Supplementary Information

Homodinuclear Lanthanide {Ln_2} (Ln = Gd, Tb, Dy, Eu) Complexes Prepared from *o*-Vanillin based Ligand: Luminescence and Single-Molecule Magnetism Behavior

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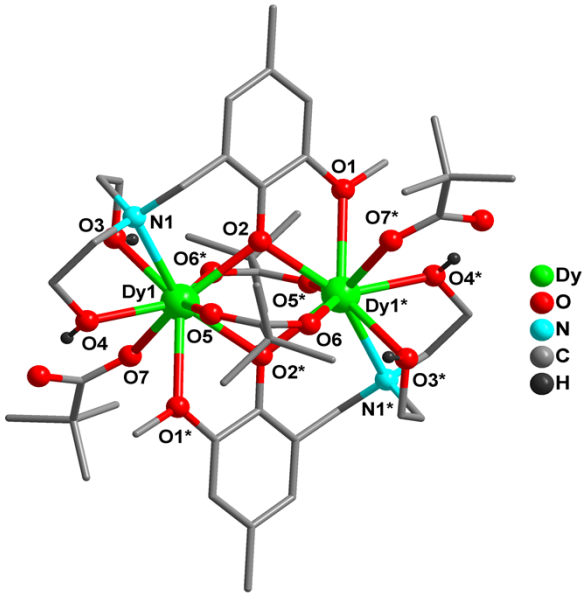


Fig. S1 Molecular structure of **3 (**hydrogen atoms and solvent molecules are omitted for clarity).

Table S1. Selected Bond distances and bond angles for compound **3**

Bond lengths (Å)		Bond angles (°)	
Bond Lengths around Dysprosium(1)		O(2)-Dy(1)-O(3)	96.43(9)
Dy(1)-O(2)*	2.305(3)	O(2)*-Dy(1)-O(4)	133.63(9)
Dy(1)-O(2)	2.337(3)	Dy(1)*-O(2)-Dy(1)	103.02(10)
Dy(1)-O(7)	2.338(3)	O(2)-Dy(1)-O(1)*	126.01(9)
Dy(1)-O(5)	2.344(3)		
Dy(1)-O(4)	2.361(3)		
Dy(1)-O(6)*	2.472(3)		
Dy(1)-O(3)	2.524(3)		
Dy(1)-O(1)*	2.675(3)		
Dy(1)-N(1)	2.679(3)		
Dy(1)-Dy(1)*	3.6331(13)		

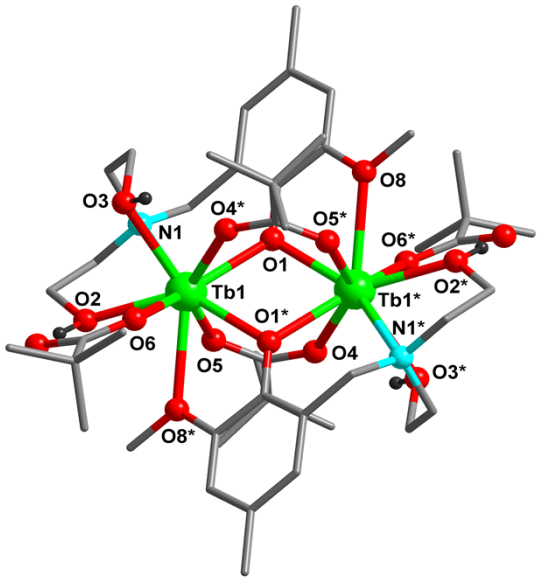


Fig. S2 Molecular structure of **2 (**hydrogen atoms and solvent molecules are omitted for clarity).

Table S2. Selected Bond distances and bond angles for compound **2**

Bond lengths (Å)		Bond angles (°)	
Bond Lengths around Terbium(1)			
Tb(1)-O(5)	2.365(3)	Tb(1)-O(1)-Tb(1)*	103.19(10)
Tb(1)-O(6)	2.351(3)	O(1)-Tb(1)-O(1)*	76.81(10)
Tb(1)-O(8)*	2.677(3)	O(1)-Tb(1)-O(3)	132.90(10)
Tb(1)-O(1)*	2.348(3)	O(1)*-Tb(1)-O(2)	134.08(10)
Tb(1)-O(2)	2.378(3)	O(1)-Tb(1)*-O(8)	63.11(9)
Tb(1)-O(4)*	2.474(3)		
Tb(1)-O(3)	2.538(3)		
Tb(1)-N(1)	2.682(3)		
Tb(1)-Tb(1)*	3.6532(14)		

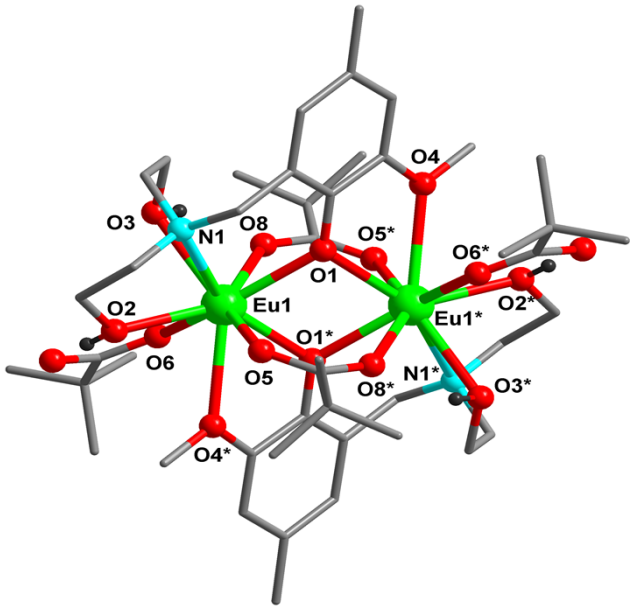


Fig. S3 Molecular structure of **4 (**hydrogen atoms and solvent molecules are omitted for clarity).

Table S3. Selected Bond distances and bond angles for compound **4**

Bond lengths (Å)		Bond angles (°)	
Bond Lengths around Europium(1)			
Eu(1)-O(1)	2.340(3)	Eu(1)*-O(1)-Eu(1)	102.76(12)
Eu(1)-O(1)	2.372(3)	O(1)*-Eu(1)-O(6)	85.00(11)
Eu(1)-O(6)	2.378(3)	O(1)-Eu(1)-N(1)	75.20(11)
Eu(1)-O(5)	2.394(3)	O(1)-Eu(1)-O(6)	143.63(11)
Eu(1)-O(2)	2.401(3)	O(6)-Eu(1)-O(5)	135.56(11)
Eu(1)-O(8)*	2.493(3)		
Eu(1)-O(3)	2.561(3)		
Eu(1)-O(4)*	2.674(3)		
Eu(1)-N(1)	2.704(4)		
Eu(1)-Eu(1)*	3.6816(6)		

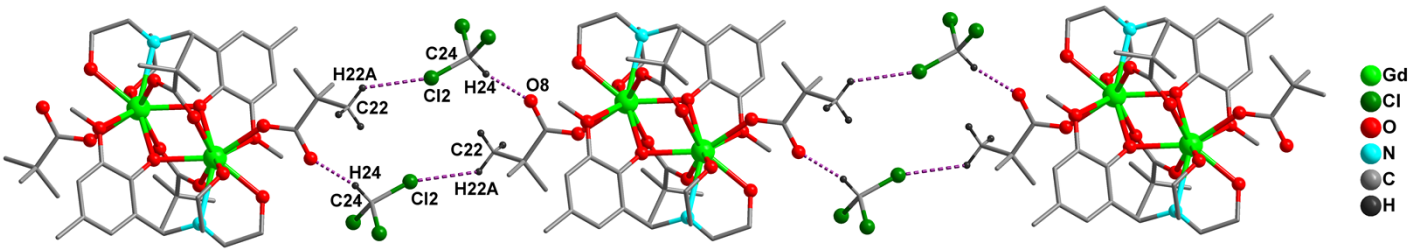


Fig. S4 1D polymeric supramolecular association through C-H…Cl and C-H…O hydrogen bonding of compound **1**.

Table S4. Hydrogen bond parameters for compound **1**

	D-H….A	d(D-H) Å	d(H….A) Å	d(D….A) Å	<(DHA)°	Symmetry of A
1	C22-H22A….Cl2	0.958(5)	2.885(2)	3.556(5)	128.99(28)	1-x, 0.5+y, 1.5-z
	C24-H24….O8	0.979(4)	2.026(4)	2.975(5)	158.02(25)	1-x, 3-y, 1-z

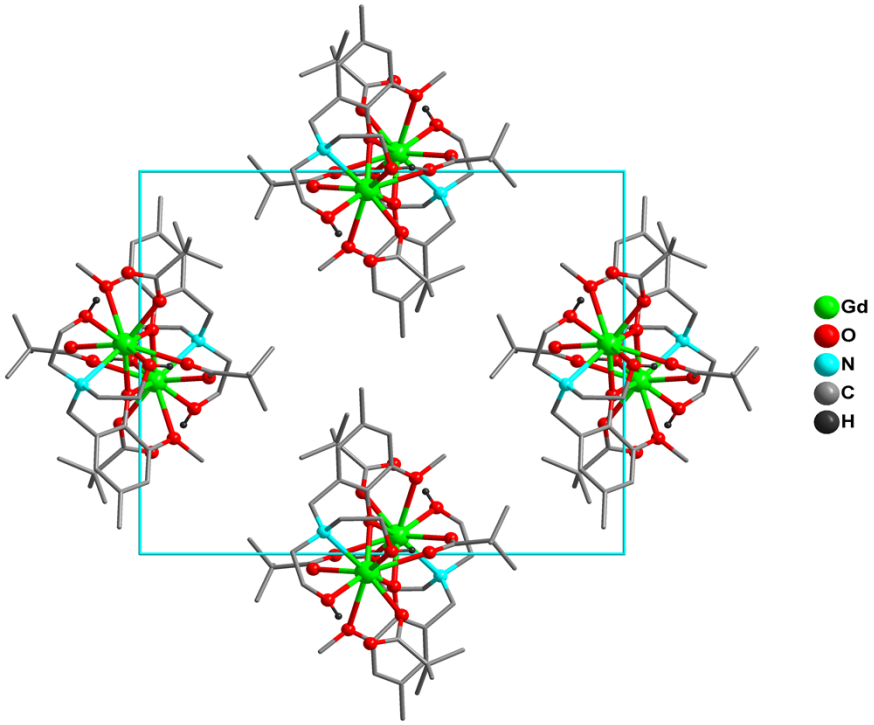


Fig. S5 Packing diagram compound **1.**

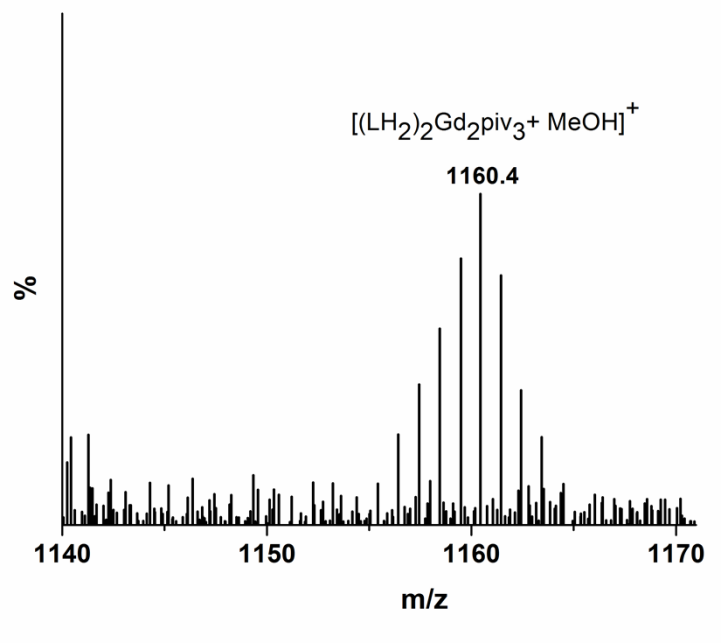


Fig. S6 ESI-MS of **1** (picture shows isotopic distribution pattern of one fragment).

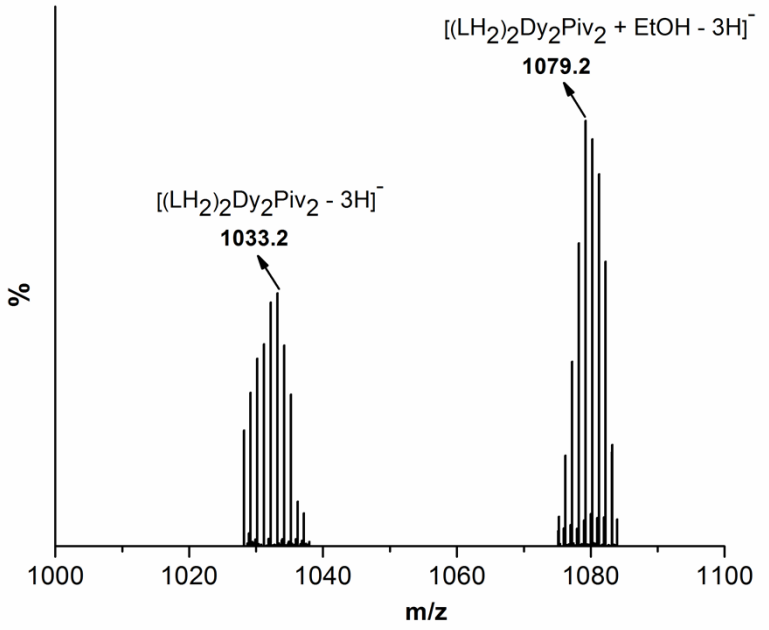


Fig. S7 ESI-MS of **3** (picture shows isotopic distribution pattern of the two fragments)

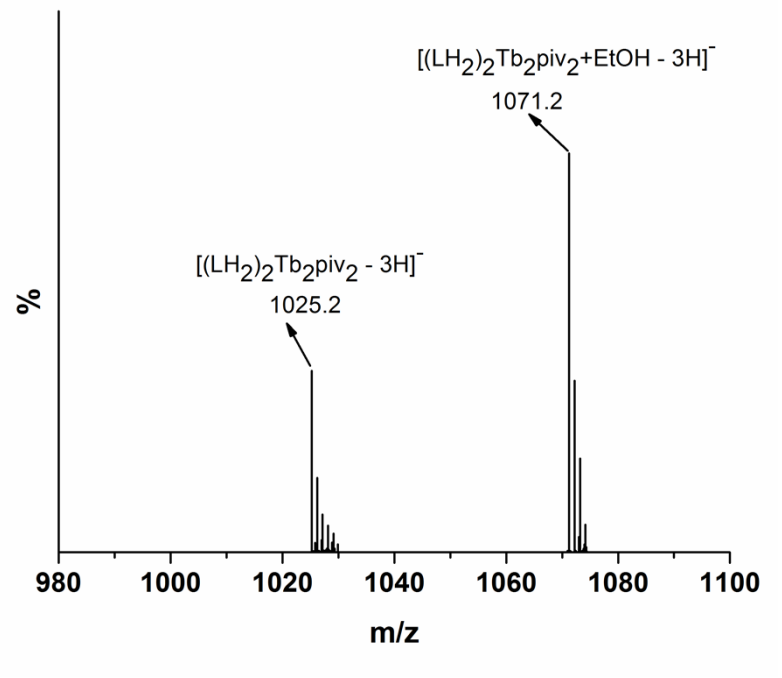


Fig. S8 ESI-MS of **2** (picture shows isotopic distribution pattern of the two fragments)

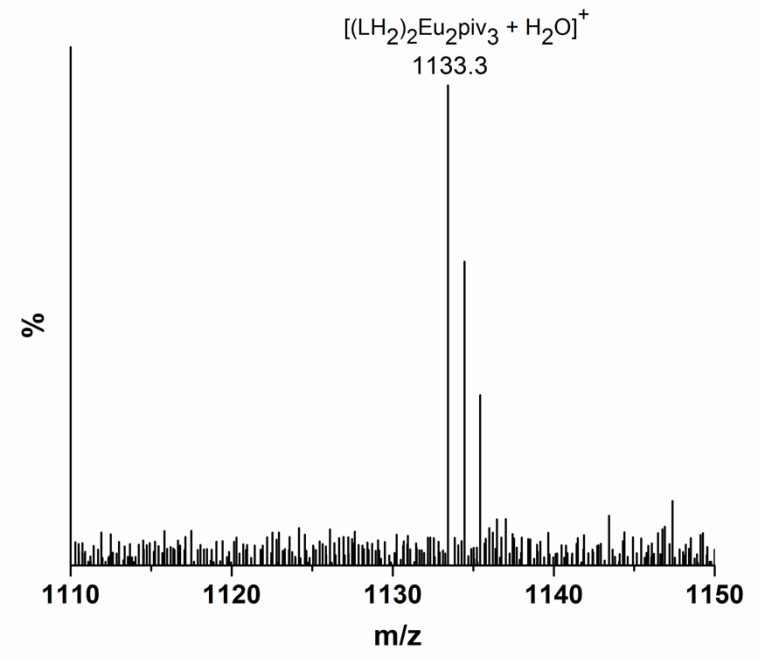


Fig. S9 ESI-MS of **4** (picture shows isotopic distribution pattern of one fragment).

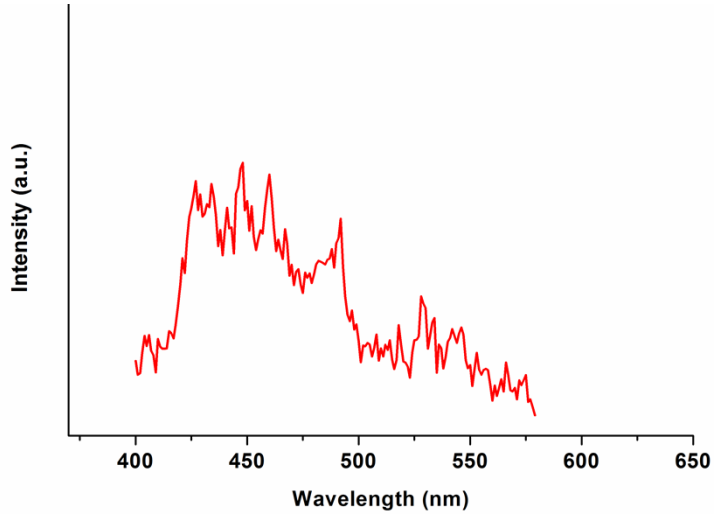
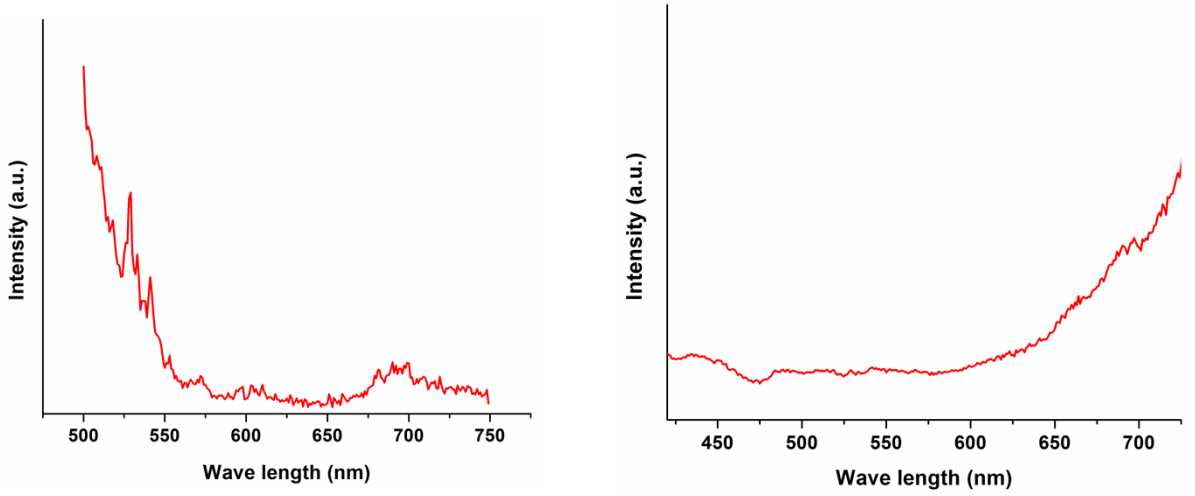


Fig. S10 Emission spectra of **4** (Eu_2) upon excitation at 300 nm.

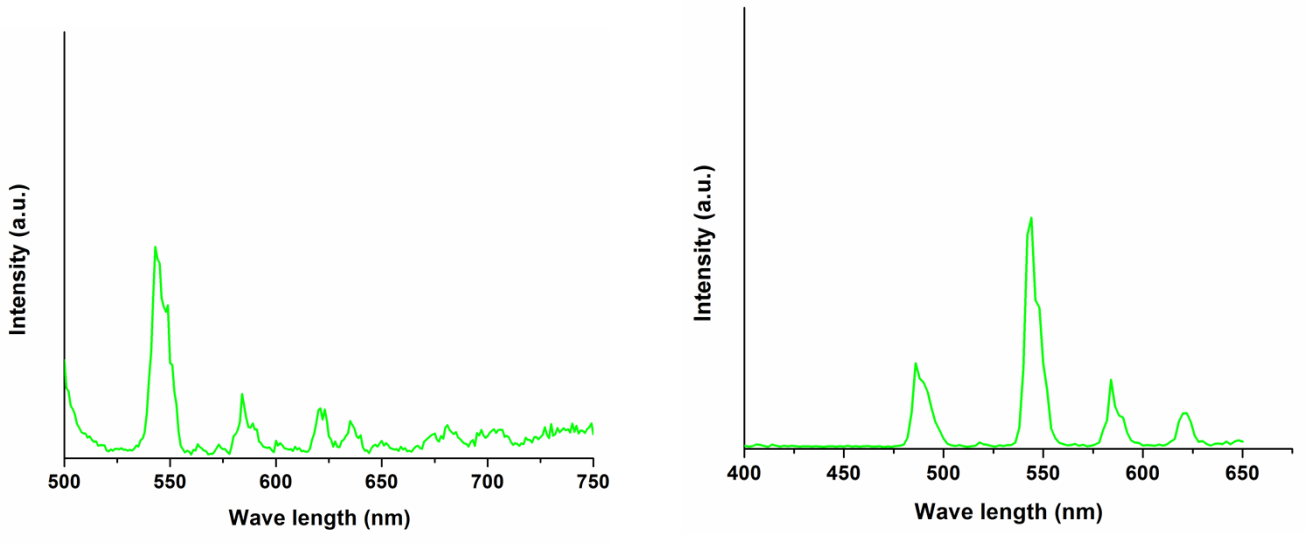
Table S5. Life time of the complex **4**

Complex	Room Temperature Life time (τ_a) (μs), λ_{ex} = 300 (nm), λ_{em} = 450 (nm)
4	1.38



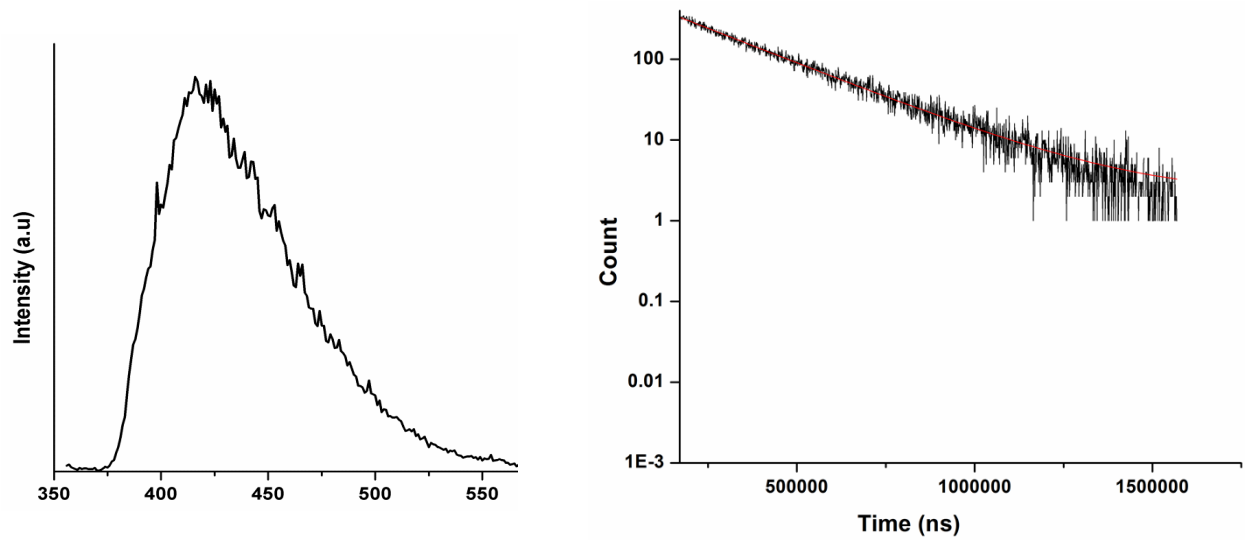
(a) (b)

Fig. S11 Emission spectra of **4** (Eu_2) upon excitation directly through the *f-f* transitions at (a) 464 nm and (b) 395 nm.



(a) (b)

Fig. S12 Emission spectra of **2** (Tb_2) upon excitation directly through the *f-f* transitions at (a) 488 nm and (b) 355 nm.

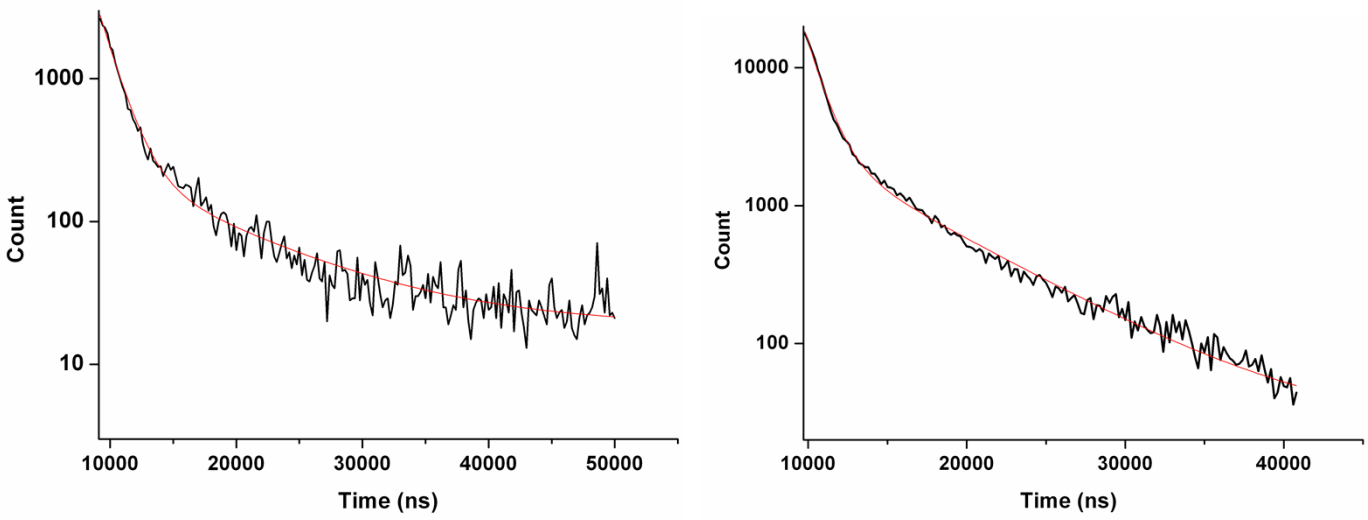


(a) (b)

Fig. S13 Room temperature (298 K) (a) phosphorescence spectra and (b) life time decay profile of Gd_2 (**1**) compound (λ_{ex} = 300 nm). The emission was monitored at 410 nm (The solid red line represent monoexponential fit to the decay curve with a τ value 250 μs.

Table S6. Life time of the ligand in presence and absence of acceptor.

Complex	Room Temperature Life time (τ_a) (μs), λ_{ex} = 300 (nm)	Room Temperature Life time (τ_0) (μs), λ_{ex} = 300 (nm)
1	-	250.33
2	1.66,	-
3	1.51	-



(a) (b)

Fig. S14 Phosphorescence decay profile (blue curve) of compounds **2** (a) and **3** (b) (λ_{ex} = 300 nm and emission monitored at 410 nm (ligand emission). The solid red line represents biexponential fit to the decay curve

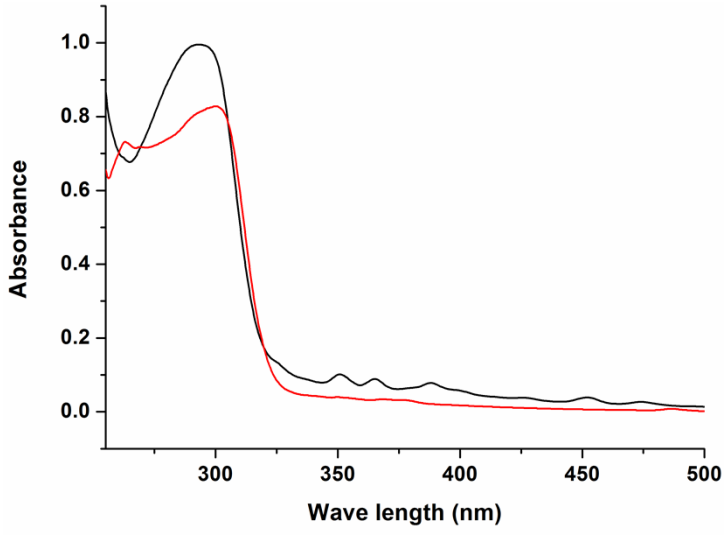
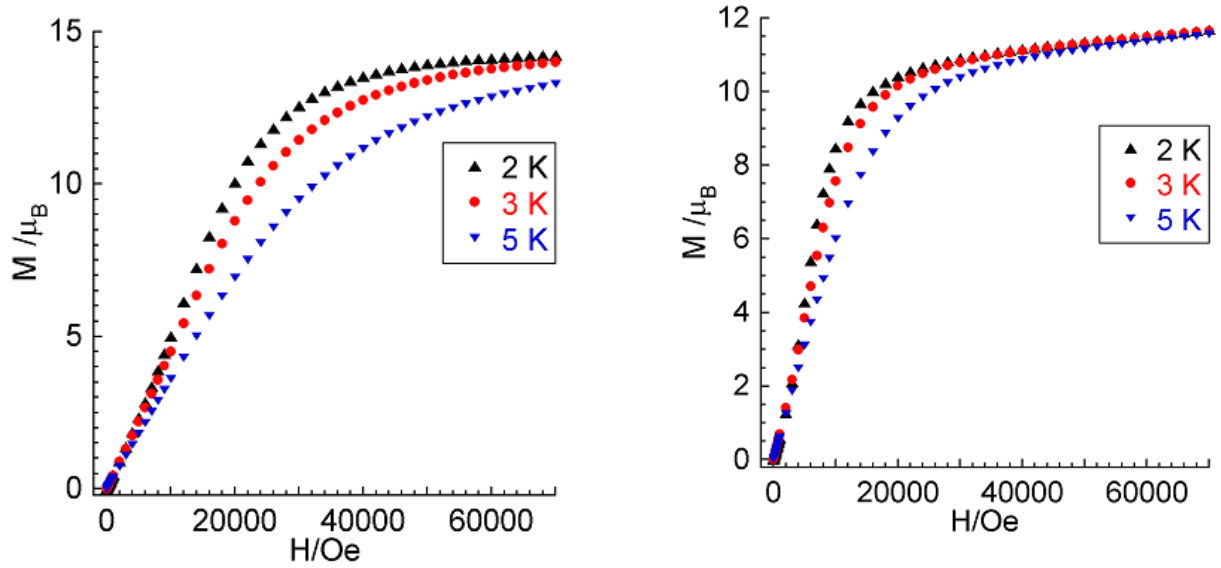


Fig. S15 Solid state absorption spectra of **2** (Tb_2, red line), **3** (Dy_2, black line).



(a) (b)

Fig. S16 M versus H plot at 2, 3 and 5 K for compound **1** (a), **3** (b)

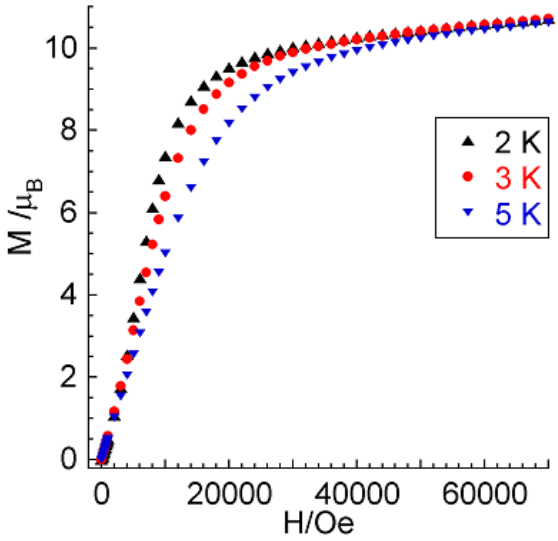
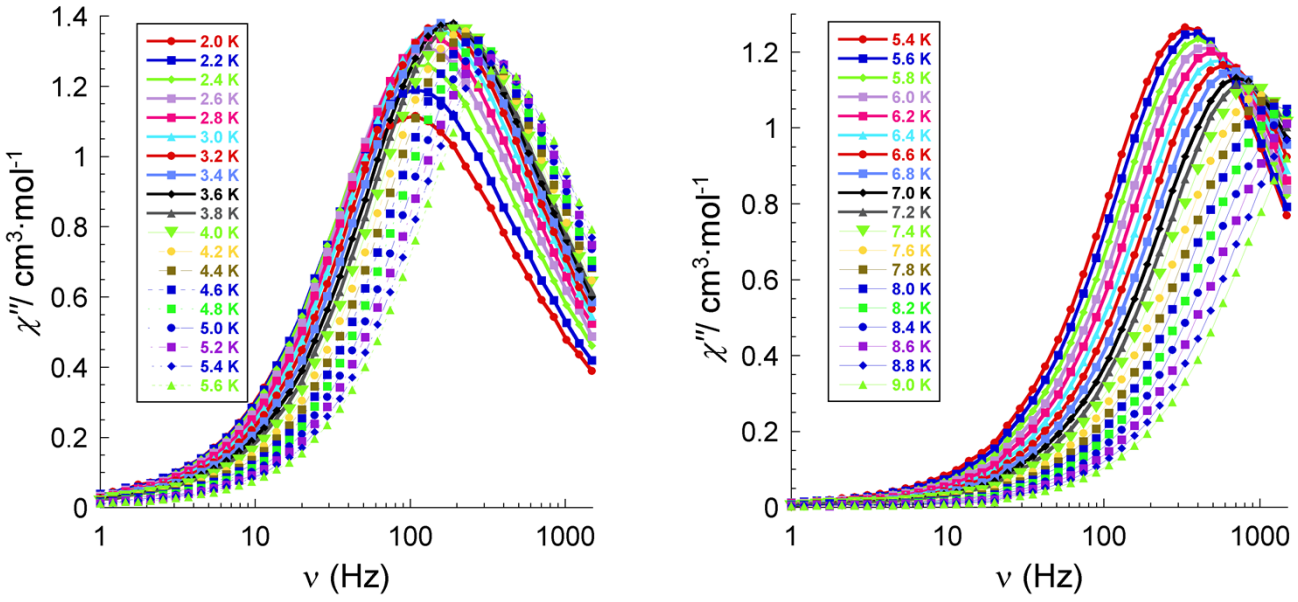


Fig. S17 M versus H plot at 2, 3 and 5 K for compound **2**



(a) (b)

Fig. S18 Frequency dependent of the out-of-phase ac signals (χ''_M) under zero applied dc field for **3** at low temperature (a) and at high temperature (b) region. Solid lines are a guide to the eye.

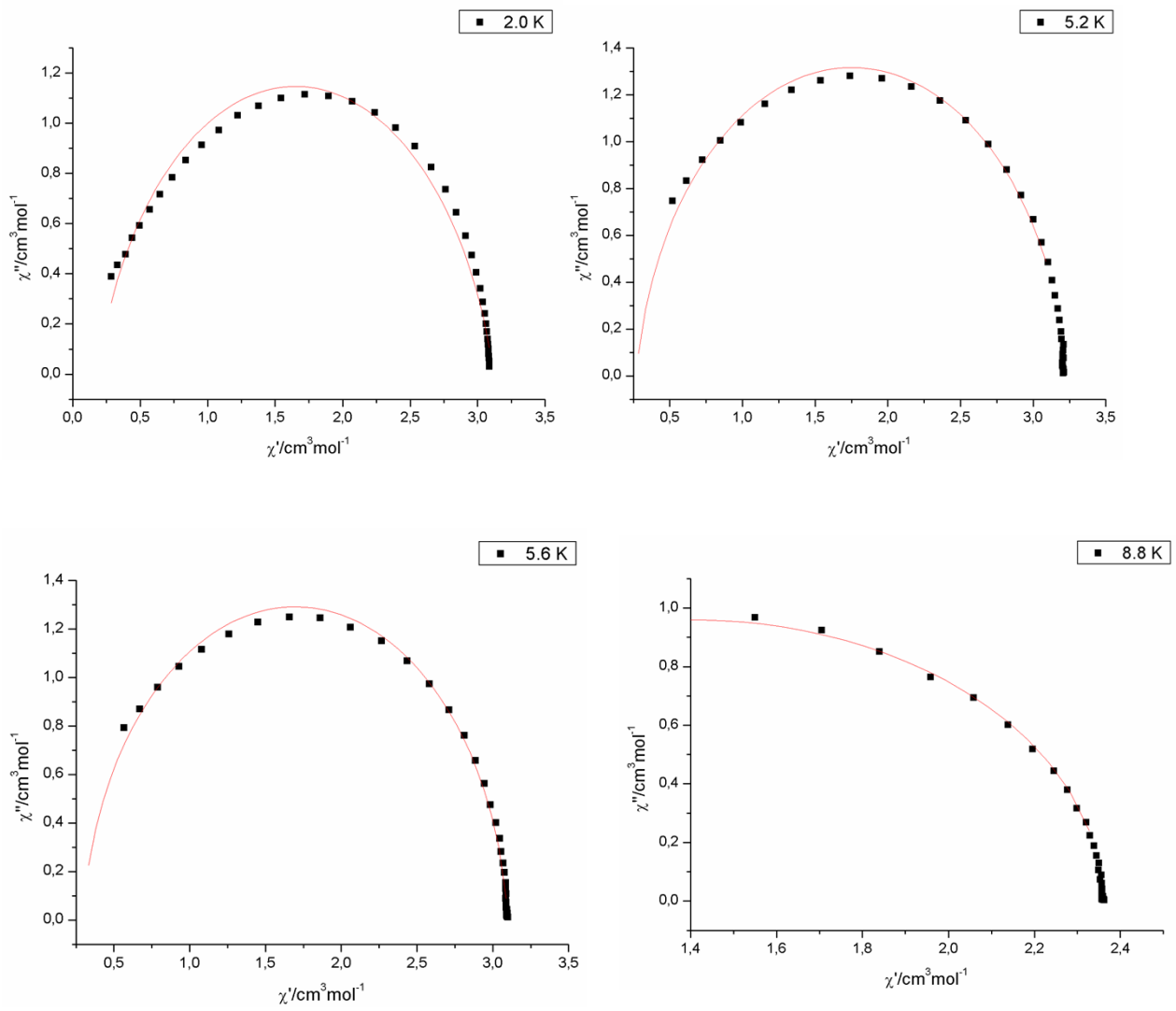


Fig. S19 Cole-Cole plot using the ac susceptibility data shown in Fig. S18 for **3**. The solid lines are the best fit obtained with a generalized Debye model (with α always smaller than 0.15).

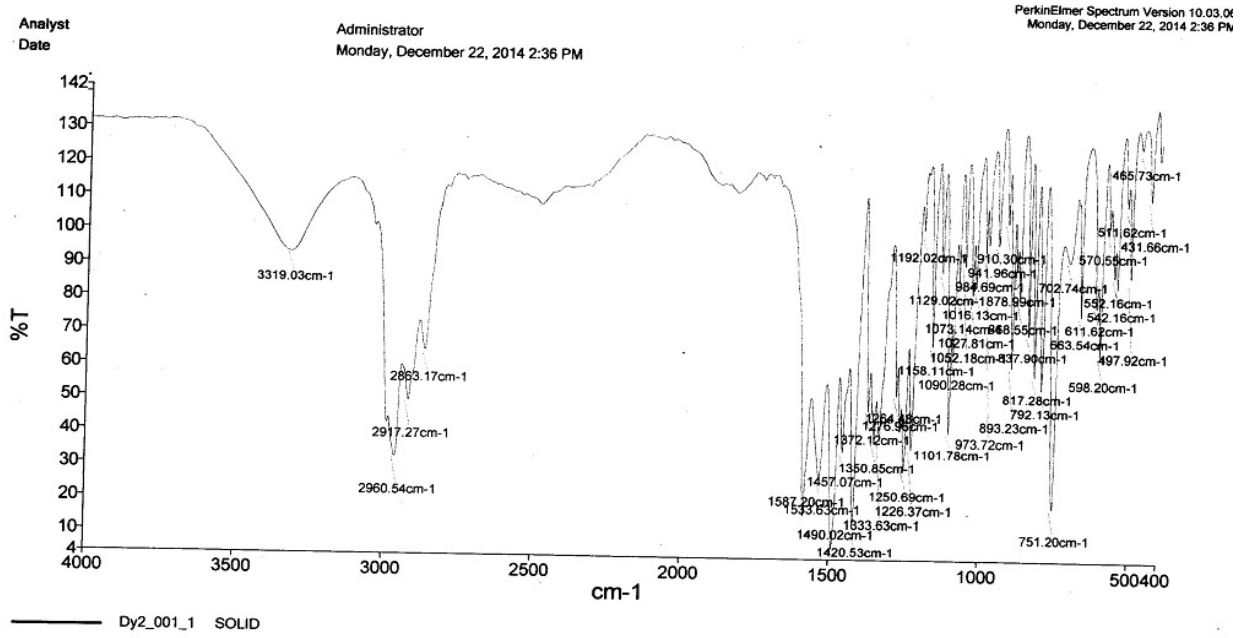


Fig. S20 IR spectra of compound **3** (Dy_2)

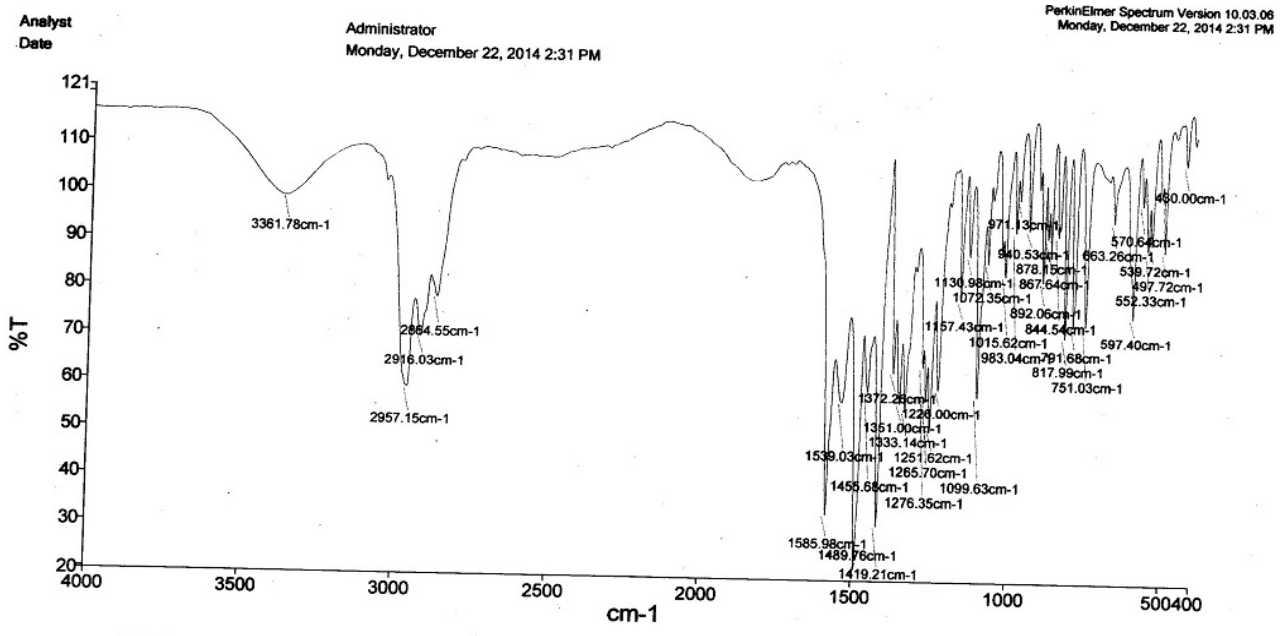


Fig. S21 IR spectra of compound **1** (Gd_2)

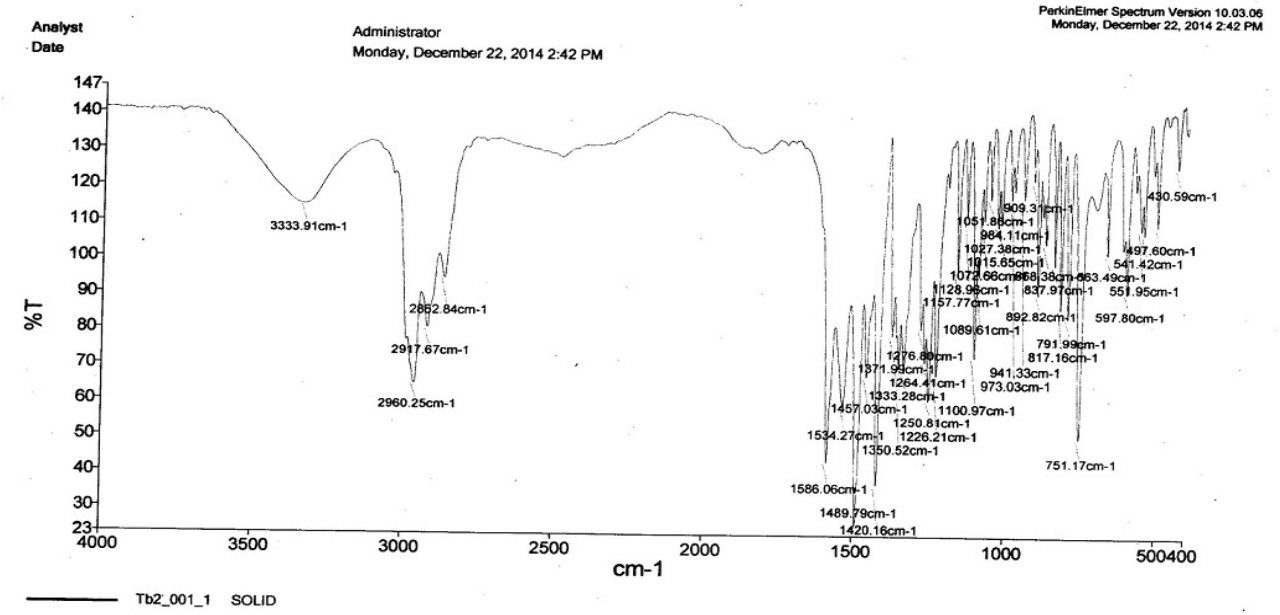


Fig. S22 IR spectra of compound **2** (Tb_2).

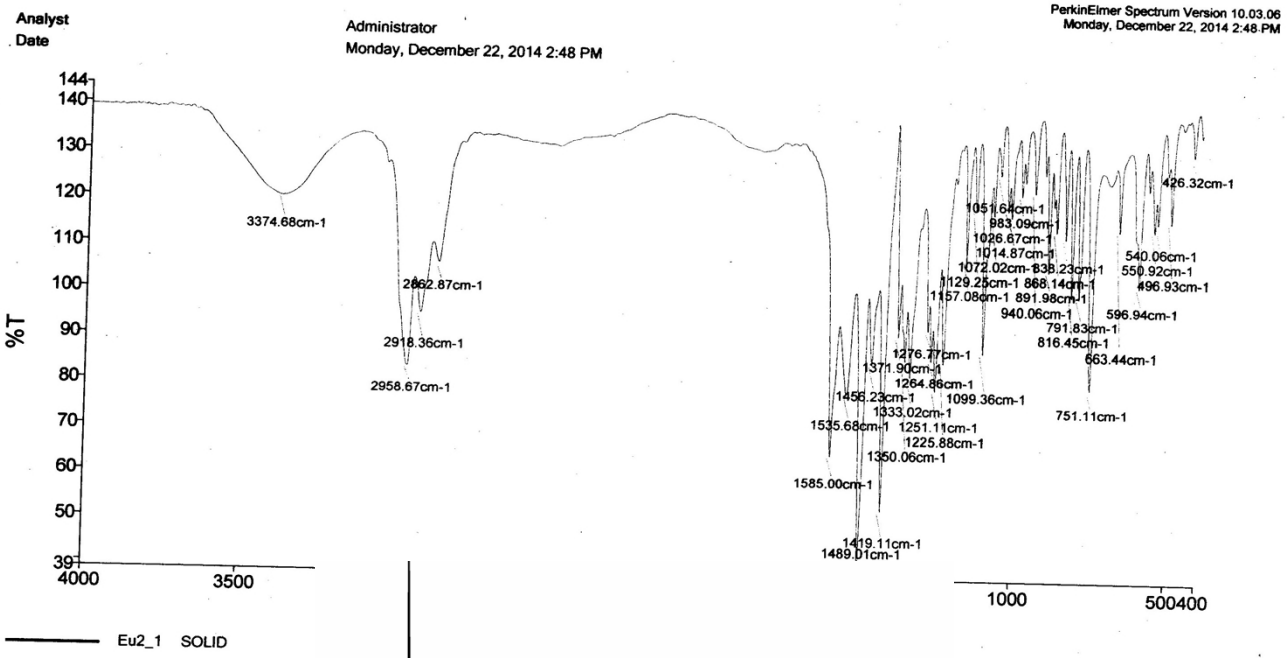
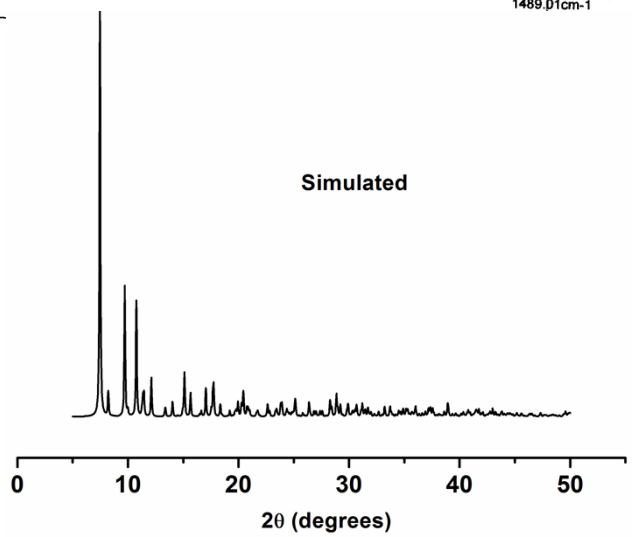


Fig. S23 IR spectra of compound **4** (Eu_2).



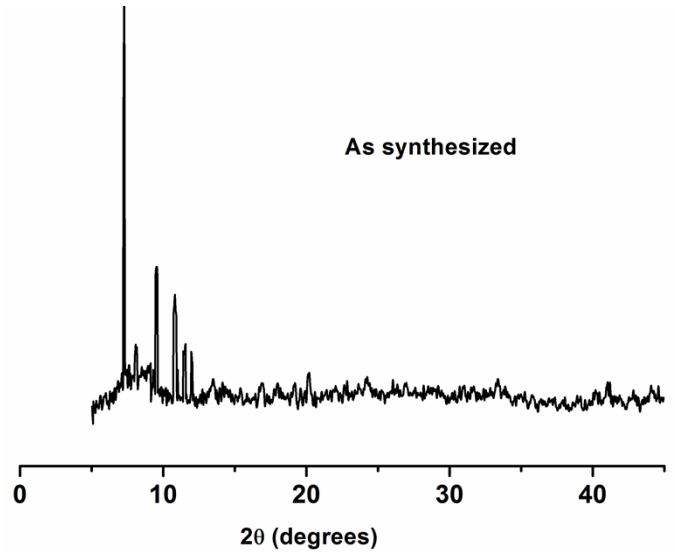


Fig. S24 Room temperature PXRD of compound **1** (Gd_2).

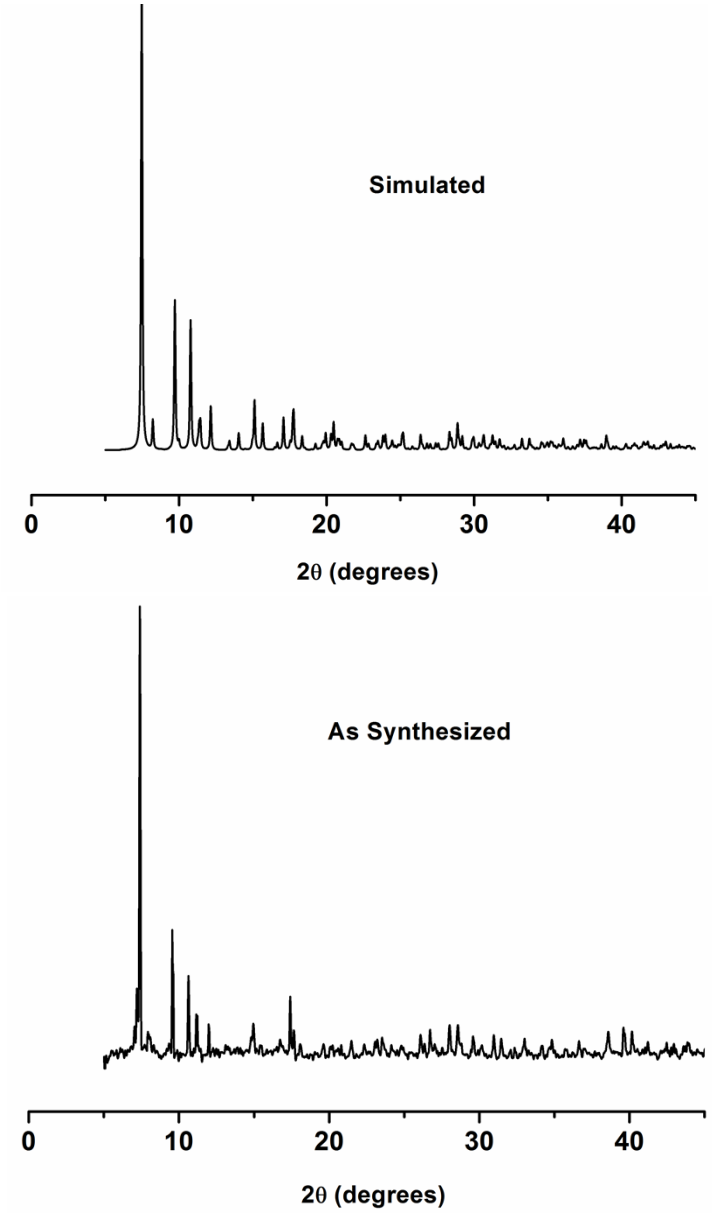
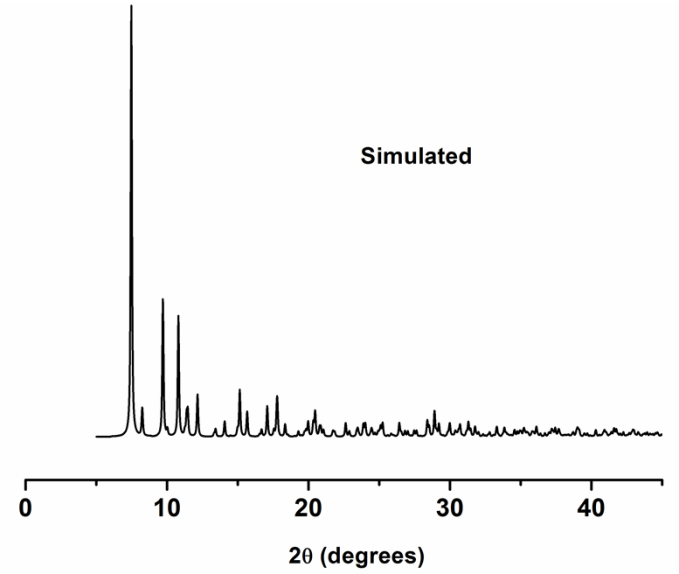
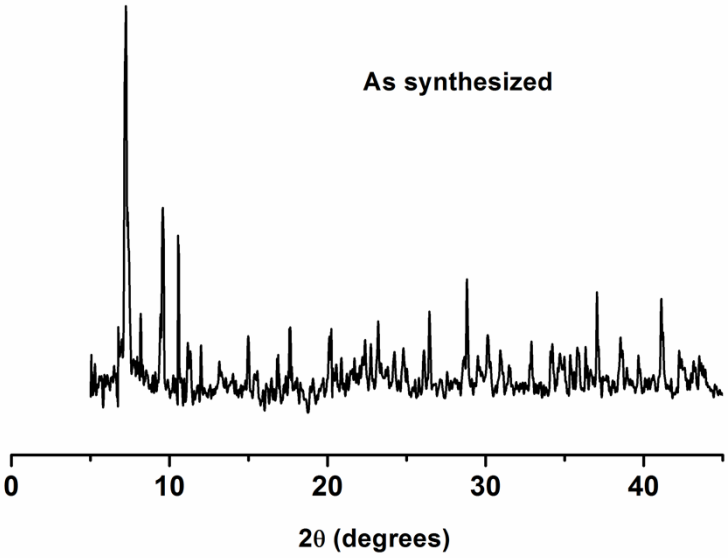


Fig. S25 Room temperature PXRD of compound **2** (Tb_2).





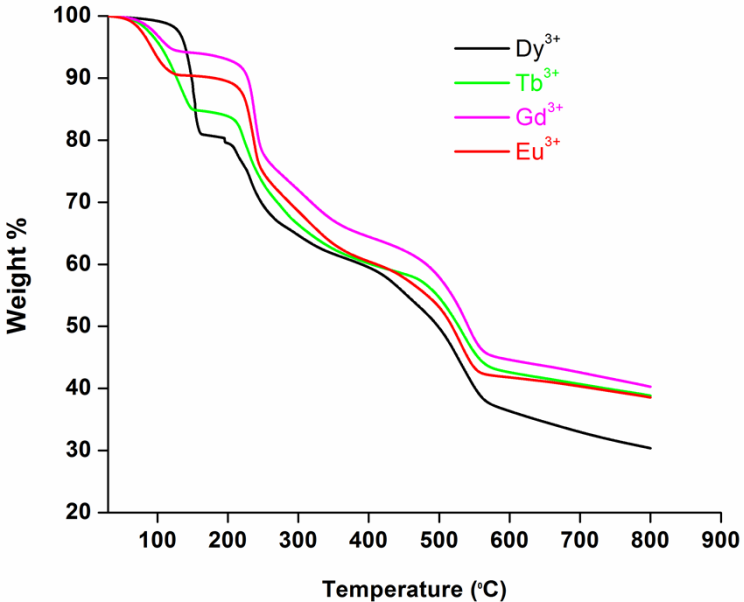


Fig. S26 Room temperature PXRD of compound **3** (Dy_2).

Fig. S27 Thermo gravimetric analysis curve of **1-4** (Heating rate: 10 °C per min) under argon atmosphere.