Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

A Series of dinuclear lanthanide(III) complexes constructed by Schiff Base and β-diketonate Ligands: synthesis, structure, luminescence and SMM behavior

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Synthesis of L

Pyridylaldehyde (2.14 g, 20mmol) was dissolved in 10 mL EtOH, 5 mL MeOH solution of 1,2-ethylenediamine (0.60 g, 10 mmol) was added, and the mixture was kept refluxed for 4 h to ensure the completion of the reaction, and then it was cooled and washed with diethyl ether. The solid was collected by filtration and dried under vacuum. Yield: 1.76 g (74 %). Elemental analysis (%) calcd for $C_{14}H_{14}N_4$(238.29)**:** C, 70.57, H, 5.92, N, 23.51. found: C, 70.60, H, 5.88, N, 23.52. IR (KBr, cm^{-1}): 3048(w), 2887 (m), 1647 (s), 1492 (s), 1280 (s), 867(s), 782 (*v*s), 734 (s). UV−vis [MeOH, λ]: 201, 235, 272 nm.

Synthesis of $Sm(DBM)_3 \cdot 2H_2O$

All complexes were synthesized by the same method. Dibenzoylmethane (DBM, 3.25

g, 15 mmol) and $SmCl_3\cdot 6H_2O$ (1.82 g, 5 mmol) was dissolved in 80 mL of ethanol, followed with dropwise addition of an aqueous solution of NaOH (10 ml, 1 M) for neutralization, then 150 ml H_2O was added . The system was warmed to 50 ℃ and stirred for 3 h. The yellow solid was collected by filtration and dried under vacuum. Yield: 3.78 g (87 %). Elemental analysis (%) calcd for $C_{45}H_{40}O_8Sm$ (859.15)**:** C, 62.91, H, 4.69. found: C, 62.90, H, 4.71. IR (KBr, cm^{-1}): 3059(m), 15223 (*v*s), 1372 (*v*s), 1255 (m), 1174 (w), 1126(w), 789 (m), 717 (s), 519 (s). UV−vis [MeOH, λ]: 206, 300 nm.

Synthesis of Eu(DBM)$_3\cdot$2H$_2$O

Yield: 3.87 g (90 %). Elemental analysis (%) calcd for $C_{45}H_{40}O_8Eu$ (860.76)**:** C, 62.91, H, 4.69. found: C, 62.90, H, 4.71. IR (KBr, cm^{-1}): 3058(m), 1524 (*v*s), 1372 (*v*s), 1255 (m), 1175 (w), 1128(w), 788 (m), 715 (s), 519 (s). UV−vis [MeOH, λ]: 206, 300 nm.

Synthesis of Gd(DBM)$_3\cdot$2H$_2$O

Yield: 3.81 g (88%). Elemental analysis (%) calcd for $C_{45}H_{40}O_8Gd$ (866.20)**:** C, 62.41, H, 4.66. found: C, 62.41, H, 4.70. IR (KBr, cm^{-1}): 3059(m), 1523 (*v*s), 1372 (*v*s), 1257 (m), 1171 (w), 1124(w), 789 (m), 719 (s), 520 (s). UV−vis [MeOH, λ]: 206, 300 nm.

Synthesis of Dy(DBM)$_3\cdot$2H$_2$O

Yield: 3.71 g (85 %). Elemental analysis (%) calcd for $C_{45}H_{40}O_8Dy$ (872.20)**:** C, 62.03, H, 4.63. found: C, 62.05, H, 4.63. IR (KBr, cm^{-1}): 3060(m), 1524 (*v*s), 1372 (*v*s), 1257 (m), 1174 (w), 1127(w), 786 (m), 714 (s), 519 (s). UV−vis [MeOH, λ]: 206, 300 nm.

Synthesis of Yb(DBM)$_3\cdot$2H$_2$O

Yield: 3.92 g (89 %). Elemental analysis (%) calcd for $C_{45}H_{40}O_8Yb$ (881.85)**:** C, 61.29, H, 4.57. found: C, 61.30, H, 4.55. IR (KBr, cm^{-1}): 3059(m), 1521 (*v*s), 1372 (*v*s), 1257 (m), 1173 (w), 1126(w), 785 (m), 717 (s), 516 (s). UV−vis [MeOH, λ]: 206, 300 nm.

Table S1. Selected bond distances (Å) for **1–5**

	1		
Sm(1)–O(5)	2.383(3)	Sm(1)–O(4)	2.376(3)
Sm(1)–O(2)	2.381(3)	Sm(1)–O(3)	2.353(3)
Sm(1)–O(1)	2.364(3)	Sm(1)–O(6)	2.333(3)
Sm(1)–N(2)	2.685(4)	Sm(1)–N(1)	2.625(4)
	2		
Eu(1)–O(5)	2.325(3)	Eu(1)–O(4)	2.365(3)
Eu(1)–O(2)	2.367(3)	Eu(1)–O(3)	2.337(3)
Eu(1)–O(1)	2.353(3)	Eu(1)–O(6)	2.366(3)
Eu(1)–N(2)	2.667(3)	Eu(1)–N(1)	2.609(3)
	3		
Gd(1)–O(5)	2.354(3)	Gd(1)–O(4)	2.360(3)
Gd(1)–O(2)	2.363(3)	Gd(1)–O(3)	2.330(3)
Gd(1)–O(1)	2.348(3)	Gd(1)–O(6)	2.315(4)
Gd(1)–N(2)	2.655(4)	Gd(1)–N(1)	2.600(4)
	4		
Dy(1)–O(5)	2.283(3)	Dy(1)–O(4)	2.331(3)
Dy(1)–O(2)	2.327(3)	Dy(1)–O(3)	2.396(3)
Dy(1)–O(1)	2.321(3)	Dy(1)–O(6)	2.329(3)
Dy(1)–N(2)	2.613(4)	Dy(1)–N(1)	2.560(4)
	5		
Yb(1)–O(5)	2.253(3)	Yb(1)–O(4)	2.300(4)
Yb(1)–O(2)	2.290(3)	Yb(1)–O(3)	2.260(3)
Yb(1)–O(1)	2.276(3)	Yb(1)–O(6)	2.294(3)
Yb(1)–N(2)	2.580(4)	Yb(1)–N(1)	2.535(4)

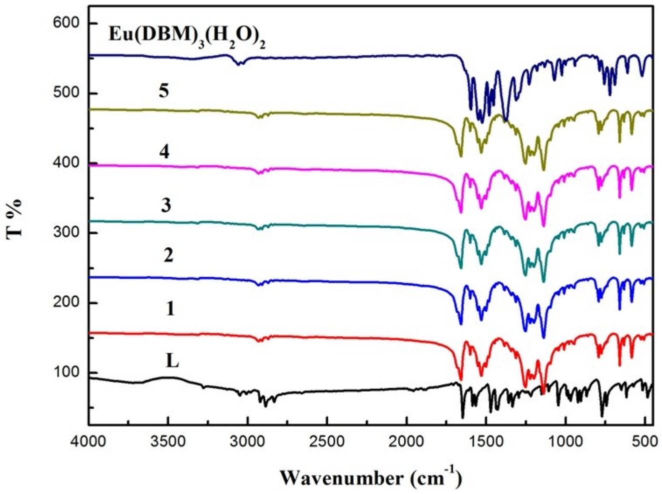

Fig. S1 Infrared spectra of ligand L, Eu(DBM)$_3$(H$_2$O)$_2$ and complexes **1**−**5**

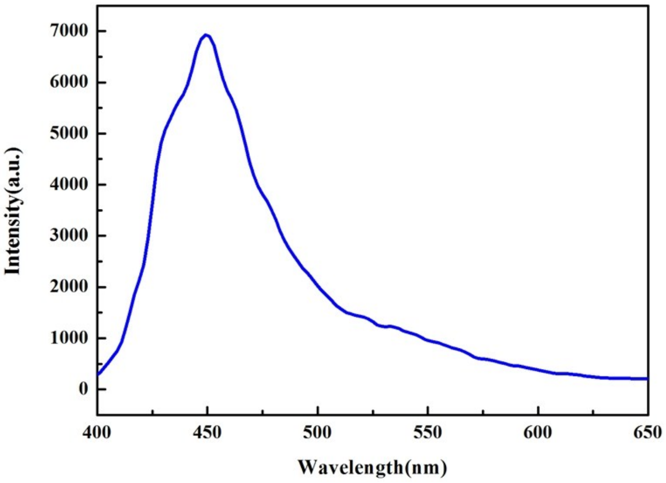

Fig. S2 The luminescent emission spectrum of ligand L in solid state at room temperature.

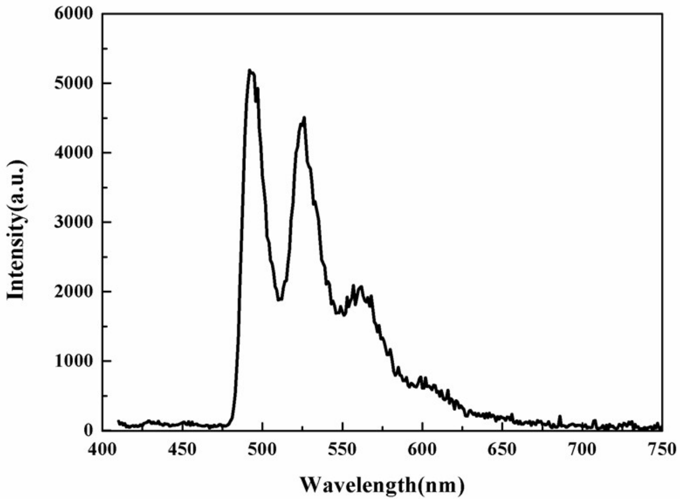

Fig. S3 Phosphorescence spectrum of the complex **3**.

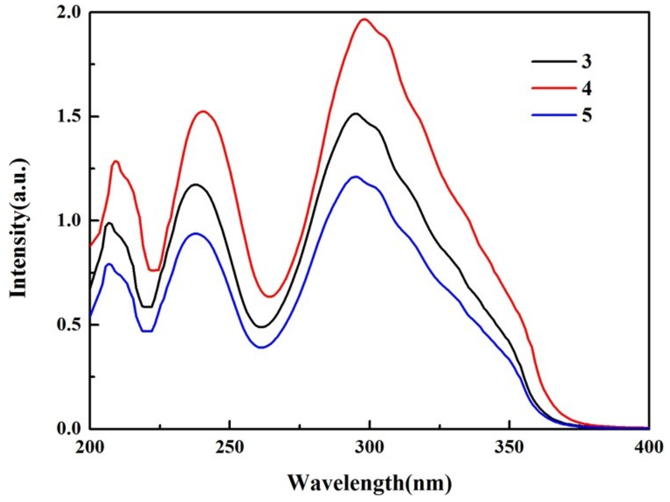

Fig. S4 UV spectra of the complex **3–5**.

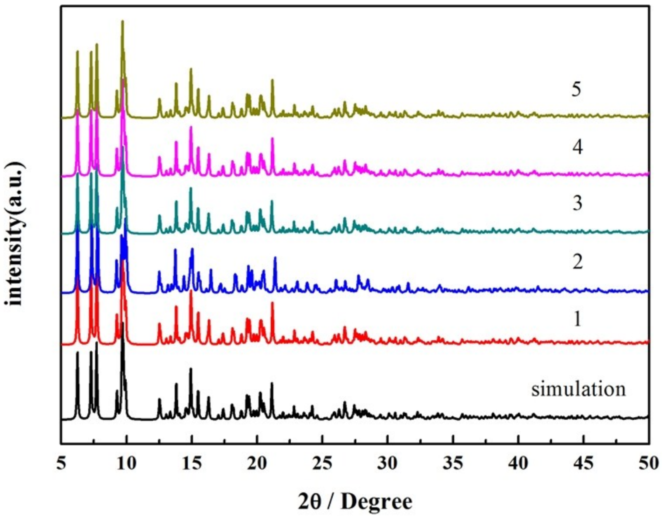

Fig. S5 The powder X-ray diffraction patterns and the simulated patterns of complexes **1–5**.

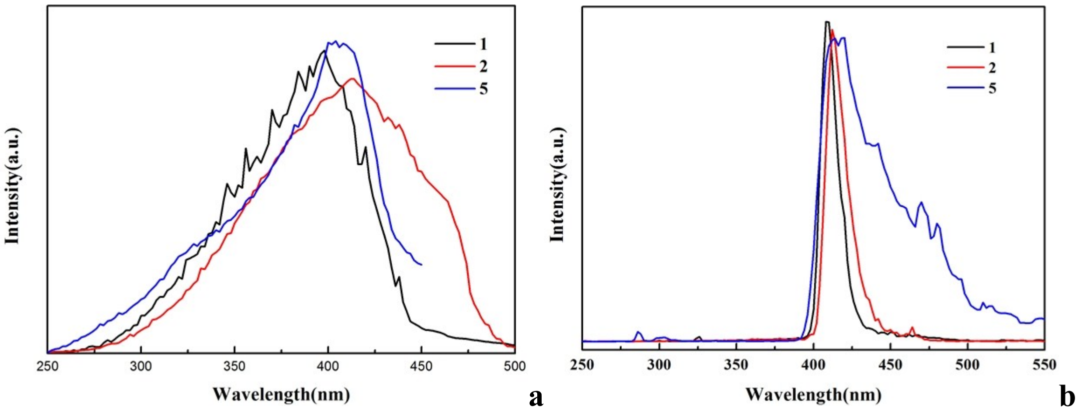

Fig. S6 The luminescence emission spectra for complexes **1** (black), **2**(red) and **5**(blue) in the solid state (a) and in CH_3OH solution (b) at room temperature.

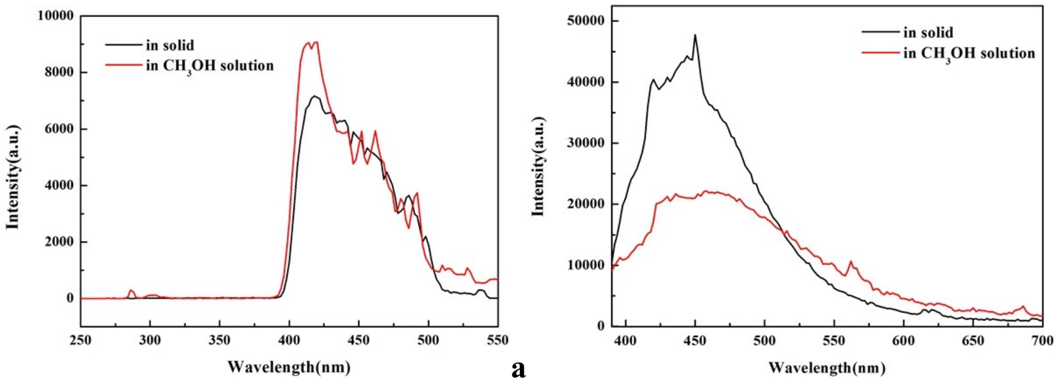

Fig. S7 The luminescence excitation spectra (a) and emission spectra (b) for complex **4** in solid state and CH_3OH solution at room temperature.

Table S2. Photophysical properties of the L and complexes **1–5** in solid at room temperature.

Compd	Absorption λ_{ab}/nm[log(ε/dm^{3}mol^{-1}cm^{-1})]	Excitation λex/nm	Emission λem/nm
L	201(1.61), 235(1.54), 272(1.01)	416	449
1	206(0.90), 237(1.07), 294(1.38)	398	565; 601; 615; 645; 704
2	214(0.60), 242(0.72), 294(0.92)	412	580; 592; 612; 650; 679
3	206(0.99), 237(1.17), 294(1.51)		
4	208(1.29), 240(1.52), 297(1.67)	418	449
5	206(0.79), 237(0.94), 294(1.21)	408	976; 993; 1028

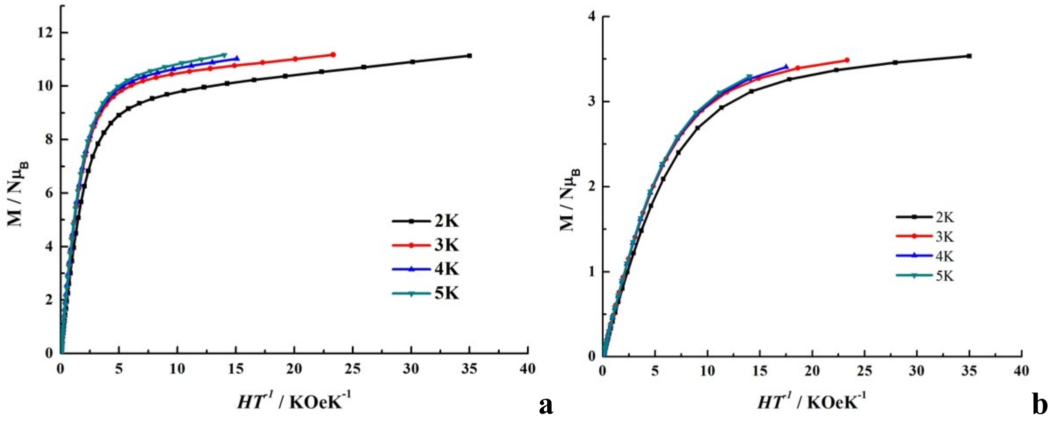

Fig. S8 Experimental M vs. H/T plots at 2–5 K for complexes **4**(a) and **5**(b) .

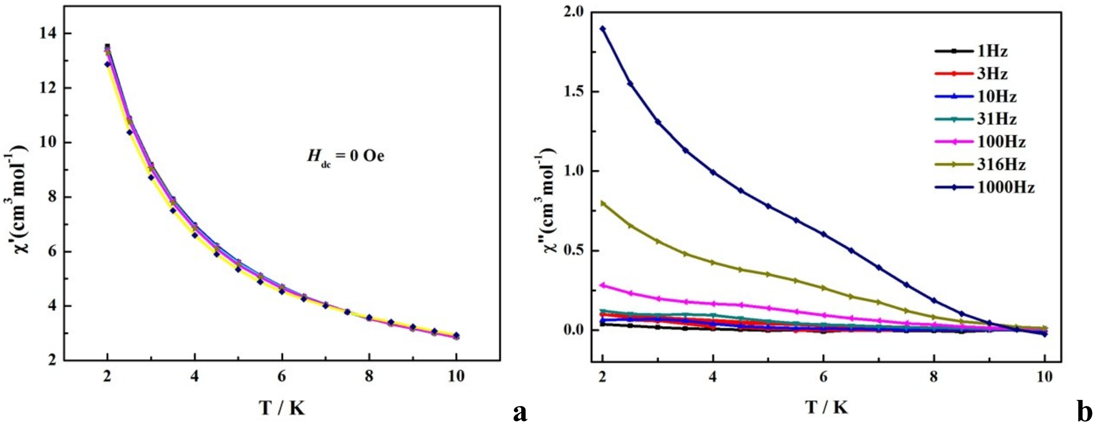

Fig. S9 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility of **4** under 0 Oe in the frequency range of 1–1000 Hz in the temperature range of 2–10 K .

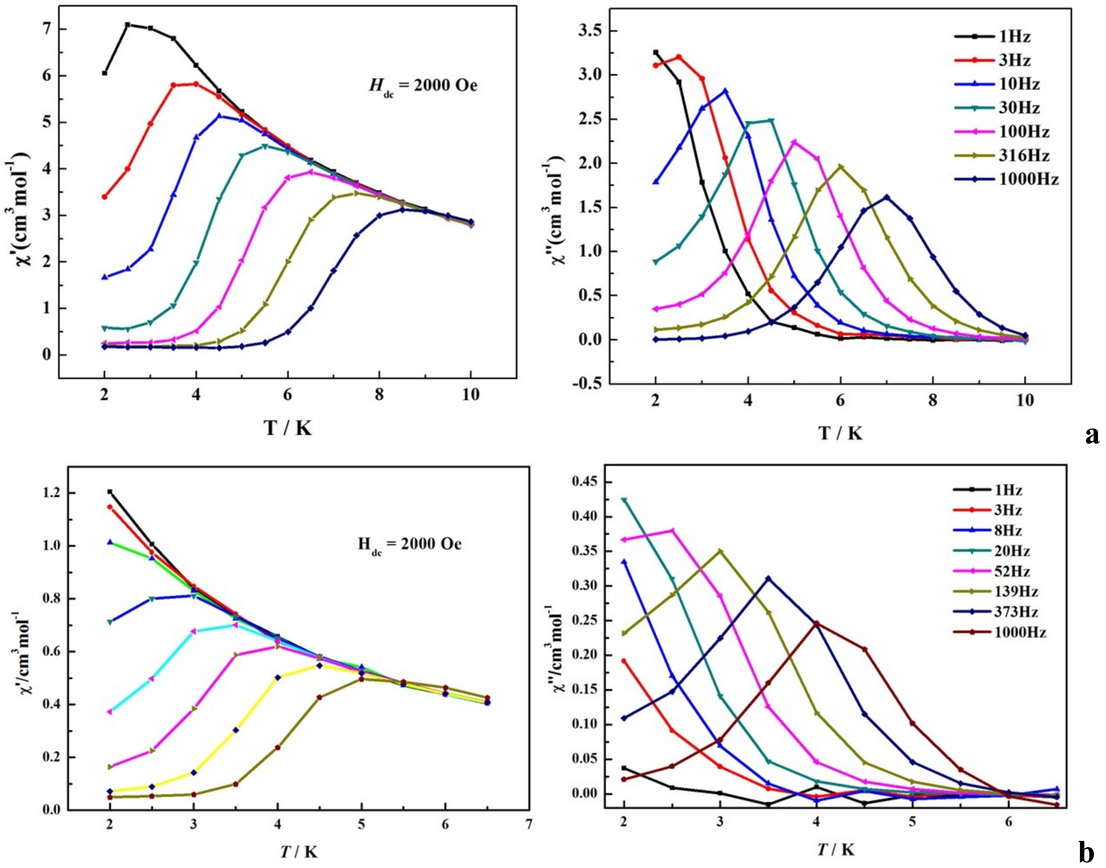

Fig. S10 Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility of **4** and **5** under 2000 Oe in the frequency range of 1–1000 Hz in the temperature range of 2–10 K (**4**) and 2–6.5 K (**5**).

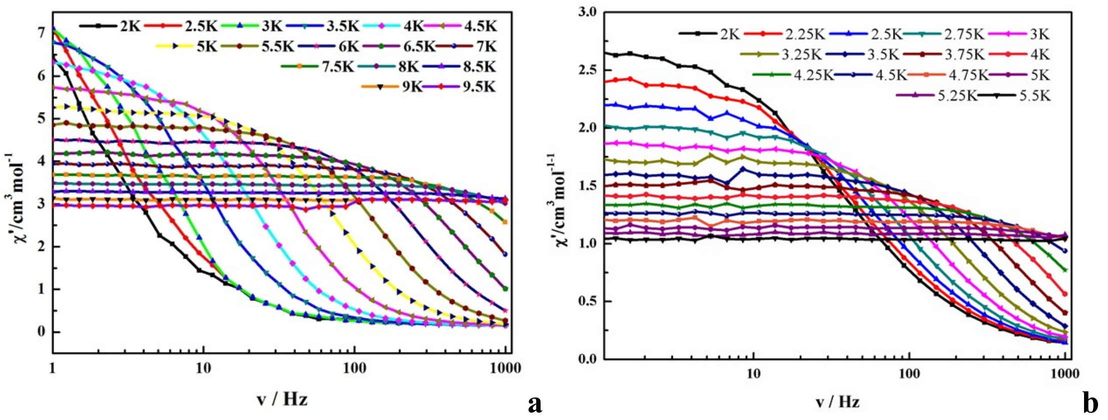

Fig. S11 Frequency dependence of the in-phase (χ') ac susceptibility of **4** and **5** under 2000 Oe in the frequency range of 1–1000 Hz in the temperature range of 2–10 K (**4**) and 2–6.5 K (**5**).