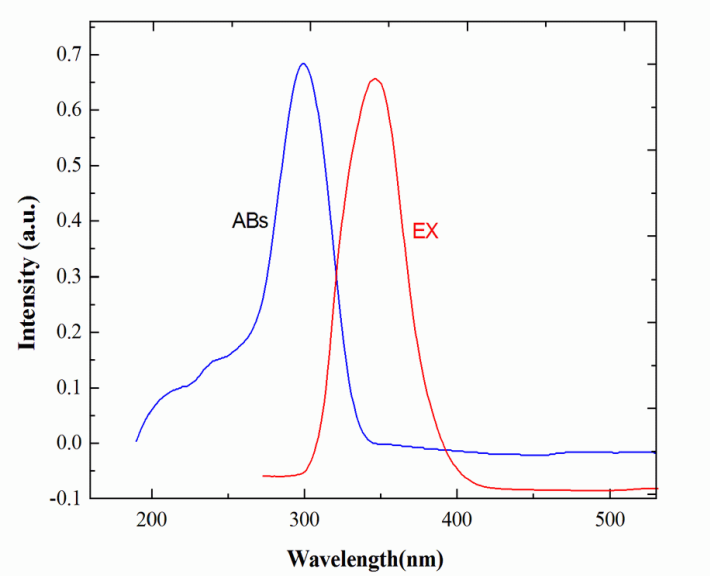
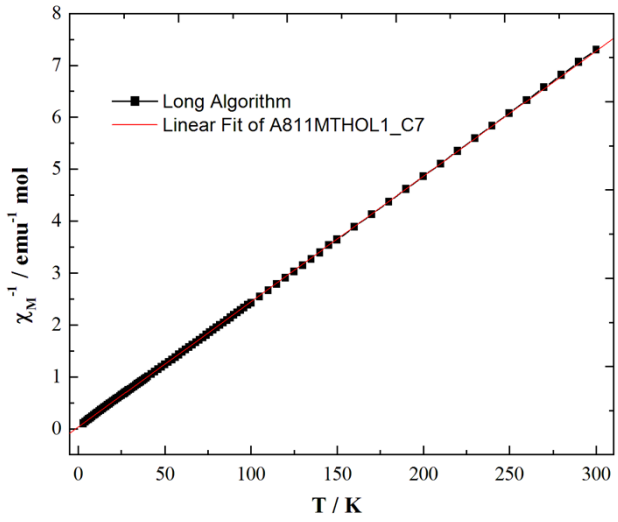
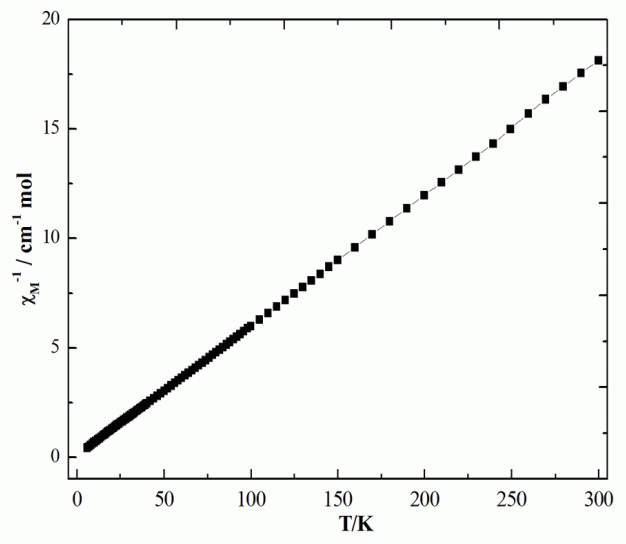


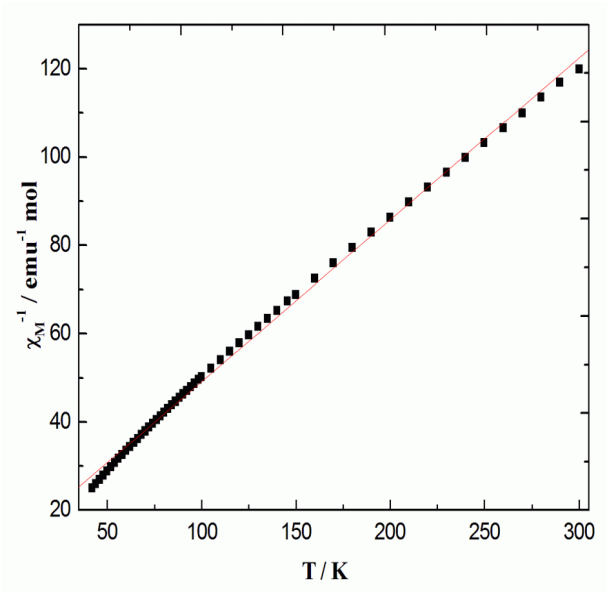
Fig. S14. Photophysical analysis of polymer **6** in methanolic suspension: absorbance spectrum (blue) and excitation spectrum (red) normalized on emission at 576 nm.



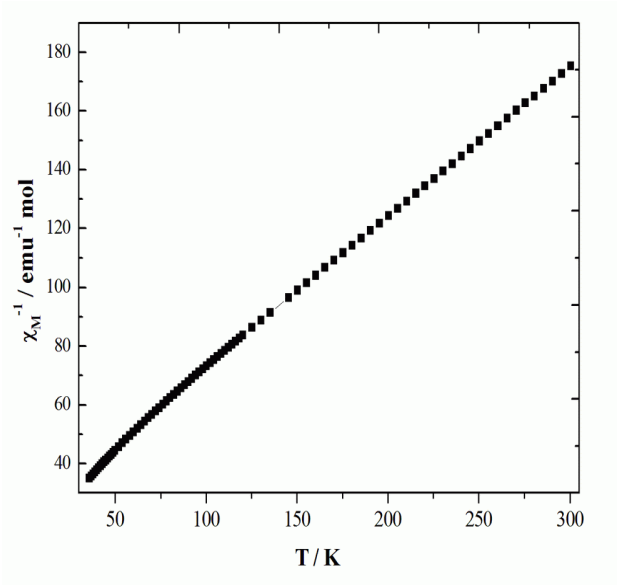
(a)



(b)



(c)



(d)

Fig. S 15. Plot of inverse molar susceptibility against temperature under a 0.2 T field for **2** (a)**, 3** (b), **4** (c)**, 5** (d)**,** the Solid lines present the best fit indicated in the text.

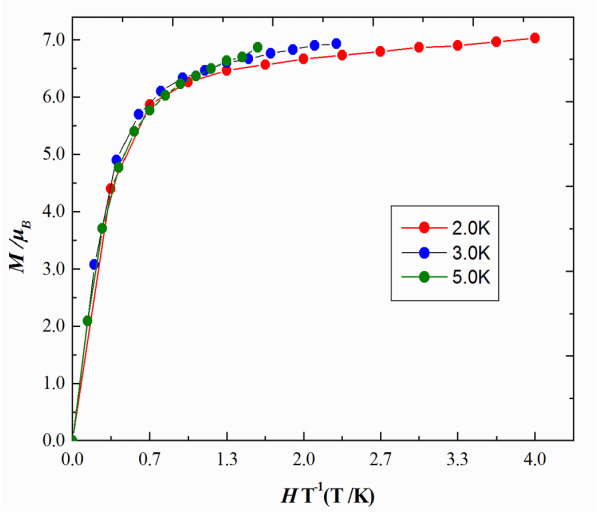


Fig. S 16. Magnetization plots (M vs H/T) from 2 to 5 K for **2** after the sample being heated

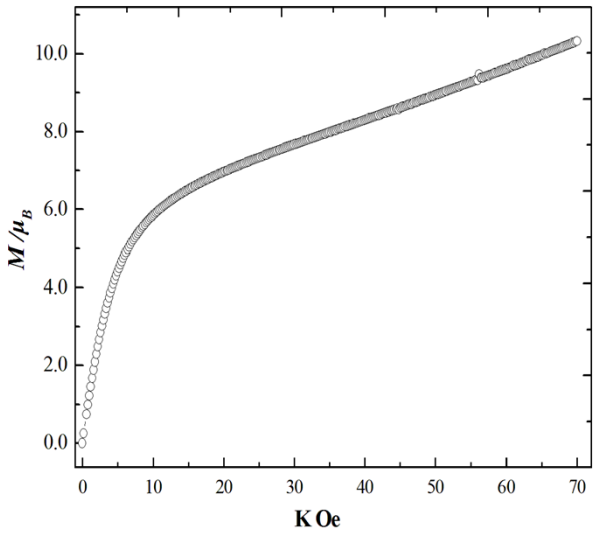


Fig. S 17. Magnetization plots (M vs H/T) for **5** at 2 K.

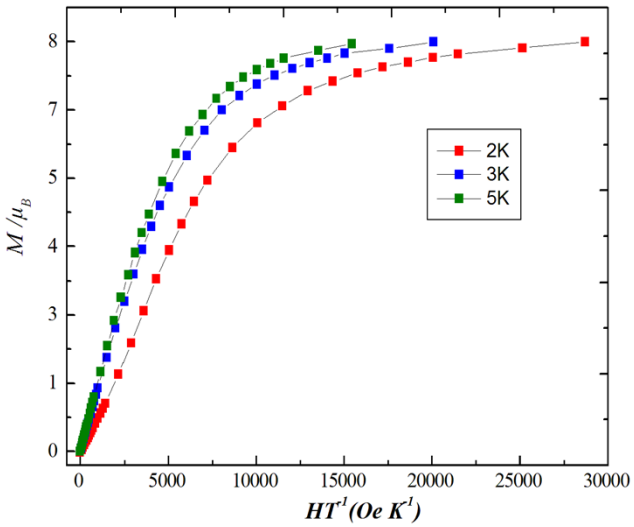


Fig. S 18. Magnetization plots (M vs H/T) for **6** from 2 to 5 K

1.2. Additional Tables:

Table S1 Selected bond lengths [Å] and angles [°] for complexes **1**–**6**

Complex 1					
Bond	Length	Bond	Length	Bond	Length
Bond	Length	Bond	Length	Bond	Length
Nd(1)-O(1)	2.241(7)	Nd(1)-O(7)	2.300(7)	Zn(1)-O(4)	2.156(6)
Nd(1)-O(3)	2.213(7)	Nd(1)-O(8)#2	2.322(7)	Zn(1)-O(1w)	1.992(8)
Nd(1)-O(5)	2.342(8)	Nd(1)-N(3)#2	2.568(8)	Zn(1)-N(1)	1.992(8)
Nd(1)-O(6)#1	2.264(8)	Zn(1)-O(2)#3	2.213(6)	Zn(1)-N(2)#3	1.988(8)
Bond	Angle	Bond	Angle	Bond	Angle
O(3)-Nd(1)-O(1)	80.9(3)	O(1)-Nd(1)-O(5)	78.9(3)	N(2)#3-Zn(1)-O(1w)	110.7(4)
O(3)-Nd(1)-O(6)#1	91.8(3)	O(6)#1-Nd(1)-O(5)	104.9(3)	N(1)-Zn(1)-O(1w)	110.9(3)
O(1)-Nd(1)-O(6)#1	171.2(3)	O(7)-Nd(1)-O(5)	74.5(3)	N(2)#3-Zn(1)-O(4)	95.8(3)
O(3)-Nd(1)-O(7)	77.1(3)	O(8)#2-Nd(1)-O(5)	73.4(2)	N(1)-Zn(1)-O(4)	79.5(3)
O(1)-Nd(1)-O(7)	94.0(3)	O(3)-Nd(1)-N(3)#2	75.6(3)	O(1w)-Zn(1)-O(4)	94.1(3)
O(6)#1-Nd(1)-O(7)	79.6(3)	O(1)-Nd(1)-N(3)#2	105.0(3)	N(2)#3-Zn(1)-O(2)#3	78.2(3)
O(3)-Nd(1)-O(8)#2	135.1(3)	O(6)#1-Nd(1)-N(3)	77.5(3)	N(1)-Zn(1)-O(2)#3	101.8(3)
O(1)-Nd(1)-O(8)#2	86.6(3)	O(7)-Nd(1)-N(3)#2	143.5(3)	O(1w)-Zn(1)-O(2)#3	92.4(3)
O(6)#1-Nd(1)-O(8)#2	102.1(3)	O(8)#2-Nd(1)-N(3)	66.4(2)	O(4)-Zn(1)-O(2)#3	172.4(3)
O(7)-Nd(1)-O(8)#2	147.1(3)	O(5)-Nd(1)-N(3)#2	139.1(2)	O(3)-Nd(1)-O(5)	143.5(2)
Complex 2					
Bond	Length	Bond	Length	Bond	Length
Ho(1)-O(1)	2.218(4)	Ho(1)-O(3)#1	2.517(3)	O(3)-Ho(1)#1	2.517(3)
Ho(1)-O(5)	2.278(4)	Zn(1)-N(3)#2	2.052(5)	O(4)-Ho(1)#1	2.434(4)
Ho(1)-O(7)	2.281(4)	Zn(1)-N(4)#3	2.067(5)	O(6)-Zn(1)#2	2.210(4)
Ho(1)-O(2w)	2.316(4)	Zn(1)-N(1)	2.113(5)	O(8)-Zn(1)#4	2.247(4)
Ho(1)-O(1w)	2.393(4)	Zn(1)-O(2)	2.168(4)	N(3)-Zn(1)#2	2.052(5)
Ho(1)-O(3)	2.400(4)	Zn(1)-O(6)#2	2.210(4)	N(4)-Zn(1)#4	2.067(5)
Ho(1)-O(4)#1	2.434(4)	Zn(1)-O(8)#3	2.247(4)	O(3)-Ho(1)#1	2.517(3)
Bond	Angle	Bond	Angle	Bond	Angle
O(1)-Ho(1)-O(5)	78.43(17)	O(1w)-Ho(1)-O(3)	146.32(13)	N(3)#2-Zn(1)-N(1)	162.39(18)
O(1)-Ho(1)-O(7)	107.17(17)	O(1)-Ho(1)-O(4)#1	164.74(16)	N(4)#3-Zn(1)-N(1)	99.60(18)
O(5)-Ho(1)-O(7)	76.86(14)	O(5)-Ho(1)-O(4)#1	95.22(14)	N(3)#2-Zn(1)-O(2)	89.49(17)
O(1)-Ho(1)-O(2w)	82.44(17)	O(7)-Ho(1)-O(4)#1	84.50(15)	N(4)#3-Zn(1)-O(2)	160.73(17)
O(5)-Ho(1)-O(2w)	136.09(15)	O(2w)-Ho(1)-O(4)#1	93.08(15)	N(1)-Zn(1)-O(2)	76.67(16)
O(7)-Ho(1)-O(2w)	146.95(14)	O(1w)-Ho(1)-O(4)#1	76.54(15)	N(3)#2-Zn(1)-O(6)#2	77.79(16)
O(1)-Ho(1)-O(1w)	88.21(17)	O(3)-Ho(1)-O(4)#1	116.94(12)	N(4)#3-Zn(1)-O(6)#2	100.65(16)
O(5)-Ho(1)-O(1w)	68.35(14)	O(1)-Ho(1)-O(3)#1	139.11(14)	N(1)-Zn(1)-O(6)#2	93.33(15)
O(7)-Ho(1)-O(1w)	138.20(15)	O(5)-Ho(1)-O(3)#1	139.61(14)	O(2)-Zn(1)-O(6)#2	98.46(16)
O(2w)-Ho(1)-O(1w)	71.92(14)	O(7)-Ho(1)-O(3)#1	77.01(12)	N(3)#2-Zn(1)-O(8)#3	100.82(17)

O(1)-Ho(1)-O(3)	76.31(14)	O(2w)-Ho(1)-O(3)#1	75.69(13)	N(4)#3-Zn(1)-O(8)#3	76.58(16)
O(5)-Ho(1)-O(3)	134.56(13)	O(1w)-Ho(1)-O(3)#1	116.20(13)	N(1)-Zn(1)-O(8)#3	88.76(17)
O(7)-Ho(1)-O(3)	75.42(14)	O(3)-Ho(1)-O(3)#1	65.27(13)	O(2)-Zn(1)-O(8)#3	84.40(16)
O(2w)-Ho(1)-O(3)	76.46(13)	O(4)#1-Ho(1)-O(3)	52.02(13)	O(6)#2-Zn(1)-O(8)#3	176.78(15)

Complex 3

Bond	Length	Bond	Length	Bond	Length
Er(1)-O(1)	2.210(3)	Er(1)-O(7)	2.273(3)	O(3)-Er(1)-O(3)#1	65.23(11)
Er(1)-O(3)	2.397(3)	Er(1)-O(1w)	2.393(3)	O(4)#1-Er(1)-O(3)#1	52.25(11)
Er(1)-O(3)#1	2.522(3)	Er(1)-O(2w)	2.324(3)	N(3)#2-Zn(1)-N(4)#3	96.55(15)
Er(1)-O(4)#1	2.441(3)	Zn(1)-O(2)	2.175(3)	N(3)#2-Zn(1)-N(1)	162.96(14)
Er(1)-O(5)	2.269(3)	Zn(1)-O(6)#2	2.214(3)	N(4)#3-Zn(1)-N(1)	99.54(15)
Bond	Angle	Bond	Angle	N(3)#2-Zn(1)-O(2)	89.78(13)
O(1)-Er(1)-O(5)	78.69(13)	O(2w)-Er(1)-O(3)	76.64(11)	N(4)#3-Zn(1)-O(2)	160.77(15)
O(1)-Er(1)-O(7)	107.44(14)	O(1w)-Er(1)-O(3)	146.23(11)	N(1)-Zn(1)-O(2)	76.78(13)
O(5)-Er(1)-O(7)	77.12(11)	O(1)-Er(1)-O(4)#1	164.82(12)	N(3)#2-Zn(1)-O(6)#2	77.84(13)
O(1)-Er(1)-O(2w)	82.15(14)	O(5)-Er(1)-O(4)#1	94.13(12)	N(4)#3-Zn(1)-O(6)#2	100.55(14)
O(5)-Er(1)-O(2w)	135.66(12)	O(7)-Er(1)-O(4)#1	83.59(12)	N(1)-Zn(1)-O(6)#2	93.66(13)
O(7)-Er(1)-O(2w)	147.14(12)	O(2w)-Er(1)-O(4)#1	94.20(13)	O(2)-Zn(1)-O(6)#2	98.52(14)
O(1)-Er(1)-O(1w)	88.75(14)	O(1w)-Er(1)-O(4)#1	76.15(12)	N(3)#2-Zn(1)-O(8)#3	100.77(14)
O(5)-Er(1)-O(1w)	68.72(12)	O(3)-Er(1)-O(4)#1	117.05(9)	O(3)-Er(1)-O(3)#1	65.23(11)
O(7)-Er(1)-O(1w)	138.41(12)	O(1)-Er(1)-O(3)#1	139.43(11)	O(4)#1-Er(1)-O(3)#1	52.25(11)
O(2w)-Er(1)-O(1w)	71.27(12)	O(5)-Er(1)-O(3)#1	139.07(11)	N(3)#2-Zn(1)-N(4)#3	96.55(15)
O(1)-Er(1)-O(3)	76.59(11)	O(7)-Er(1)-O(3)#1	76.53(10)	N(3)#2-Zn(1)-N(1)	162.96(14)
O(5)-Er(1)-O(3)	135.04(11)	O(2w)-Er(1)-O(3)#1	76.37(11)	N(4)#3-Zn(1)-N(1)	99.54(15)
O(7)-Er(1)-O(3)	75.35(11)	O(1w)-Er(1)-O(3)#1	115.47(11)	N(3)#2-Zn(1)-O(2)	89.78(13)

Complex 4

Bond	Length	Bond	Length	Bond	Length
Yb(1)-O(1)	2.192(3)	Yb(1)-O(2w)	2.299(3)	O(3)-Yb(1)#1	2.499(3)
Yb(1)-O(3)	2.390(3)	Zn(1)-O(2)	2.173(3)	O(4)-Yb(1)#1	2.420(3)
Yb(1)-O(3)#1	2.499(3)	Zn(1)-O(6)#2	2.221(3)	O(6)-Zn(1)#2	2.221(3)
Yb(1)-O(4)#1	2.420(3)	Zn(1)-O(8)#3	2.254(3)	O(8)-Zn(1)#4	2.254(3)
Yb(1)-O(5)	2.258(3)	Zn(1)-N(1)	2.122(3)	N(3)-Zn(1)#2	2.064(3)
Yb(1)-O(7)	2.256(3)	Zn(1)-N(3)#2	2.064(3)	N(4)-Zn(1)#4	2.079(3)
Yb(1)-O(1w)	2.376(3)	Zn(1)-N(4)#3	2.079(3)		
Bond	Angle	Bond	Angle	Bond	Angle
O(1)-Yb(1)-O(7)	106.58(12)	O(7)-Yb(1)-O(4)#1	83.86(11)	N(4)#3-Zn(1)-O(2)	161.10(13)
O(1)-Yb(1)-O(5)	78.66(12)	O(5)-Yb(1)-O(4)#1	93.02(11)	N(1)-Zn(1)-O(2)	76.72(12)
O(7)-Yb(1)-O(5)	77.45(10)	O(2w)-Yb(1)-O(4)#1	94.57(12)	N(3)#2-Zn(1)-O(6)#2	77.92(12)

O(1)-Yb(1)-O(2w)	82.87(13)	O(1w)-Yb(1)-O(4)#1	76.29(11)	N(4)#3-Zn(1)-O(6)#2	100.28(12)
O(7)-Yb(1)-O(2w)	146.74(11)	O(3)-Yb(1)-O(4)#1	117.25(9)	N(1)-Zn(1)-O(6)#2	94.02(11)
O(5)-Yb(1)-O(2w)	135.73(11)	O(1)-Yb(1)-O(3)#1	139.75(10)	O(2)-Zn(1)-O(6)#2	98.48(12)
O(1)-Yb(1)-O(1w)	88.56(12)	O(7)-Yb(1)-O(3)#1	76.91(9)	N(3)#2-Zn(1)-O(8)#3	100.61(12)
O(7)-Yb(1)-O(1w)	139.17(11)	O(5)-Yb(1)-O(3)#1	138.90(10)	N(4)#3-Zn(1)-O(8)#3	76.51(11)
O(5)-Yb(1)-O(1w)	68.53(10)	O(2w)-Yb(1)-O(3)#1	75.90(10)	N(1)-Zn(1)-O(8)#3	88.25(12)
O(2w)-Yb(1)-O(1w)	71.15(11)	O(1w)-Yb(1)-O(3)#1	115.38(10)	O(2)-Zn(1)-O(8)#3	84.81(12)
O(1)-Yb(1)-O(3)	77.02(10)	O(3)-Yb(1)-O(3)#1	65.02(10)	O(6)#2-Zn(1)-O(8)#3	176.36(11)
O(7)-Yb(1)-O(3)	75.01(10)	O(4)#1-Yb(1)-O(3)	52.73(10)	C(1)-O(1)-Yb(1)	153.8(3)
O(5)-Yb(1)-O(3)	135.85(10)	N(3)#2-Zn(1)-N(4)#3	96.54(14)	C(1)-O(2)-Zn(1)	116.7(3)
O(2w)-Yb(1)-O(3)	76.35(10)	N(3)#2-Zn(1)-N(1)	163.05(13)	C(4)-O(3)-Yb(1)	150.7(2)
O(1w)-Yb(1)-O(3)	145.80(10)	N(4)#3-Zn(1)-N(1)	99.59(14)	C(4)-O(3)-Yb(1)#1	91.9(2)
O(1)-Yb(1)-O(4)#1	164.60(11)	N(3)#2-Zn(1)-O(2)	89.62(12)	Yb(1)-O(3)-Yb(1)#1	114.98(10)

Complex 5

Bond	Length	Bond	Length	Bond	Length
Tb(1)-O(1)	2.241(5)	Co(1)-O(6)#3	2.162(5)	Tb(1)-O(4)#1	2.474(4)
Tb(1)-O(5)	2.288(5)	Co(1)-O(8)#2	2.178(5)	Tb(1)-O(3)#1	2.557(4)
Tb(1)-O(7)	2.298(5)	O(4)-Tb(1)#1	2.474(4)	Co(1)-N(4)#2	2.081(5)
Tb(1)-O(2W)	2.361(5)	O(6)-Co(1)#3	2.162(5)	Co(1)-N(3)#3	2.081(5)
Tb(1)-O(3)	2.413(5)	O(8)-Co(1)#4	2.178(5)	Co(1)-O(2)	2.111(5)
Tb(1)-O(1W)	2.418(5)	N(4)-Co(1)#4	2.081(5)	Co(1)-N(1)	2.135(6)
Bond	Angle	Bond	Angle	Bond	Angle
O(1)-Tb(1)-O(5)	78.68(19)	O(2W)-Tb(1)-O(3)#1	76.66(2)	O(1W)-Tb(1)-O(4)#1	76.51(17)
O(1)-Tb(1)-O(7)	107.6(2)	O(3)-Tb(1)-O(3)#1	65.83(2)	O(1)-Tb(1)-O(3)#1	139.20(17)
O(5)-Tb(1)-O(7)	76.96(17)	O(1W)-Tb(1)-O(3)#1	115.33(2	O(5)-Tb(1)-O(3)#1	139.21(16)
O(1)-Tb(1)-O(3)	75.79(17)	O(4)#1-Tb(1)-O(3)#1	51.45(2)	O(7)-Tb(1)-O(3)#1	76.43(15)
O(5)-Tb(1)-O(3)	134.28(2)	N(4)#2-Co(1)-N(3)#3	94.6(2)	N(4)#2-Co(1)-O(6)#3	99.1(2)
O(7)-Tb(1)-O(3)	75.58(17)	N(4)#2-Co(1)-O(2)	163.9(2)	N(3)#3-Co(1)-O(6)#3	78.1(2)
O(2W)-Tb(1)-O(3)	76.86(16)	N(3)#3-Co(1)-O(2)	91.4(2)	O(2)-Co(1)-O(6)#3	96.73(19)
O(5)-Tb(1)-O(4)#1	95.19(17)	N(4)#2-Co(1)-N(1)	98.2(2)	O(7)-Tb(1)-O(1W)	138.22(18)
O(1)-Tb(1)-O(4)#1	165.54(2)	N(3)#3-Co(1)-N(1)	166.4(2)	O(3)-Tb(1)-O(4)#1	116.87(14)
O(6)#3-Co(1)-O(8)#2	175.58(2)	O(2)-Co(1)-N(1)	77.42(2)	O(2)-Co(1)-O(8)#2	86.49(18)
O(7)-Tb(1)-O(4)#1	83.34(17)	N(1)-Co(1)-O(6)#3	95.2(2)	N(1)-Co(1)-O(8)#2	88.4(2)
N(4)#2-Co(1)-O(8)	77.82(19)	N(3)#3-Co(1)-O(8)#2	98.8(2)	O(1W)-Tb(1)-O(4)#1	76.51(17)
O(1)-Tb(1)-O(5)	78.68(19)	O(2W)-Tb(1)-O(3)#1	76.66(2)		

Complex 6

Bond	Length	Bond	Length	Bond	Length
Dy(1)-O(1)	2.233(5)	Dy(1)-O(1w)	2.408(6)	Co(1)-N(3)#2	2.090(6)

Dy(1)-O(3)#1	2.545(5)	Dy(1)-O(2w)	2.352(5)	Co(1)-N(4)#3	2.089(6)
Dy(1)-O(3)	2.408(5)	Co(1)-O(2)	2.121(5)	O(3)-Dy(1)#1	2.545(5)
Dy(1)-O(4)#1	2.459(5)	Co(1)-O(6)#2	2.163(5)	O(4)-Dy(1)#1	2.459(5)
Dy(1)-O(5)	2.285(5)	Co(1)-O(8)#3	2.187(5)	O(6)-Co(1)#2	2.163(5)
Dy(1)-O(7)	2.292(5)	Co(1)-N(1)	2.143(6)	O(8)-Co(1)#4	2.187(5)
Bond	Angle	Bond	Angle	Bond	Angle
O(1)-Dy(1)-O(5)	78.3(2)	O(7)-Dy(1)-O(3)	75.67(18)	O(2w)-Dy(1)-O(3)#1	76.45(17)
O(1)-Dy(1)-O(7)	107.4(2)	O(2w)-Dy(1)-O(3)	76.16(17)	O(1w)-Dy(1)-O(3)#1	114.89(18)
O(5)-Dy(1)-O(7)	77.10(18)	O(1w)-Dy(1)-O(3)	145.79(17)	O(3)-Dy(1)-O(3)#1	65.48(17)
O(1)-Dy(1)-O(2w)	82.0(2)	O(1)-Dy(1)-O(4)#1	165.4(2)	O(4)#1-Dy(1)-O(3)#1	51.76(16)
O(5)-Dy(1)-O(2w)	135.81(19)	O(5)-Dy(1)-O(4)#1	94.91(19)	O(3)-Dy(1)-C(4)#1	91.16(16)
O(7)-Dy(1)-O(2w)	146.96(19)	O(7)-Dy(1)-O(4)#1	83.31(19)	N(4)#3-Co(1)-N(3)#2	93.9(2)
O(1)-Dy(1)-O(1w)	89.3(2)	O(2w)-Dy(1)-O(4)#1	94.3(2)	N(4)#3-Co(1)-O(2)	164.0(2)
O(5)-Dy(1)-O(1w)	69.41(18)	O(1w)-Dy(1)-O(4)#1	76.10(19)	N(3)#2-Co(1)-O(2)	91.7(2)
O(7)-Dy(1)-O(1w)	138.5(2)	O(3)-Dy(1)-O(4)#1	116.83(15)	N(4)#3-Co(1)-N(1)	98.7(2)
O(2w)-Dy(1)-O(1w)	71.17(19)	O(1)-Dy(1)-O(3)#1	139.42(18)	N(3)#2-Co(1)-N(1)	166.6(2)
O(1)-Dy(1)-O(3)	76.23(18)	O(5)-Dy(1)-O(3)#1	139.29(18)	O(2)-Co(1)-N(1)	77.3(2)
O(5)-Dy(1)-O(3)	134.70(17)	O(7)-Dy(1)-O(3)#1	76.38(16)	N(4)#3-Co(1)-O(6)#2	99.2(2)

Symmetry codes for Symmetry codes for **1**: #1 -x+1,y+1/2,-z+1/2 ,#2 x,-y+3/2,z-1/2, #3 -x, y+1/2,-z+1/2, #4 -x,y-1/2,-z+1/2, #5 -x+1,y-1/2,-z+1/2, #6 x,-y+3/2,z+1/2, #7 -x+1,-y+1,-z+1, #8 x,y-1, z. for **2**: #1 -x+3/2,-y+1/2,-z+1, #2 -x+1,-y,-z+1, #3 -x+3/2,y-1/2,-z+1/2 , #4 -x+3/2,y+1/2,-z+1/2. for **3**: #1 -x+1,-y,-z+1, #2 -x+1/2,y+1/2,-z+1/2, #3 x,-y,z+1/2, #4 -x+1/2,y-1/2,-z+1/2, #5 x,-y, z-1/2. for **4**: #1 -x+1,-y+1,-z+1, #2 -x+3/2,y-1/2,-z+3/2; #3 x+1/2,y-1/2, z, #4 -x+3/2,y+1/2,-z+3/2,#5 x-1/2,y+1/2, z. for **5**: #1 -x+1/2,-y+1/2,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+1/2,y+1/2,-z+3/2; #4 -x+1/2,y-1/2,-z+3/2, for **6**: #1 -x+1,-y,-z+1 ,#2 -x+1/2,y+1/2,-z+1/2, #3 x,-y, z+1/2, #4 -x+1/2, y-1/2,-z+1/2, #5 x,-y,z-1/2.

Table S2 The hydrogen bond lengths (Å) and angles (°) for polymers **1- 6**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Complex **1**				
O(1w)-H(11)...O(2)#6	0.84	1.94	2.76(1)	166
O(1w)-H(12)...O(2w)	0.84	1.92	2.70(1)	152
O(2w)-H(21)...O(6)#6	0.84	2.26	3.04(1)	155
O(2w)-H(22)...O(8)	0.84	2.09	2.86(1)	152
O(3w)-H(31)...O(4)#7	0.84	1.96	2.78(1)	167
O(3w)-H(32)...O(8)#8	0.84	2.32	2.98(2)	136
N(4)-H(4)...O(3w)	0.88	1.90	2.78(2)	172
Complex **2**				

O(1w)-H(11)...O(4)#5	0.84	2.16	2.853(6)	139.0
O(1w)-H(12)...O(3w)	0.84	2.23	2.712(6)	116.2
O(2w)-H(21)...O(7)#1	0.84	2.00	2.835(6)	171.9
O(2w)-H(22)...O(5w)	0.84	2.10	2.666(7)	124.3
O(3w)-H(31)...O(4w)	0.84	1.95	2.793(9)	177.9
O(3w)-H(32)...O(6w)	0.84	2.36	3.169(18)	162.3
O(4w)-H(41)...O(2)#6	0.84	1.93	2.750(10)	166.3
O(4w)-H(42)...O(1w)#6	0.84	2.40	2.979(10)	127.0
O(5w)-H(51)...O(4w)	0.84	1.92	2.745(13)	168.7
N(2)-H(2)...O(6)#7	0.88	2.26	2.843(6)	123.8
Complex **3**				
O(1w)-H(11)...O(4)#5	0.84	2.16	2.849(5)	139.1
O(1w)-H(12)...O(3w)	0.84	2.24	2.698(5)	114.7
O(2w)-H(21)...O(7)#1	0.84	2.01	2.847(5)	171.8
O(2w)-H(22)...O(5w)	0.84	2.09	2.649(8)	123.7
O(3w)-H(31)...O(4w)	0.84	1.94	2.779(10)	178.9
O(3w)-H(32)...O(6w)	0.84	2.35	3.167(15)	163.2
O(4w)-H(41)...O(2)#6	0.84	1.90	2.725(11)	167.6
O(4w)-H(42)...O(1w)#6	0.84	2.41	2.999(10)	128.1
O(5w)-H(51)...O(4w)	0.84	1.85	2.681(15)	168.4
N(2)-H(2)...O(6)#7	0.88	2.27	2.845(5)	123.3
Complex **4**				
O(1w)-H(11)...O(4)#5	0.84	2.19	2.864(4)	138.0
O(1w)-H(12)...O(3w)	0.84	2.23	2.696(4)	115.2
O(2w)-H(21)...O(7)#1	0.84	1.99	2.822(4)	172.9
O(2w)-H(22)...O(5w)	0.84	2.08	2.641(6)	124.0
O(3w)-H(31)...O(4w)	0.84	1.97	2.808(8)	178.1
O(3w)-H(32)...O(6w)	0.84	2.36	3.177(12)	163.2
O(4w)-H(41)...O(2)#6	0.84	1.91	2.737(9)	167.9
O(4w)-H(42)...O(1w)#6	0.84	2.38	2.960(8)	127.0
O(5w)-H(51)...O(4w)	0.84	1.89	2.723(12)	169.0
N(2)-H(2)...O(6)#7	0.88	2.27	2.848(5)	122.9
Complex **5**				
O(1W)-H(11)...O(4)#5	0.84	2.12	2.803(7)	138.8
O(1W)-H(12)...O(3W)	0.84	2.23	2.699(7)	115.0
O(2W)-H(21)...O(7)#1	0.84	2.04	2.869(7)	171.4
O(2W)-H(22)...O(5W)	0.85	2.06	2.626(16)	123.7
O(3W)-H(31)...O(4W)	0.84	1.84	2.659(17)	163.4

O(3W)-H(32)...O(6W)	0.84	2.21	3.013(19)	160.0
O(4W)-H(41)...O(2)#6	0.84	1.87	2.701(18)	171.5
O(4W)-H(42)...O(1W)#6	0.84	2.48	3.170(17)	140.4
O(5W)-H(51)...O(4W)	0.84	1.43	2.25(3)	163.5
N(2)-H(2)...O(6)#7	0.88	2.33	2.858(8)	118.7
Complex **6**				
O(1w)-H(11)...O(4)#5	0.84	2.13	2.821(8)	139.4
O(1w)-H(12)...O(3w)	0.84	2.22	2.681(8)	114.2
O(2w)-H(21)...O(7)#1	0.84	2.02	2.850(8)	171.7
O(3w)-H(31)...O(4w)	0.84	1.85	2.687	176.6
O(4w)-H(41)...O(2)#6	0.84	1.90	2.691(7)	156.4
O(4w)-H(42)...O(1w)#6	0.84	2.72	3.146(8)	113.5
N(2)-H(2)...O(6)#7	0.88	2.31	2.859(8)	120.7

Symmetry codes for Symmetry codes for **1**: #1 -x+1,y+1/2,-z+1/2 ,#2 x,-y+3/2,z-1/2, #3 -x, y+1/2,-z+1/2, #4 -x,y-1/2,-z+1/2, #5 -x+1,y-1/2,-z+1/2, #6 x,-y+3/2,z+1/2, #7 -x+1,-y+1,-z+1, #8 x,y-1, z. for **2**: #1 -x+3/2,-y+1/2,-z+1, #2 -x+1,-y,-z+1, #3 -x+3/2,y-1/2,-z+1/2 , #4 -x+3/2,y+1/2,-z+1/2. for **3**: #1 -x+1,-y,-z+1, #2 -x+1/2,y+1/2,-z+1/2, #3 x,-y,z+1/2, #4 -x+1/2,y-1/2,-z+1/2, #5 x,-y, z-1/2. for **4**: #1 -x+1,-y+1,-z+1, #2 -x+3/2,y-1/2,-z+3/2; #3 x+1/2,y-1/2, z, #4 -x+3/2,y+1/2,-z+3/2,#5 x-1/2,y+1/2, z. for **5**: #1 -x+1/2,-y+1/2,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+1/2,y+1/2,-z+3/2; #4 -x+1/2,y-1/2,-z+3/2, for **6**: #1 -x+1,-y,-z+1 ,#2 -x+1/2,y+1/2,-z+1/2, #3 x,-y,z+1/2, #4 -x+1/2, y-1/2,-z+1/2, #5 x,-y,z-1/2.

References

1. Song, J. F.; Zhou, R. S.; Hu, T. P.; Chen, Z.; Wang, B. B. *J. Coord. Chem*., **2010**, 63, 42014.

2. Feng, X.; Miao S. B.; Li, T. F. and Wang, L. Y. *Russ. J. Coord. Chem*., **2011**, 37, 572.

3. Sun, Y. G.; Wu,Y. L.; Philippe, G. X.; Smet, F.; Ding, F.; Guo, M. Y.; Zhu, M. C.; Gao, E. J.; Poelman, D and Verpoort ,F. *Dalton Trans,* **2010**, 39, 11383.

4. Paira, M. K., Dinda, J., Lu, T.H., et al., *Polyhedron*, **2007**, 26, 4131.