Supporting Information

A New Family of Boat-Shaped Ln_8 Clusters Exhibiting Magnetocaloric Effect, Slow Magnetic Relaxation

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Luminescence Properties.

The luminescence properties of **3-Eu** were investigated in the solid state at ambient temperature. As can be seen in Fig. S1, under the maximum excitation wavelength of 394 nm, the **3-Eu** exhibits the characteristic emission peaks of Eu(III) cation. The **3-Eu** exhibits the characteristic emission peaks of Eu(III) at 580, 593, 613, 653, and 702 nm, which can be derived from $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, and 4) transitions. Among them, the strong emission at 613 nm is ascribed to the $^5D_0 \rightarrow {}^7F_2$ electric dipolar transition, while the medium emission at 593 nm is attributed to magnetic dipolar $^5D_0 \rightarrow {}^7F_1$ transition. Additionally, the peaks at 653 and 702 nm pertain to the transition of $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively. Those characteristic peaks are in agreement with the reported Eu(III) compounds.[1,2]

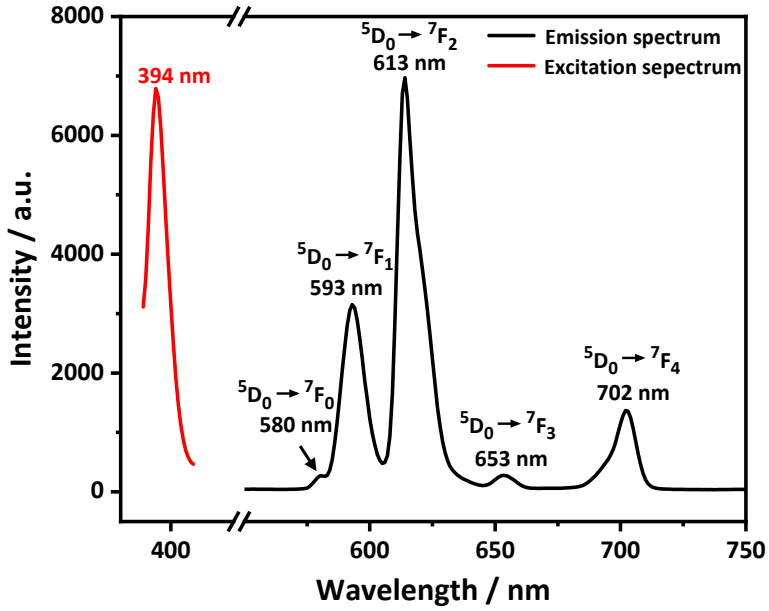


Fig. S1 The solid-state excitation and emission spectra of the powder samples of **3-Eu** under room temperature.

Experimental Section

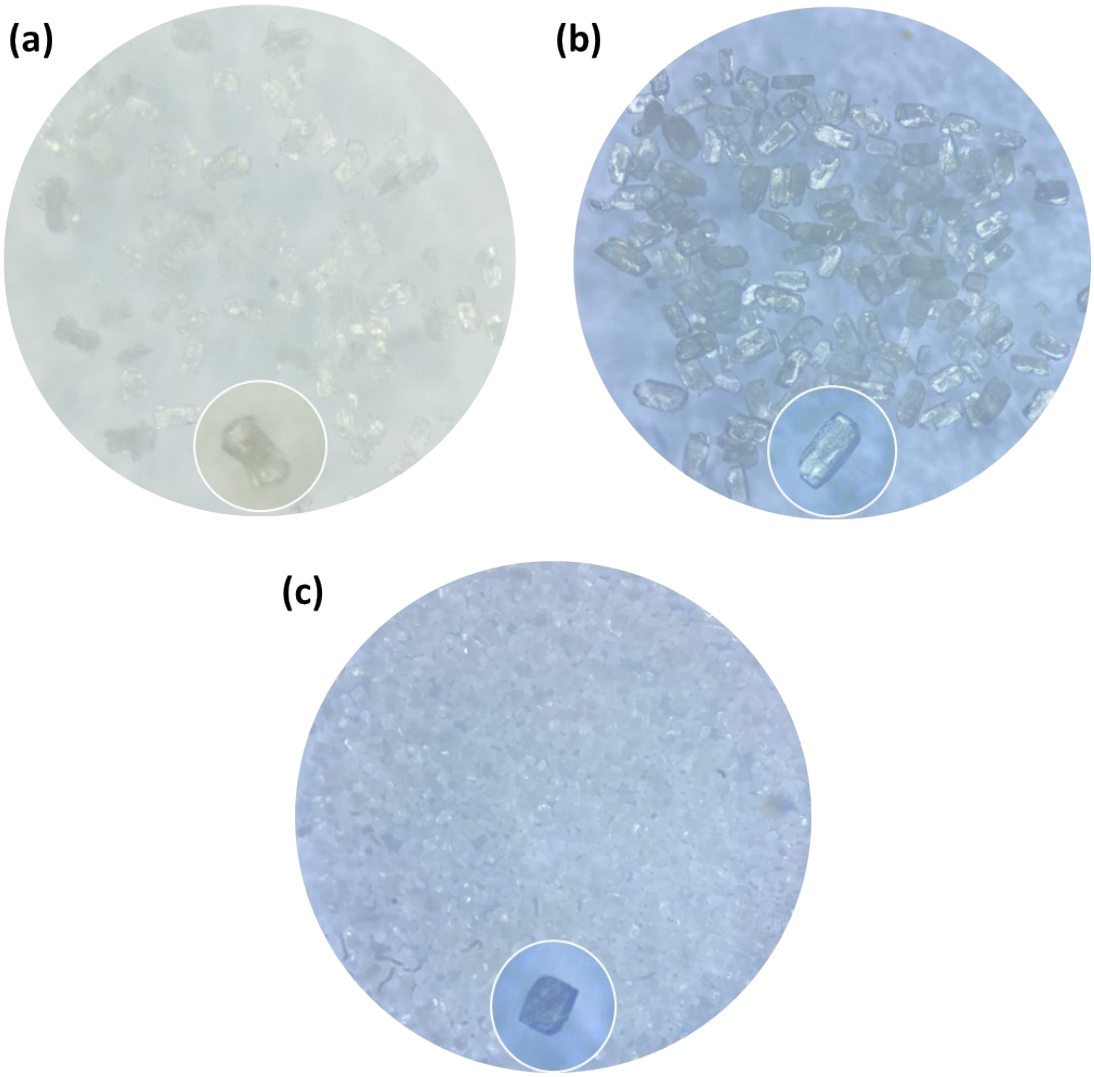


Fig. S2 The images of (a) **1-Gd**, (b) **2-Dy**, (c) **3-Eu** under optical microscope.

Structure

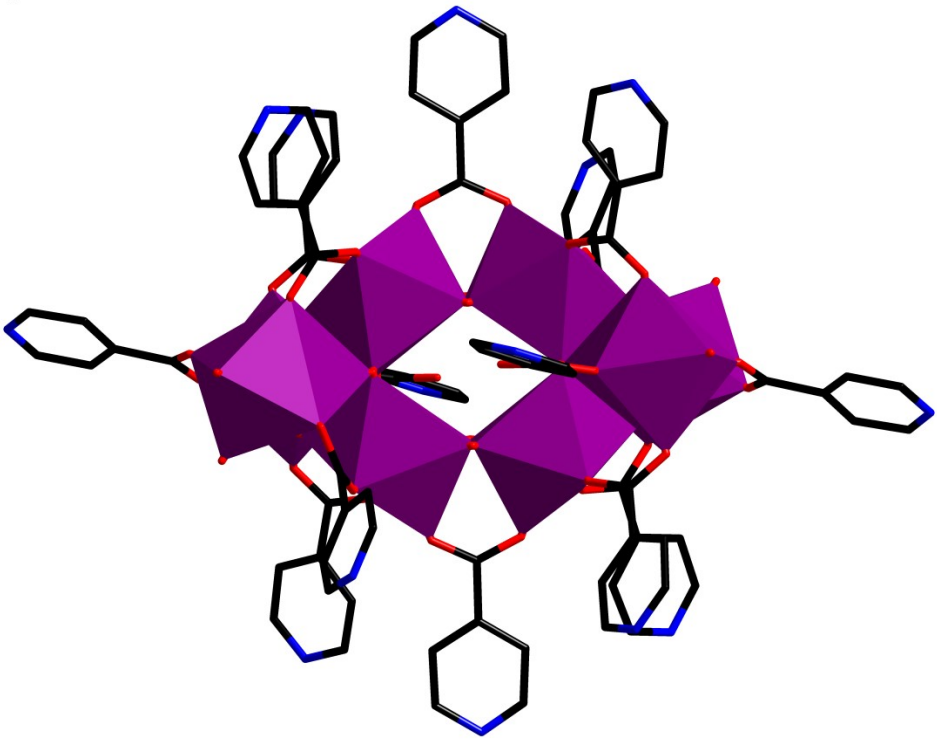


Fig. S3 Polyhedral view of compound **2-Dy**.

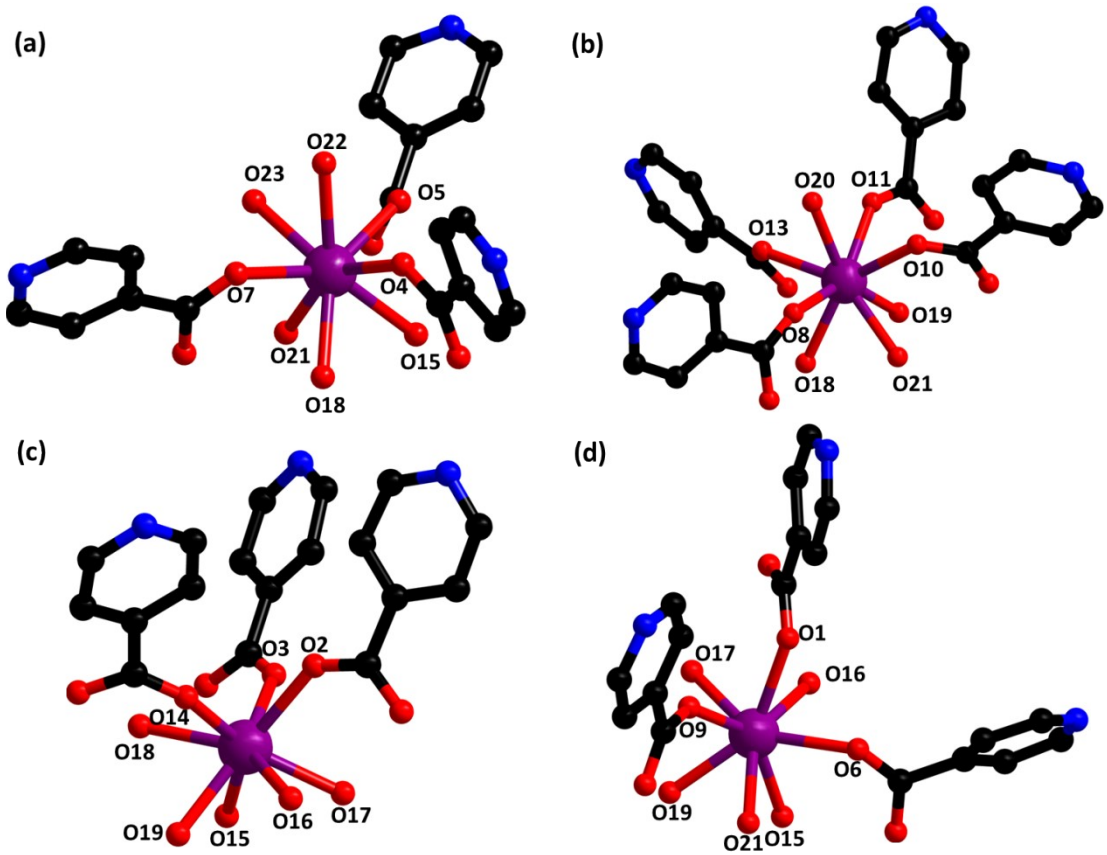


Fig. S4 Ball-and-stick of coordination mode of Dy1 (a), Dy2 (b), Dy3 (c), Dy4 (d).

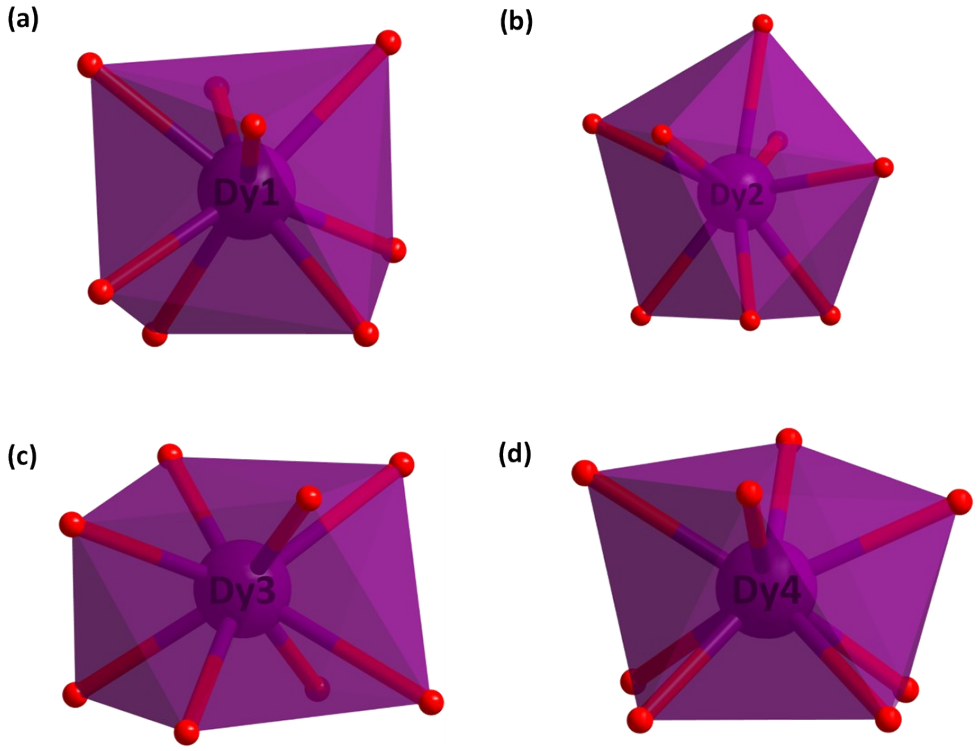
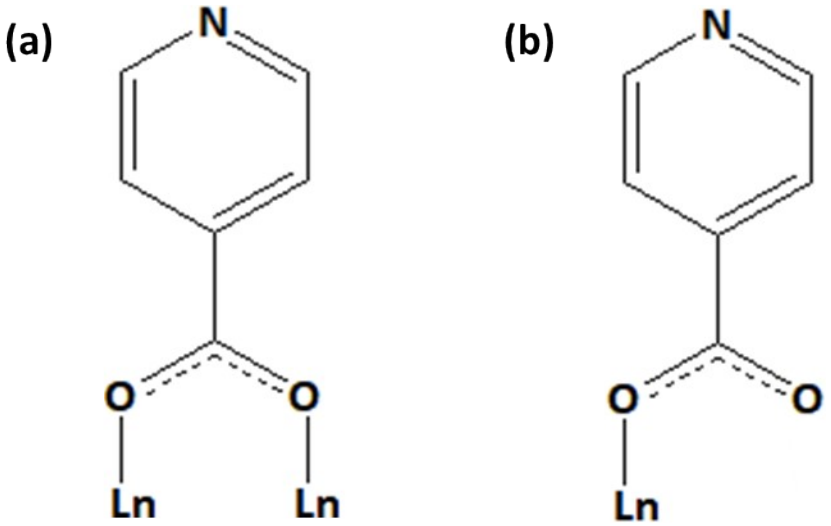


Fig. S5 The coordination geometries of Dy atoms in compound **2-Dy**.

Scheme S1. Coordination modes of HIN in **2-Dy**.



PXRD patterns

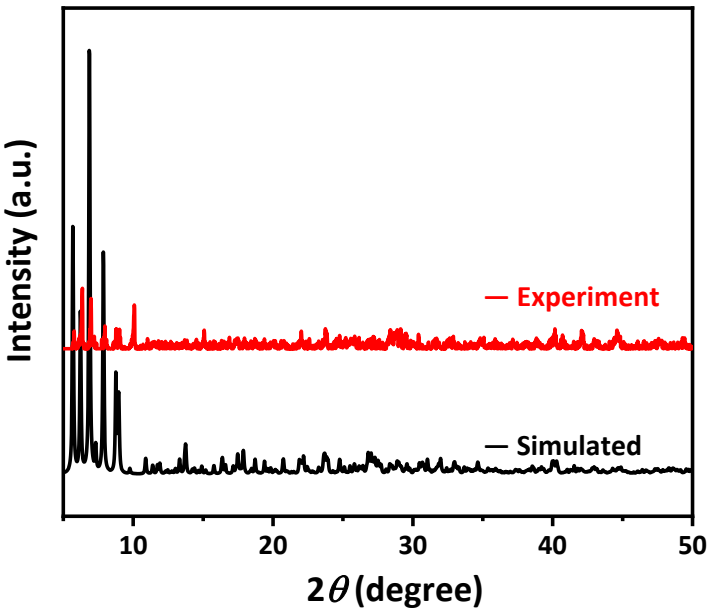


Fig. S6 The PXRD spectrum of compound **1-Gd**.

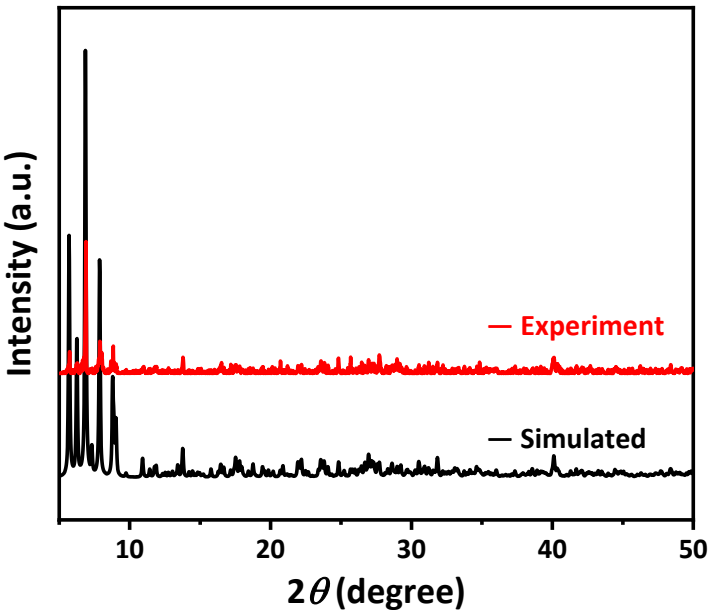


Fig. S7 The PXRD spectrum of compound **2-Dy**.

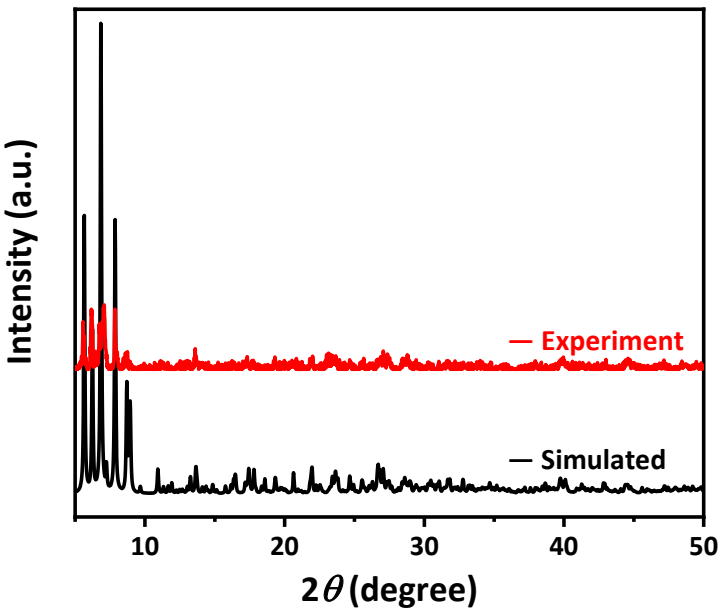


Fig. S8 The PXRD spectrum of compound **3-Eu**.

FT-IR patterns

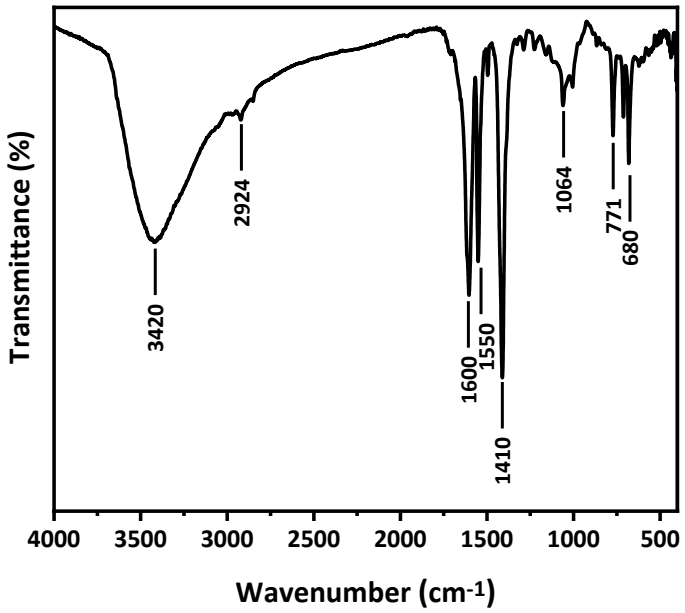


Fig. S9 The IR spectrum of compound **1-Gd**.

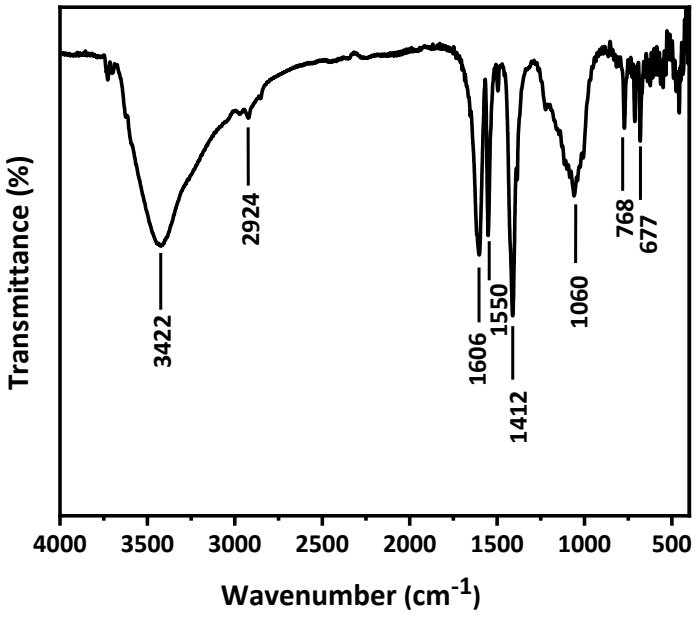


Fig. S10 The IR spectrum of compound **2-Dy**.

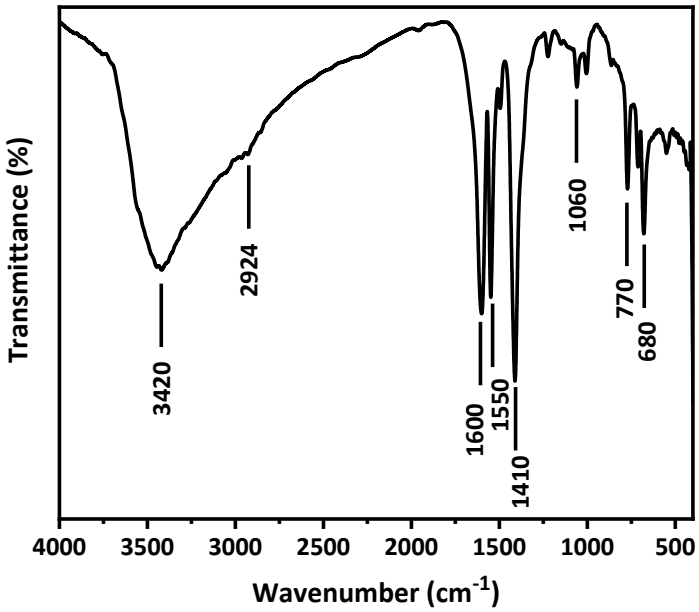


Fig. S11 The IR spectrum of compound **3-Eu**.

TG

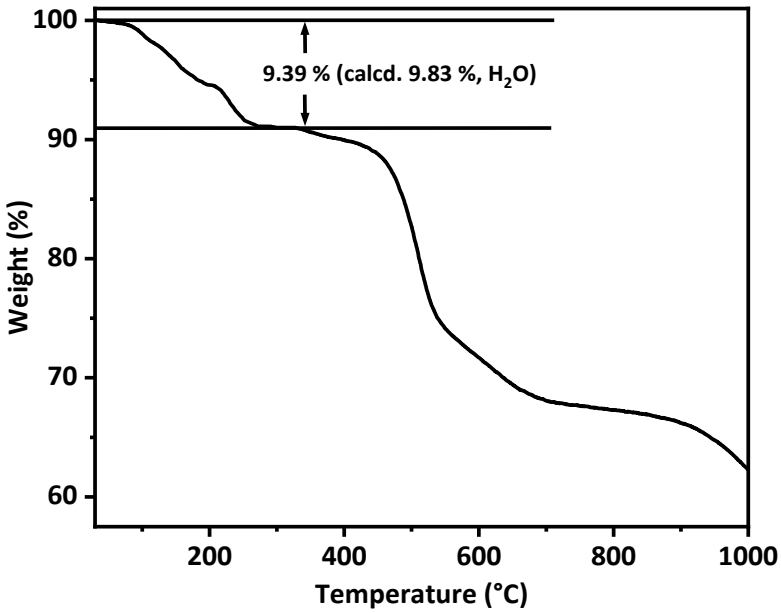


Fig. S12 TGA curve of compound **1-Gd**.

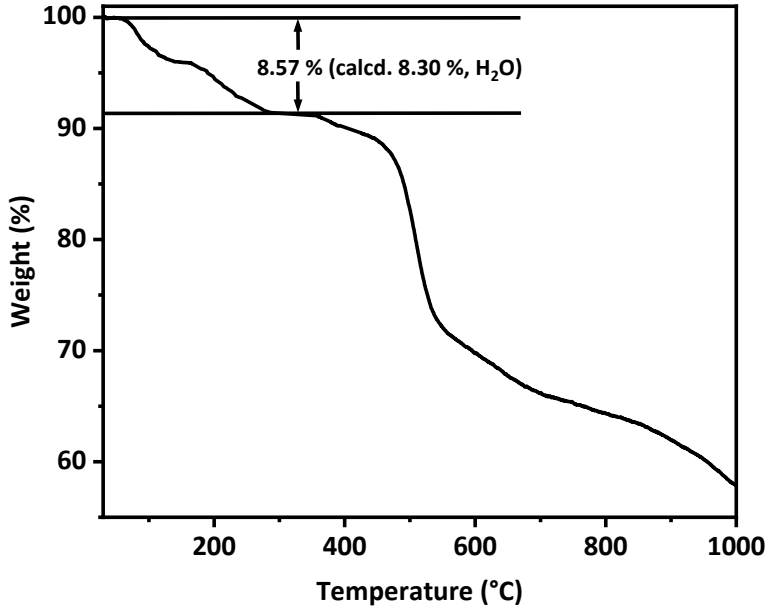


Fig. S13 TGA curve of compound **2-Dy**.

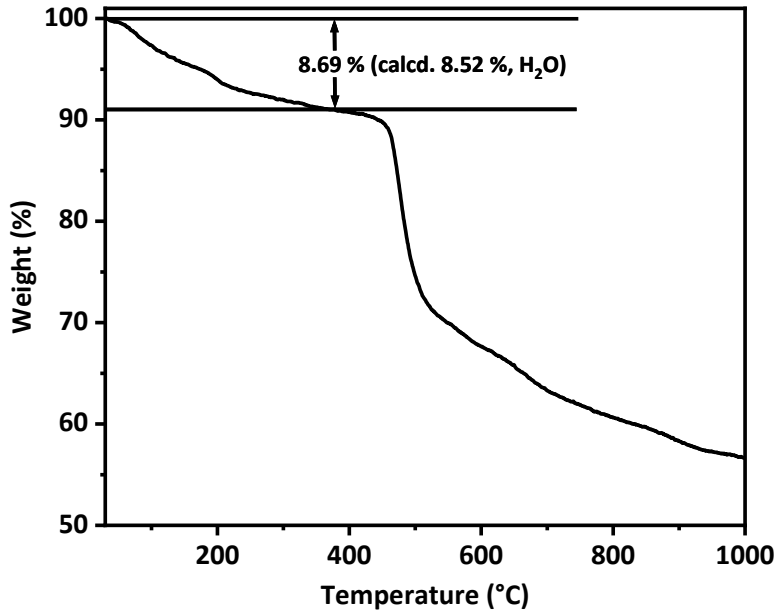


Fig. S14 TGA curve of compound **3-Eu**.

The thermogravimetric analyses of compounds **1-Gd** and **3-Eu** were also investigated (Fig. S12 and S14). For **1-Gd**, the weight loss of 5.45 % (calculated value: 5.69 %) corresponds to the loss of lattice H_2O molecules, which ranges from 25 to 190 °C. The second step in the range of 190–280 °C is considered as the the removal of coordinated H_2O molecules (calculated value: 4.14 %; found: 3.94 %). When temperature increases from 280 to 1000 °C, the entire compound framework gradually collapses as the organic ligands isonicotinic acid are lost. For **3-Eu**, the loss of 4.37 % is within the scope of 25–150 °C, which may be due to the lattice H_2O molecules (calculated value: 4.26 %). The loss of 4.32 % between 150 and 350 °C corresponds to the coordinated H_2O molecules (calculated value: 4.26 %). Above 350 °C, HIN ligands are removed and the framework collapses.

Magnetic property

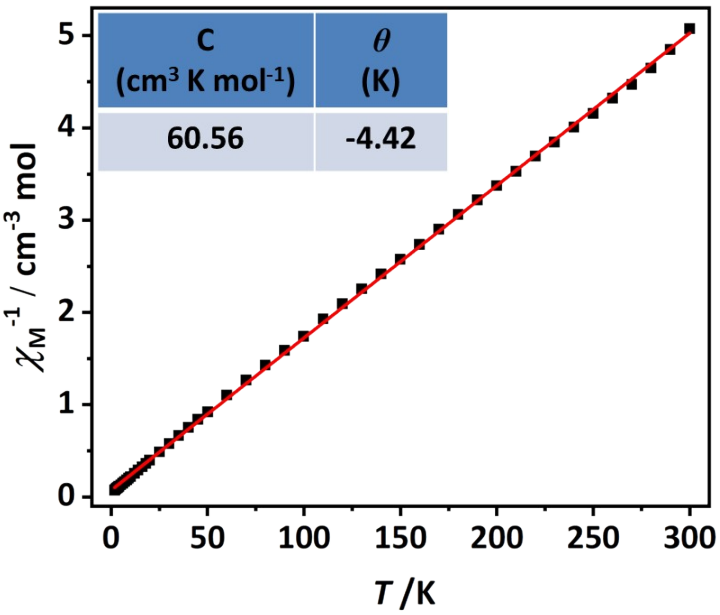


Fig. S15 χ_M^{-1} versus *T* plot of **1-Gd**. The red line is fitting result with $\chi_M = C / (T - \theta)$.

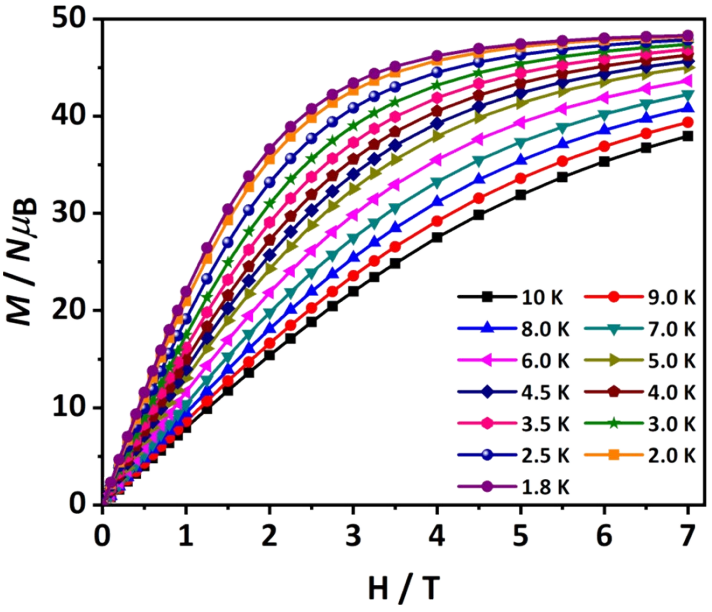


Fig. S16 Plot of *M-H* for **1-Gd** under different temperatures.

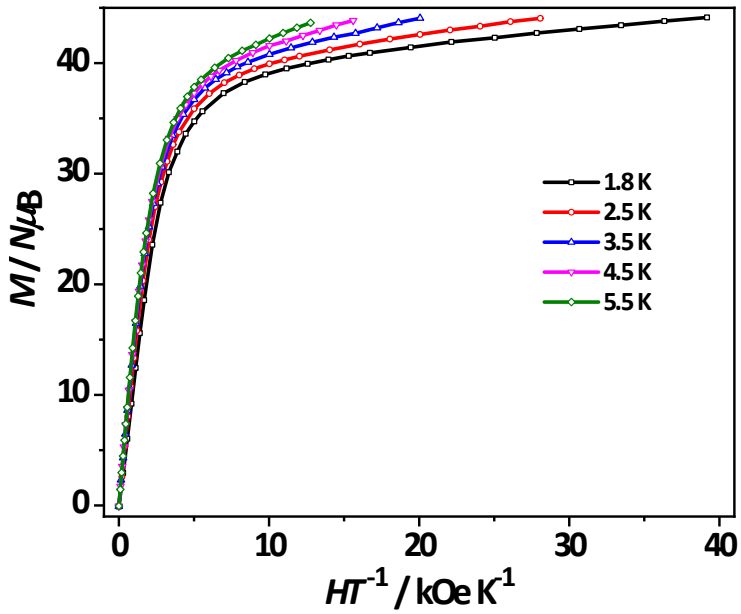


Fig. S17 Plot of reduced magnetization (*M*) vs HT^{-1} in the range of 1.8 to 5.5 K for compound **2-Dy**.

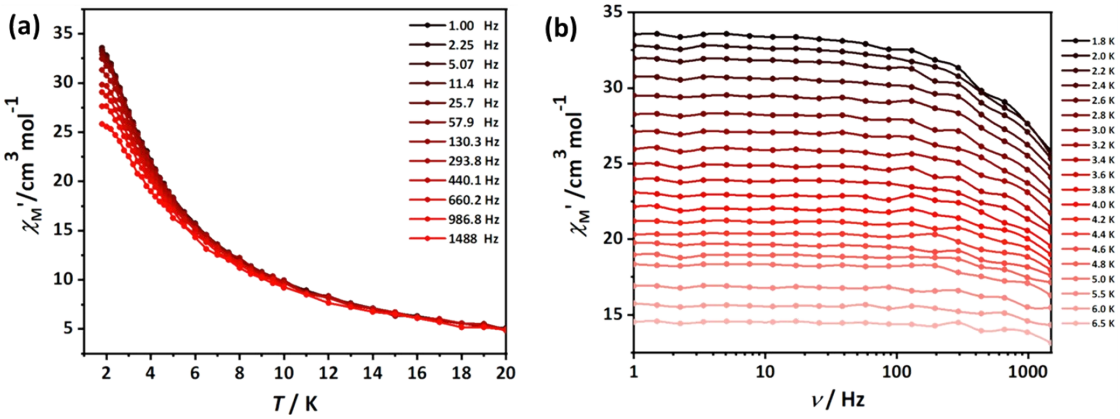


Fig. S18 The isothermal or equifrequent lines of in-phase susceptibilities of compound **2-Dy** for the observation of frequency dependence.

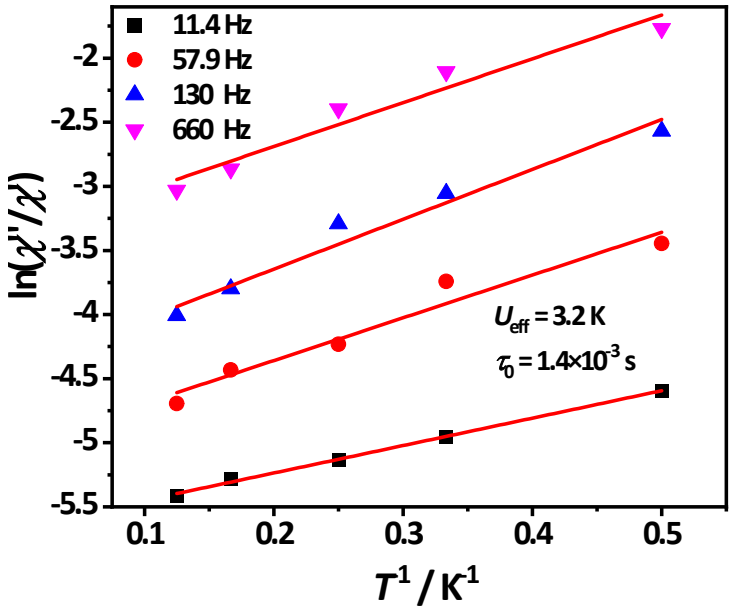


Fig. S19 Natural logarithm of the ratio of χ'' over χ' versus T^{-1} of the data for compound **2-Dy**.

Table S1. Selected Bond lengths (Å) and Bond angles (°) of main metal atoms for compound **1-Gd**.

Gd(1)-O(4)	2.302(7)	Gd(2)-O(4)	2.279(7)
Gd(1)-O(9)	2.368(7)	Gd(2)-O(3)	2.346(7)
Gd(1)-O(18)#1	2.385(8)	Gd(2)-O(10)	2.356(8)
Gd(1)-O(3)#1	2.388(7)	Gd(2)-O(14)	2.378(8)
Gd(1)-O(2)#1	2.409(6)	Gd(2)-O(1)	2.391(7)
Gd(1)-O(12)	2.427(7)	Gd(2)-O(13)	2.401(8)
Gd(1)-O(21)#1	2.471(8)	Gd(2)-O(9)#1	2.426(7)
Gd(1)-O(1W)	2.546(7)	Gd(2)-O(1W)	2.633(7)
Gd(4)-O(2)	2.344(7)	Gd(3)-O(3)	2.339(7)
Gd(4)-O(11)	2.355(8)	Gd(3)-O(23)	2.363(8)
Gd(4)-O(1)	2.366(7)	Gd(3)-O(1)	2.391(7)
Gd(4)-O(22)	2.377(7)	Gd(3)-O(19)	2.395(9)
Gd(4)-O(20)	2.428(8)	Gd(3)-O(2)	2.419(7)
Gd(4)-O(9)#1	2.443(7)	Gd(3)-O(15)	2.431(8)
Gd(4)-O(4W)	2.447(7)	Gd(3)-O(17)	2.433(10)
Gd(4)-O(3W)	2.489(7)	Gd(3)-O(2W)	2.447(9)
O(4)-Gd(1)-O(9)	110.5(2)	O(4)-Gd(2)-O(3)	105.1(2)
O(4)-Gd(1)-O(18)#1	81.5(3)	O(4)-Gd(2)-O(10)	85.9(3)
O(9)-Gd(1)-O(18)#1	141.7(2)	O(3)-Gd(2)-O(10)	142.6(3)
O(4)-Gd(1)-O(3)#1	74.2(2)	O(4)-Gd(2)-O(14)	139.4(3)
O(9)-Gd(1)-O(3)#1	68.5(2)	O(3)-Gd(2)-O(14)	81.0(3)
O(18)#1-Gd(1)-O(3)#1	81.2(3)	O(10)-Gd(2)-O(14)	113.8(3)
O(4)-Gd(1)-O(2)#1	139.0(2)	O(4)-Gd(2)-O(1)	146.6(2)
O(9)-Gd(1)-O(2)#1	71.5(2)	O(3)-Gd(2)-O(1)	70.7(2)
O(18)#1-Gd(1)-O(2)#1	76.2(2)	O(10)-Gd(2)-O(1)	80.6(3)
O(3)#1-Gd(1)-O(2)#1	68.7(2)	O(14)-Gd(2)-O(1)	73.7(3)
O(4)-Gd(1)-O(12)	79.8(3)	O(4)-Gd(2)-O(13)	79.7(3)
O(9)-Gd(1)-O(12)	143.4(3)	O(3)-Gd(2)-O(13)	142.4(3)
O(18)#1-Gd(1)-O(12)	73.1(3)	O(10)-Gd(2)-O(13)	74.2(3)
O(3)#1-Gd(1)-O(12)	145.7(3)	O(14)-Gd(2)-O(13)	73.0(3)
O(2)#1-Gd(1)-O(12)	124.2(2)	O(1)-Gd(2)-O(13)	124.6(2)
O(4)-Gd(1)-O(21)#1	145.2(3)	O(4)-Gd(2)-O(9)#1	77.7(2)
O(9)-Gd(1)-O(21)#1	79.3(3)	O(3)-Gd(2)-O(9)#1	68.2(3)
O(18)#1-Gd(1)-O(21)#1	111.9(3)	O(10)-Gd(2)-O(9)#1	79.9(3)
O(3)#1-Gd(1)-O(21)#1	137.8(3)	O(14)-Gd(2)-O(9)#1	138.3(3)
O(2)#1-Gd(1)-O(21)#1	75.7(2)	O(1)-Gd(2)-O(9)#1	70.0(2)
O(12)-Gd(1)-O(21)#1	74.4(3)	O(13)-Gd(2)-O(9)#1	146.5(3)
O(4)-Gd(1)-O(1W)	70.4(2)	O(4)-Gd(2)-O(1W)	69.1(2)
O(9)-Gd(1)-O(1W)	78.3(2)	O(3)-Gd(2)-O(1W)	74.1(2)
O(18)#1-Gd(1)-O(1W)	138.5(2)	O(10)-Gd(2)-O(1W)	141.7(2)

O(3)#1-Gd(1)-O(1W)	117.7(2)	O(14)-Gd(2)-O(1W)	74.5(2)
O(2)#1-Gd(1)-O(1W)	143.9(2)	O(1)-Gd(2)-O(1W)	135.3(2)
O(12)-Gd(1)-O(1W)	72.4(3)	O(13)-Gd(2)-O(1W)	73.2(3)
O(21)#1-Gd(1)-O(1W)	79.7(2)	O(9)#1-Gd(2)-O(1W)	120.0(2)
O(2)-Gd(4)-O(11)	146.9(3)	O(3)-Gd(3)-O(23)	140.8(3)
O(2)-Gd(4)-O(1)	72.0(2)	O(3)-Gd(3)-O(1)	70.8(2)
O(11)-Gd(4)-O(1)	80.4(3)	O(23)-Gd(3)-O(1)	77.5(3)
O(2)-Gd(4)-O(22)	95.3(3)	O(3)-Gd(3)-O(19)	93.9(3)
O(11)-Gd(4)-O(22)	94.8(3)	O(23)-Gd(3)-O(19)	98.9(3)
O(1)-Gd(4)-O(22)	75.1(3)	O(1)-Gd(3)-O(19)	144.2(3)
O(2)-Gd(4)-O(20)	99.4(3)	O(3)-Gd(3)-O(2)	69.4(2)
O(11)-Gd(4)-O(20)	90.5(3)	O(23)-Gd(3)-O(2)	78.8(3)
O(1)-Gd(4)-O(20)	140.8(3)	O(1)-Gd(3)-O(2)	70.3(2)
O(22)-Gd(4)-O(20)	144.0(3)	O(19)-Gd(3)-O(2)	74.1(3)
O(2)-Gd(4)-O(9)#1	71.3(2)	O(3)-Gd(3)-O(15)	104.5(3)
O(11)-Gd(4)-O(9)#1	82.6(3)	O(23)-Gd(3)-O(15)	89.4(3)
O(1)-Gd(4)-O(9)#1	70.1(2)	O(1)-Gd(3)-O(15)	76.6(3)
O(22)-Gd(4)-O(9)#1	145.1(3)	O(19)-Gd(3)-O(15)	139.2(3)
O(20)-Gd(4)-O(9)#1	70.9(3)	O(2)-Gd(3)-O(15)	146.5(3)
O(2)-Gd(4)-O(4W)	73.7(3)	O(3)-Gd(3)-O(17)	73.2(3)
O(11)-Gd(4)-O(4W)	139.3(3)	O(23)-Gd(3)-O(17)	145.9(3)
O(1)-Gd(4)-O(4W)	132.3(3)	O(1)-Gd(3)-O(17)	126.0(3)
O(22)-Gd(4)-O(4W)	76.1(3)	O(19)-Gd(3)-O(17)	76.0(3)
O(20)-Gd(4)-O(4W)	76.9(3)	O(2)-Gd(3)-O(17)	129.5(3)
O(9)#1-Gd(4)-O(4W)	126.8(2)	O(15)-Gd(3)-O(17)	75.0(4)
O(2)-Gd(4)-O(3W)	143.4(3)	O(3)-Gd(3)-O(2W)	147.1(3)
O(11)-Gd(4)-O(3W)	69.6(3)	O(23)-Gd(3)-O(2W)	71.7(3)
O(1)-Gd(4)-O(3W)	135.1(2)	O(1)-Gd(3)-O(2W)	136.9(3)
O(22)-Gd(4)-O(3W)	75.1(3)	O(19)-Gd(3)-O(2W)	71.3(3)
O(20)-Gd(4)-O(3W)	73.6(3)	O(2)-Gd(3)-O(2W)	129.6(3)
O(9)#1-Gd(4)-O(3W)	134.2(3)	O(15)-Gd(3)-O(2W)	73.7(3)
O(4W)-Gd(4)-O(3W)	69.7(3)	O(17)-Gd(3)-O(2W)	74.8(3)

Table S2. Selected Bond lengths (Å) and Bond angles (°) of main metal atoms for compound **2-Dy**.

Dy(1)-O(4)	2.332(7)	Dy(2)-O(19)	2.334(6)
Dy(1)-O(21)	2.339(6)	Dy(2)-O(8)	2.337(7)
Dy(1)-O(18)	2.346(7)	Dy(2)-O(10)	2.361(7)
Dy(1)-O(7)	2.367(7)	Dy(2)-O(13)	2.394(7)
Dy(1)-O(5)	2.398(8)	Dy(2)-O(18)	2.395(6)
Dy(1)-O(15)#1	2.429(7)	Dy(2)-O(21)	2.402(7)
Dy(1)-O(23)	2.450(7)	Dy(2)-O(11)	2.434(8)
Dy(1)-O(22)	2.476(7)	Dy(2)-O(20)	2.437(8)
Dy(3)-O(17)	2.233(6)	Dy(4)-O(17)	2.272(6)
Dy(3)-O(19)	2.326(6)	Dy(4)-O(19)#1	2.362(6)
Dy(3)-O(14)	2.359(7)	Dy(4)-O(15)	2.366(6)
Dy(3)-O(3)	2.363(7)	Dy(4)-O(9)#1	2.368(7)
Dy(3)-O(18)	2.384(7)	Dy(4)-O(21)#1	2.388(7)
Dy(3)-O(2)	2.400(7)	Dy(4)-O(1)	2.403(7)
Dy(3)-O(15)#1	2.410(7)	Dy(4)-O(6)#1	2.465(7)
Dy(3)-O(16)	2.644(6)	Dy(4)-O(16)	2.490(7)
O(4)-Dy(1)-O(21)	147.7(2)	O(19)-Dy(2)-O(8)	140.7(2)
O(4)-Dy(1)-O(18)	80.8(2)	O(19)-Dy(2)-O(10)	94.9(2)
O(21)-Dy(1)-O(18)	72.8(2)	O(8)-Dy(2)-O(10)	97.0(3)
O(4)-Dy(1)-O(7)	95.7(3)	O(19)-Dy(2)-O(13)	105.1(3)
O(21)-Dy(1)-O(7)	94.9(2)	O(8)-Dy(2)-O(13)	89.7(3)
O(18)-Dy(1)-O(7)	74.6(2)	O(10)-Dy(2)-O(13)	139.1(3)
O(4)-Dy(1)-O(5)	89.1(3)	O(19)-Dy(2)-O(18)	71.5(2)
O(21)-Dy(1)-O(5)	99.8(3)	O(8)-Dy(2)-O(18)	77.1(2)
O(18)-Dy(1)-O(5)	141.2(2)	O(10)-Dy(2)-O(18)	144.3(2)
O(7)-Dy(1)-O(5)	144.1(2)	O(13)-Dy(2)-O(18)	76.5(3)
O(4)-Dy(1)-O(15)#1	82.1(2)	O(19)-Dy(2)-O(21)	69.7(2)
O(21)-Dy(1)-O(15)#1	71.9(2)	O(8)-Dy(2)-O(21)	78.1(3)
O(18)-Dy(1)-O(15)#1	70.7(2)	O(10)-Dy(2)-O(21)	73.5(2)
O(7)-Dy(1)-O(15)#1	145.1(2)	O(13)-Dy(2)-O(21)	146.9(3)
O(5)-Dy(1)-O(15)#1	70.8(2)	O(18)-Dy(2)-O(21)	70.8(2)
O(4)-Dy(1)-O(23)	139.0(3)	O(19)-Dy(2)-O(11)	72.7(3)
O(21)-Dy(1)-O(23)	73.3(2)	O(8)-Dy(2)-O(11)	146.6(3)
O(18)-Dy(1)-O(23)	132.6(2)	O(10)-Dy(2)-O(11)	76.3(3)
O(7)-Dy(1)-O(23)	76.5(3)	O(13)-Dy(2)-O(11)	76.3(3)
O(5)-Dy(1)-O(23)	76.7(3)	O(18)-Dy(2)-O(11)	126.7(3)
O(15)#1-Dy(1)-O(23)	126.6(2)	O(21)-Dy(2)-O(11)	128.6(3)
O(4)-Dy(1)-O(22)	69.9(3)	O(19)-Dy(2)-O(20)	146.3(3)
O(21)-Dy(1)-O(22)	142.4(3)	O(8)-Dy(2)-O(20)	72.6(3)
O(18)-Dy(1)-O(22)	134.6(2)	O(10)-Dy(2)-O(20)	70.7(3)

O(7)-Dy(1)-O(22)	74.7(3)	O(13)-Dy(2)-O(20)	73.1(3)
O(5)-Dy(1)-O(22)	73.6(3)	O(18)-Dy(2)-O(20)	136.7(3)
O(15)#1-Dy(1)-O(22)	134.6(3)	O(21)-Dy(2)-O(20)	129.7(3)
O(23)-Dy(1)-O(22)	69.2(3)	O(11)-Dy(2)-O(20)	74.3(3)
O(17)-Dy(3)-O(19)	103.7(2)	O(17)-Dy(4)-O(19)#1	73.9(2)
O(17)-Dy(3)-O(14)	138.2(3)	O(17)-Dy(4)-O(15)	110.4(2)
O(19)-Dy(3)-O(14)	82.0(3)	O(19)#1-Dy(4)-O(15)	68.8(2)
O(17)-Dy(3)-O(3)	86.7(3)	O(17)-Dy(4)-O(9)#1	81.7(3)
O(19)-Dy(3)-O(3)	143.2(2)	O(19)#1-Dy(4)-O(9)#1	81.1(3)
O(14)-Dy(3)-O(3)	113.6(3)	O(15)-Dy(4)-O(9)#1	141.8(3)
O(17)-Dy(3)-O(18)	147.4(2)	O(17)-Dy(4)-O(21)#1	139.2(2)
O(19)-Dy(3)-O(18)	71.8(2)	O(19)#1-Dy(4)-O(21)#1	69.5(2)
O(14)-Dy(3)-O(18)	74.1(3)	O(15)-Dy(4)-O(21)#1	72.2(2)
O(3)-Dy(3)-O(18)	80.5(2)	O(9)#1-Dy(4)-O(21)#1	75.6(2)
O(17)-Dy(3)-O(2)	79.5(3)	O(17)-Dy(4)-O(1)	80.1(2)
O(19)-Dy(3)-O(2)	143.1(2)	O(19)#1-Dy(4)-O(1)	145.7(2)
O(14)-Dy(3)-O(2)	72.9(3)	O(15)-Dy(4)-O(1)	143.2(3)
O(3)-Dy(3)-O(2)	73.1(3)	O(9)#1-Dy(4)-O(1)	73.1(3)
O(18)-Dy(3)-O(2)	124.1(2)	O(21)#1-Dy(4)-O(1)	123.2(2)
O(17)-Dy(3)-O(15)#1	77.9(2)	O(17)-Dy(4)-O(6)#1	145.0(2)
O(19)-Dy(3)-O(15)#1	68.6(2)	O(19)#1-Dy(4)-O(6)#1	138.4(2)
O(14)-Dy(3)-O(15)#1	139.3(3)	O(15)-Dy(4)-O(6)#1	79.7(2)
O(3)-Dy(3)-O(15)#1	79.6(2)	O(9)#1-Dy(4)-O(6)#1	111.7(3)
O(18)-Dy(3)-O(15)#1	70.4(2)	O(21)#1-Dy(4)-O(6)#1	75.6(2)
O(2)-Dy(3)-O(15)#1	145.3(3)	O(1)-Dy(4)-O(6)#1	73.7(3)
O(17)-Dy(3)-O(16)	67.9(2)	O(17)-Dy(4)-O(16)	70.2(2)
O(19)-Dy(3)-O(16)	73.5(2)	O(19)#1-Dy(4)-O(16)	117.3(2)
O(14)-Dy(3)-O(16)	74.6(2)	O(15)-Dy(4)-O(16)	78.0(2)
O(3)-Dy(3)-O(16)	141.4(2)	O(9)#1-Dy(4)-O(16)	138.7(2)
O(18)-Dy(3)-O(16)	135.7(2)	O(21)#1-Dy(4)-O(16)	144.2(2)
O(2)-Dy(3)-O(16)	73.9(2)	O(1)-Dy(4)-O(16)	72.7(2)
O(15)#1-Dy(3)-O(16)	119.9(2)	O(6)#1-Dy(4)-O(16)	79.9(2)

Table S3. Selected Bond lengths (Å) and Bond angles (°) of main metal atoms for compound **3-Eu**.

Eu(1)-O(5)	2.315(4)	Eu(3)-O(9)	2.358(4)
Eu(1)-O(4)	2.393(5)	Eu(3)-O(11)	2.368(5)
Eu(1)-O(6)	2.404(4)	Eu(3)-O(3)	2.372(5)
Eu(1)-O(8)#1	2.404(4)	Eu(3)-O(12)	2.418(4)
Eu(1)-O(9)#1	2.423(4)	Eu(3)-O(19)	2.422(5)
Eu(1)-O(7)	2.446(4)	Eu(3)-O(6)#1	2.468(4)
Eu(1)-O(18)#1	2.490(5)	Eu(3)-O(1W)	2.499(5)
Eu(1)-O(2)	2.533(5)	Eu(3)-O(2W)	2.526(5)
Eu(2)-O(5)	2.271(5)	Eu(4)-O(8)	2.341(4)
Eu(2)-O(8)	2.352(4)	Eu(4)-O(13)	2.384(5)
Eu(2)-O(10)	2.385(4)	Eu(4)-O(1)#1	2.408(5)
Eu(2)-O(14)	2.395(5)	Eu(4)-O(15)	2.409(5)
Eu(2)-O(3)	2.409(4)	Eu(4)-O(3)	2.425(4)
Eu(2)-O(20)	2.412(5)	Eu(4)-O(9)	2.449(5)
Eu(2)-O(6)#1	2.438(4)	Eu(4)-O(3W)	2.476(5)
Eu(2)-O(2)	2.683(4)	Eu(4)-O(16)	2.483(5)
O(5)-Eu(1)-O(4)	82.53(17)	O(9)-Eu(3)-O(11)	148.38(15)
O(5)-Eu(1)-O(6)	110.39(16)	O(9)-Eu(3)-O(3)	72.33(14)
O(4)-Eu(1)-O(6)	140.20(16)	O(11)-Eu(3)-O(3)	81.16(15)
O(5)-Eu(1)-O(8)#1	73.88(15)	O(9)-Eu(3)-O(12)	94.90(16)
O(4)-Eu(1)-O(8)#1	81.18(17)	O(11)-Eu(3)-O(12)	94.36(18)
O(6)-Eu(1)-O(8)#1	67.76(14)	O(3)-Eu(3)-O(12)	74.62(15)
O(5)-Eu(1)-O(9)#1	138.77(16)	O(9)-Eu(3)-O(19)	98.96(16)
O(4)-Eu(1)-O(9)#1	74.52(15)	O(11)-Eu(3)-O(19)	90.65(18)
O(6)-Eu(1)-O(9)#1	71.58(15)	O(3)-Eu(3)-O(19)	140.73(15)
O(8)#1-Eu(1)-O(9)#1	69.15(14)	O(12)-Eu(3)-O(19)	144.57(17)
O(5)-Eu(1)-O(7)	80.52(16)	O(9)-Eu(3)-O(6)#1	71.53(15)
O(4)-Eu(1)-O(7)	74.30(18)	O(11)-Eu(3)-O(6)#1	83.57(15)
O(6)-Eu(1)-O(7)	143.36(16)	O(3)-Eu(3)-O(6)#1	70.06(14)
O(8)#1-Eu(1)-O(7)	146.49(15)	O(12)-Eu(3)-O(6)#1	144.53(15)
O(9)#1-Eu(1)-O(7)	123.58(15)	O(19)-Eu(3)-O(6)#1	70.89(15)
O(5)-Eu(1)-O(18)#1	145.87(16)	O(9)-Eu(3)-O(1W)	73.00(15)
O(4)-Eu(1)-O(18)#1	112.05(18)	O(11)-Eu(3)-O(1W)	138.62(16)
O(6)-Eu(1)-O(18)#1	78.71(15)	O(3)-Eu(3)-O(1W)	131.99(16)
O(8)#1-Eu(1)-O(18)#1	136.94(14)	O(12)-Eu(3)-O(1W)	76.36(16)
O(9)#1-Eu(1)-O(18)#1	75.26(15)	O(19)-Eu(3)-O(1W)	76.83(18)
O(7)-Eu(1)-O(18)#1	74.65(16)	O(6)#1-Eu(3)-O(1W)	126.64(14)
O(5)-Eu(1)-O(2)	70.68(15)	O(9)-Eu(3)-O(2W)	141.89(15)
O(4)-Eu(1)-O(2)	140.44(15)	O(11)-Eu(3)-O(2W)	69.73(16)
O(6)-Eu(1)-O(2)	77.93(14)	O(3)-Eu(3)-O(2W)	136.16(14)

O(8)#1-Eu(1)-O(2)	116.68(14)	O(12)-Eu(3)-O(2W)	75.69(17)
O(9)#1-Eu(1)-O(2)	143.64(14)	O(19)-Eu(3)-O(2W)	73.29(16)
O(7)-Eu(1)-O(2)	73.01(16)	O(6)#1-Eu(3)-O(2W)	134.55(16)
O(18)#1-Eu(1)-O(2)	79.82(15)	O(1W)-Eu(3)-O(2W)	68.90(15)
O(5)-Eu(2)-O(8)	104.06(16)	O(8)-Eu(4)-O(13)	139.39(17)
O(5)-Eu(2)-O(10)	88.47(17)	O(8)-Eu(4)-O(1)#1	96.96(16)
O(8)-Eu(2)-O(10)	141.33(16)	O(13)-Eu(4)-O(1)#1	96.09(18)
O(5)-Eu(2)-O(14)	138.44(17)	O(8)-Eu(4)-O(15)	103.62(17)
O(8)-Eu(2)-O(14)	81.52(18)	O(13)-Eu(4)-O(15)	92.00(19)
O(10)-Eu(2)-O(14)	112.98(19)	O(1)#1-Eu(4)-O(15)	137.38(19)
O(5)-Eu(2)-O(3)	147.27(16)	O(8)-Eu(4)-O(3)	70.33(14)
O(8)-Eu(2)-O(3)	70.43(14)	O(13)-Eu(4)-O(3)	76.71(16)
O(10)-Eu(2)-O(3)	79.32(16)	O(1)#1-Eu(4)-O(3)	144.19(16)
O(14)-Eu(2)-O(3)	73.87(17)	O(15)-Eu(4)-O(3)	78.35(17)
O(5)-Eu(2)-O(20)	79.33(17)	O(8)-Eu(4)-O(9)	69.71(14)
O(8)-Eu(2)-O(20)	142.43(17)	O(13)-Eu(4)-O(9)	77.21(17)
O(10)-Eu(2)-O(20)	75.33(18)	O(1)#1-Eu(4)-O(9)	74.30(16)
O(14)-Eu(2)-O(20)	73.0(2)	O(15)-Eu(4)-O(9)	148.00(16)
O(3)-Eu(2)-O(20)	125.36(15)	O(3)-Eu(4)-O(9)	69.90(14)
O(5)-Eu(2)-O(6)#1	78.00(16)	O(8)-Eu(4)-O(3W)	147.71(16)
O(8)-Eu(2)-O(6)#1	68.03(14)	O(13)-Eu(4)-O(3W)	72.66(19)
O(10)-Eu(2)-O(6)#1	79.47(16)	O(1)#1-Eu(4)-O(3W)	70.15(19)
O(14)-Eu(2)-O(6)#1	138.63(18)	O(15)-Eu(4)-O(3W)	72.6(2)
O(3)-Eu(2)-O(6)#1	69.99(14)	O(3)-Eu(4)-O(3W)	136.45(16)
O(20)-Eu(2)-O(6)#1	146.32(17)	O(9)-Eu(4)-O(3W)	129.80(18)
O(5)-Eu(2)-O(2)	68.54(15)	O(8)-Eu(4)-O(16)	72.20(17)
O(8)-Eu(2)-O(2)	73.32(14)	O(13)-Eu(4)-O(16)	148.41(19)
O(10)-Eu(2)-O(2)	143.98(15)	O(1)#1-Eu(4)-O(16)	75.74(19)
O(14)-Eu(2)-O(2)	74.15(16)	O(15)-Eu(4)-O(16)	75.72(19)
O(3)-Eu(2)-O(2)	134.32(14)	O(3)-Eu(4)-O(16)	127.11(16)
O(20)-Eu(2)-O(2)	73.44(15)	O(9)-Eu(4)-O(16)	127.34(16)
O(6)#1-Eu(2)-O(2)	119.65(13)	O(3W)-Eu(4)-O(16)	75.88(19)

Table S4. Continuous Shape Measures Calculations for metal centers in compound **2-Dy**.[3]

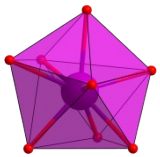
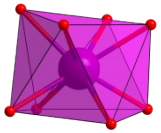
Metal Centers	Coordination Number	Geometries	SHAPE calculations result with the distortion values				
Dy1 / Dy2	8		Octagon	Heptagonal pyramid	Hexagonal bipyramid	Cube	Square antiprism
			30.961 / 30.389	24.084 / 24.138	16.850 / 15.046	10.805 / 8.798	2.430 / 2.018
			Triangular dodecahedron	Johnson-Gyrobifastigium J26	Johnson-Elongated triangular bipyramid J14	Johnson-Biaugmented trigonal prism J50	Biaugmented trigonal prism
			0.455 / 0.313	12.950 / 14.517	28.963 / 28.119	2.426 / 2.279	1.870 / 1.717
			Snub diphenoid J84	Triakis tetrahedron	Elongated trigonal bipyramid		
			2.321 / 2.629	11.491 / 9.582	25.874 / 23.972		
Dy3 / Dy4	8		Octagon	Heptagonal pyramid	Hexagonal bipyramid	Cube	Square antiprism
			28.909 / 28.593	22.776 / 22.308	17.204 / 16.062	10.439 / 9.800	**0.795 / 0.454**
			Triangular dodecahedron	Johnson-Gyrobifastigium J26	Johnson-Elongated triangular bipyramid J14	Biaugmented trigonal prism J50	Biaugmented trigonal prism
			1.582 / 2.253	14.199 / 14.969	27.269 / 27.099	1.523 / 2.400	1.514 / 1.930
			Snub diphenoid J84	Triakis tetrahedron	Elongated trigonal bipyramid		
			3.247 / 4.322	10.929 / 10.298	23.756 / 23.413		

Table S5. Summary of the reported 4f and 3d-4f clusters with isonicotinic ligand.

Compound	Formula	Dimensionality	Ref.
4f			
Ln	$[Ln(IN)(CO_3)(H_2O)]$ (Ln = La, Eu)	2D	4
Ln	$[Ln(IN)_2L]$ (Ln = Eu, Tb, Er, Dy, Ho, Gd, La, L = OCH_2CH_2OH)	1D	5
Ln	${}_L$-/${}_D$-$\{Ln[IN][HIN][CH_2OCH_2O]\}_n$ (Ln = Gd, Dy)	1D	6
Ln_3	$[Ln_3(IN)_2(bdc)_{3.5}(H_2O)_3]\cdot 0.5H_2O$ (Ln = Er, Ho)	3D	7
Ln_3	$[Ln_3(IN)_3(\mu_3\text{-}OH)(HIDA)(IDA)_2]_n$ (Ln = Eu, Sm)	2D	8
Ln_{26}	$[Ho_{26}(IN)_{28}(CH_3COO)_4(CO_3)_{10}(OH)_{26}(H_2O)_{18}]\cdot 20H_2O$	0D	9
	$[Er_{26}(IN)_{29}(CH_3COO)_3(CO_3)_{10}(OH)_{26}(H_2O)_{19}]\cdot 26H_2O$		
Ho_{48}	$K_2[Ho_{48}(IN)_{46}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}OH)_4(\mu_5\text{-}O)_2(OAc)_4(H_2O)_{14}(CO_3)Br_2]\cdot 2HIN\cdot 20H_2O$	2D	10
Dy_{30}	$Dy_{30}I(IN)_{41}(\mu_3\text{-}OH)_{24}(\mu_3\text{-}O)_6(NO_3)_9(OH)_3(H_2O)_{38}$	0D	11
Dy_{104}	$Dy_{104}I_4(IN)_{125}(\mu_3\text{-}OH)_{80}(\mu_3\text{-}O)_{24}(NO_3)_{36}(OH)_{19}\cdot(H_2O)_{167}$		
3d-4f			
LnZn	${}_L$-/${}_D$-$[LnZn(IN)_3(C_2H_4O_2)]_n$ (Ln = Eu, Sm, Gd)	3D	12
$Ln_{26}Zn_{1.5}$	$Zn_{1.5}Dy_{26}(IN)_{25}(CH_3COO)_8(CO_3)_{11}(OH)_{26}(H_2O)_{29}$	3D	13
	$Zn_{1.5}Gd_{26}(IN)_{26}(CH_3COO)_7(CO_3)_{11}(OH)_{26}(H_2O)_{28}$		
Ln_4Cu_6	$Ln_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3$ (Ln = Nd, Pr)	3D	14
Ln_2Cu_5	$\{[Ln_2Cu_5Br_4(IN)_7(H_2O)_6]H_2O\}_n$ (Ln = Eu, Gd)	3D	15
Ln_2Cu_4	$[Ln_2Cu_4Br_3(IN)_6(OH)(H_2O)_4]_n$ (Ln = Ho, Yb)	2D	16
Ln_6Cu_{10}	$[Ln_6(Cu_4Br_3)(Cu_2Br_2)_2(Cu_2Br)(IN)_{20}(H_2O)_{12}]\cdot 2H_2O$ (Ln = Gd, Sm, Eu)	3D	17
Dy_2Cu_4	$[Dy_2Cu_4I_3(IN)_7(DMF)_2]\cdot DMF$	3D	18
	$[Dy_2Cu_4I_3(IN)_7(DMA)_2]\cdot DMA$		
Ln_2Cu_4	$[Ln_2Cu_4I_3(IN)_7(DMA)_2]\cdot DMA$ (Ln = Gd, Tb)	3D	19
$Ln_{14}Cu_6$	$[Ln_{14}(\mu_6\text{-}O)(\mu_3\text{-}OH)_{20}(IN)_{22}Cu_6Cl_4(H_2O)_8]\cdot 6H_2O$ (Ln = Y, Gd, Dy)	3D	20
Ln_4Cr_4	${}_L$-/${}_D$-$[Gd_4Cr_4(IN)_{10}(\mu_3\text{-}OH)_4(\mu_4\text{-}O)_4(H_2O)_{12}]\cdot[IN]_2\cdot 8H_2O$	0D	21
	${}_L$-/${}_D$-$[Dy_4Cr_4(IN)_{11}(\mu_3\text{-}OH)_4(\mu_4\text{-}O)_4(H_2O)_8]\cdot[IN]\cdot 1.5H_2O$		
Ln_8Cr_4	$[Ln_8Cr_4(IN)_{18}(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_6(\mu_4\text{-}O)_4(H_2O)_{10}]\cdot 13H_2O$ (Ln = Gd, Tb)	1D	22
$Ln_{52}Ni_{52}$	$[Gd_{52}Ni_{52}(IN)_8(CH_3COO)_6(C_2O_4)_2(IDA)_{46}(\mu_4\text{-}O)_6(\mu_3\text{-}O)_{18}(\mu_3\text{-}OH)_{102}(H_2O)_{28}]\cdot 27.5H_2O$	0D	23
	$[Dy_{52}Ni_{52}(IN)_4(CH_3COO)_9(C_2O_4)_2(IDA)_{46}(NH_2CH_2COO)_3(\mu_3\text{-}O)_{16}(\mu_3\text{-}OH)_{106}(\mu_2\text{-}OH)_{10}(H_2O)_{26}]\cdot 25H_2O$		

References

1. Y. Liu, Y. Zhang, G. H. Hu, S. Zhou, R. Fan, Y. Yang and Y. Xu, *Chem. Eur. J.*, 2015, **21**, 10391-10399.
2. C. H. Cui, W. W. Ju, X. M. Luo, Q. F. Lin, J. P. Cao and Y. Xu, *Inorg. Chem.*, 2018, **57**, 8608-8614.
3. D. Casanova, M. Llunell, P. Alemany and S. Alvarez, *Chem. Eur. J.*, 2005, **11**, 1479-1494.
4. L. Huang, L. J. Han, D. R. Zhu, L. Chen and Y. Xu, *Inorg. Chem. Commun.*, 2012, **21**, 80-83.
5. Y. Liu, Y. Zhang, G. H. Hu, S. Zhou, R. Q. Fan, Y. L. Yang and Y. Xu, *Chem. Eur. J.*, 2015, **21**, 10391-10399.
6. N. F. Li, J. Y. Ji, W. Jiang, J. P. Cao, Y. M. Han, P. Yuan and Y. Xu, *Z. Anorg. Allg. Chem.*, 2020, **646**, 463-468.
7. L. Chen, L. Huang, D. Zhang, D. W. Yan, C. L. Wang, T. Qin, D. R. Zhu and Y. Xu, *Inorg. Chem. Commun.*, 2012, **21**, 182-185.
8. W. Xu, C. J. Zhang, H. Wang and Y. Wang, *J. Clust. Sci.*, 2017, **28**, 2005-2015.
9. L. Chen, L. Huang, C. L. Wang, J. Fu, D. Zhang, D. R. Zhu and Y. Xu, *J. Coord. Chem.*, 2012, **65**, 958-968.
10. L. Chen, J. Y. Guo, X. Xu, W. W. Ju, D. Zhang, D. R. Zhu and Y. Xu, *Chem. Commun.*, 2013, **49**, 9728-9730.
11. X. J. Gu and D. F. Xue, *Inorg. Chem.*, **46**, 3212-3216.
12. X. X. He, Y. Liu, Y. Lv, Y. Y. Dong, G. H. Hu, S. Zhou and Y. Xu, *Inorg. Chem.*, 2016, **55**, 2048-2054.
13. L. Huang, L. J. Han, W. J. Feng, L. Zheng, Z. B. Zhang, Y. Xu, Q. Chen, D. R. Zhu and S. Y. Niu, *Cryst. Growth Des.*, 2010, **10**, 2548-2552.
14. X. J. Gu and D. F. Xue, *Inorg. Chem.*, 2007, **46**, 5349−5353.
15. L. Q. Fan, J. H. Wu and Y. F. Huang, *J. Solid State Chem.*, 2011, **184**, 2472-2477.
16. L. Q. Fan, J. H. Wu and Y. F. Huang, *Z. Anorg. Allg. Chem.*, 2014, **640**, 1462-1466.
17. L. Chen, Y. Liu, D. Lou, C. D. Wei and Y. Xu, *Z. Anorg. Allg. Chem.*, 2017, **643**, 1004-1010.
18. Z. L. Wu, A. L. Gu, N. Gao, H. Y. Cui, W. M. Wang and J. Z. Cui, *Inorg. Chem.*, 2020, **59**, 15111-15119.
19. J. Ji, W. M. Wang and Y. L. Hou, *Inorg. Chem. Commun.*, 2021, **132**, 108840**.**
20. M. B. Zhang, J. Zhang, S. T. Zheng and G. Y. Yang, *Angew. Chem. Int. Ed.*, 2005, **44**, 1385-1388.
21. C. H. Cui, J. P. Cao, X. M. Luo, Q. F. Lin and Y. Xu, *Chem. Eur. J.*, 2018, **24**, 15295-15302.
22. Y. M. Han, N. F. Li, Y. Z. Yu, J. P. Cao, M. X. Yang, Y. L. Hong, R. K. Kang, P. Yuan and Y. Xu, *RSC Adv.*, 2020, **10**, 11365-11370.
23. Q. F. Lin, J. Li, Y. Y. Dong, G. P. Zhou, Y. Song and Y. Xu, *Dalton Trans.*, 2017, **46**, 9745-9749.