Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Syntheses, Crystal Structures and Magnetic Properties of a Series of Luminescent Lanthanide Complexes Containing Neutral Tetradentate Phenanthroline-amide Ligands

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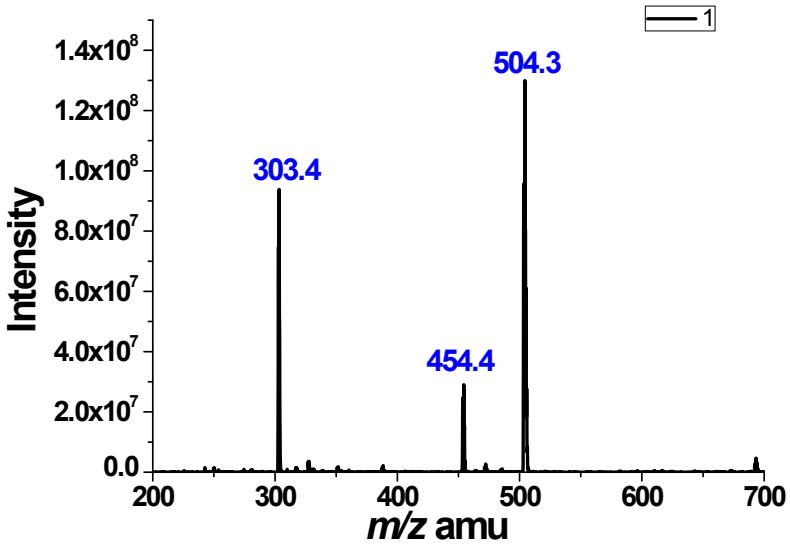

Figure S1. ESI/MS (+ve mode) of **1** in MeOH.

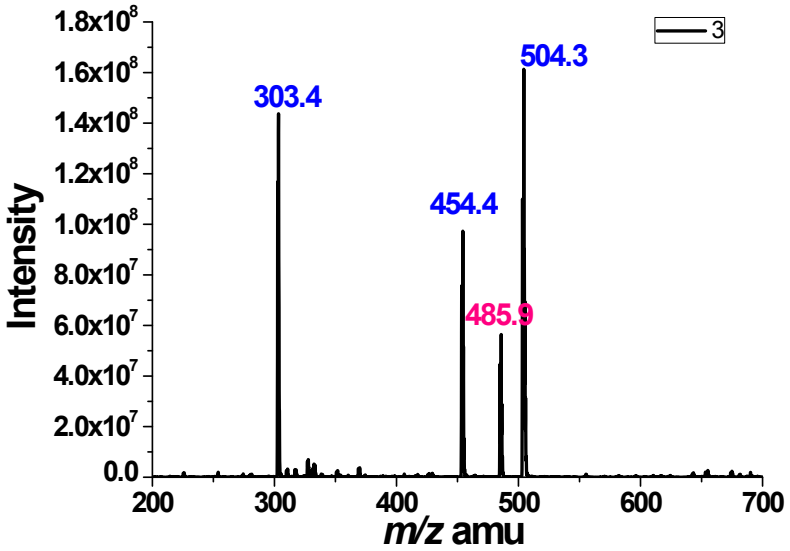

Figure S2. ESI/MS (+ve mode)of **3** in MeOH.

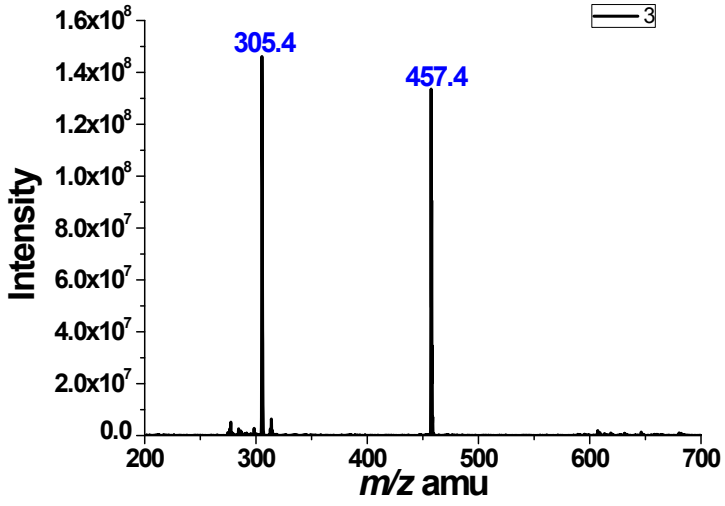

Figure S3. ESI/MS (+ve mode)of **2** in MeOH.

Table S1. Crystal data and structure refinement details for compounds **1-3**.

	1	**2**	**3**
Formula	$C_{45}H_{58}Cl_3N_8O_{18}Eu \cdot 3H_2O$	$C_{44}H_{54}Cl_3N_8O_5Tb \cdot 6H_2O$	$C_{44}H_{52}Cl_2N_9O_{15}Eu \cdot 2H_2O$
Mr	1311.35	1148.31	1205.83
T /K	100.0 (1) K	100.0 (1) K	100.0 (1) K
Crystal syst	Triclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/n$	*P*-1
a/Å	11.2219 (4)	17.7872 (5)	11.0673 (6)
b/Å	13.5403 (4)	15.8545 (4)	14.9385 (7)
c/Å	18.5761 (6)	18.2894 (5)	16.8102 (7)
α, (°)	81.020 (2)		108.393 (4)
β, (°)	82.265 (3)	90.718 (2)°	107.089 (4)
γ, (°)	82.701 (3)		92.161 (4)
V/ Å^3	2746.37 (16)	5157.3 (2)	2494.6 (2)
Z	2	4	2
ρ_{calcd}, Mg m^{-3}	1.586	1.479	1.605
F(000)	1344	2360	1232
Collected refl.	18528	36999	25802
Unique refl.	9866	9073	11765
R(int)	0.048	0.039	0.042
Final *R* indices, *I* > 2σ(I)	R_1(obs)=0.063 *w*R(all)=0.174	R_1(obs)=0.047 *w*R(all)=0.120	R_1(obs)= 0.058 *w*R(all)= 0.160
GOF	1.04	1.07	1.06
No.of par.	708	669	690

Table S2. Crystal data and structure refinement details for compounds **4-6**.

	4	**5**	**6**
Formula	$C_{44}H_{52}Cl_2N_9O_{15}Sm \cdot CH_3OH$	$C_{44}H_{52}Cl_2N_9O_{15}Tb \cdot CH_3OH \cdot H_2O$	$C_{44}H_{52}Cl_2N_9O_{15}Dy \cdot H_2O$
Mr	1200.23	1226.82	1198.36
T /K	100.0 (1) K	100.0 (1) K	100.0 (1) K
Crystal syst	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	11.0699 (3)	11.1117 (7)	10.7892 (3)
b/Å	14.8478 (5)	14.8294 (7)	13.9796 (4)
c/Å	17.1169 (6)	17.0510 (10)	17.7479 (3)
α, (°)	109.272 (3)	109.676 (5)	73.240 (2)
β, (°)	104.997 (3)	104.801 (6)	82.841 (2)
γ, (°)	93.227 (2)	93.316 (4)	72.131 (3)
V/ Å^3	2534.12 (15)	2525.7 (3)	2437.60 (12)

Z	2	2	2
ρ_{calcd}, Mg m^{-3}	1.573	1.613	1.633
F(000)	1226	1252	1218
Collected refl.	21233	16754	27593
Unique refl.	8923	9058	11556
R(int)	0.039	0.070	0.080
Final *R* indices, *I* > 2σ(I)	R_1(obs)= 0.059 *w*R(all)= 0.166	R_1(obs)= 0.073 *w*R(all)= 0.211	R_1(obs)= 0.066 *w*R(all)= 0.178
GOF	1.03	1.09	1.07
No.of par.	664	673	653

Table S3. The calculated Continuous Shape Measures (CShM) for **1**.

Hexadecahedron (D_{4h})	Tetradecahedron (C_{2v})	Staggered Dodecahedron (D_2)	Bicapped square antiprism (D_{4d})	Metabidiminished icosahedron (C_{2v})	Sphenocorona (C_{2v})
8.79	4.61	5.24	3.24	6.90	2.66

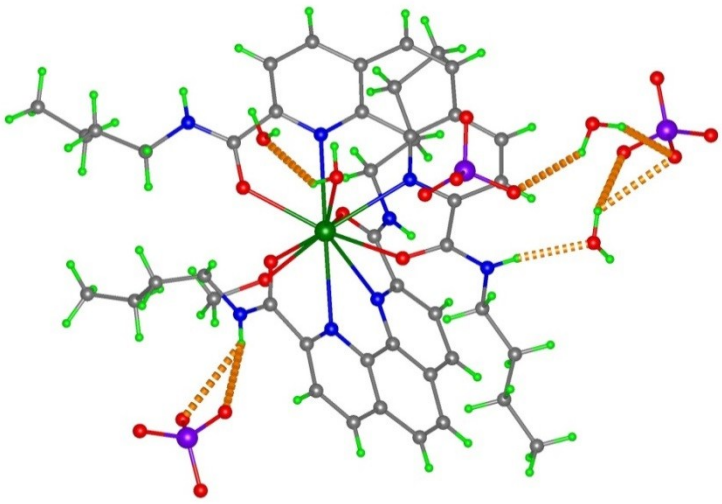

Figure S4. The H-bonding interactions among the coordinated H2O, MeOH, solvates and anion ClO_4^- in Eu^{3+} compound **1**.

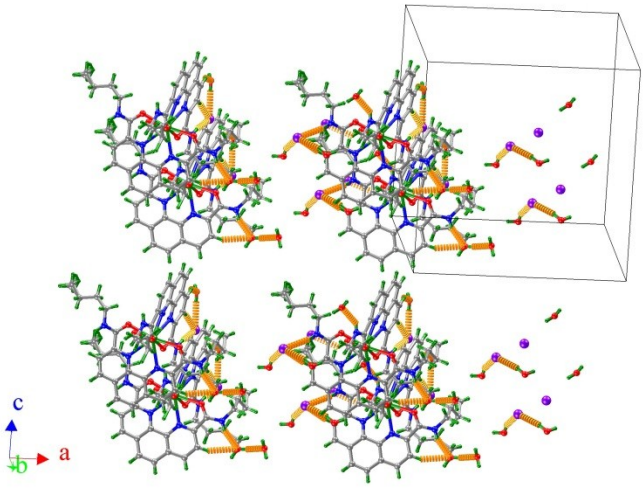

Figure S5. The H-bonding interactions among the coordinated H_2O molecule, solvate H_2O and anion Cl^- in Tb(III) compound **2**.

Table S4. The calculated Continuous Shape Measures (CShM) for **2**

Muffin (C_s)	Hula-hoop (C_{2v})	Spherical tricapped trigonal prism (D_{3h})	Tricapped trigonal prism (D_{3h})	Spherical capped square antiprism (C_{4v})	Capped square antiprism (C4v)
2.39	7.26	2.85	5.54	2.77	3.70

Table S5. The calculated Continuous Shape Measures (CShM) for **5**.

Hexadecahedron (D_{4h})	Tetradecahedron (C_{2v})	Staggered Dodecahedron (D_2)	Sphenocorona (C_{2v})	Metabidiminished icosahedron (C_{2v})	Bicapped square antiprism (D_{4d})
9.89	5.81	6.81	3.27	7.57	3.33

Table S6. The calculated Continuous Shape Measures (CShM) for **6**.

Hexadecahedron (D_{4h})	Tetradecahedron (C_{2v})	Staggered Dodecahedron (D_2)	Sphenocorona (C_{2v})	Metabidiminished icosahedron (C_{2v})	Bicapped square antiprism (D_{4d})
9.83	5.71	6.68	3.22	7.45	3.25

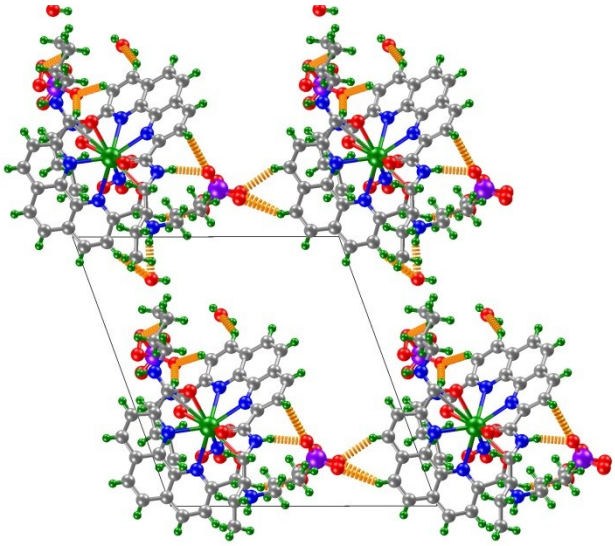

Figure S6. The H-bonding interactions in Eu^{3+} compound **3** and the closest Eu···Eu distance is 11.06 Å.

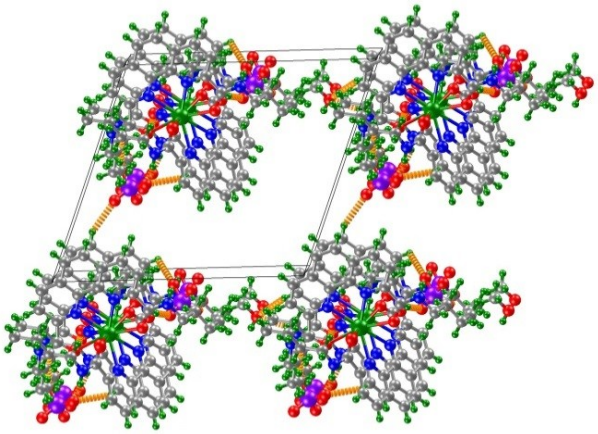

Figure S7. The H-bonding interactions in Eu^{3+} compound **4** and the closest Sm···Sm distance is 11.07 Å.

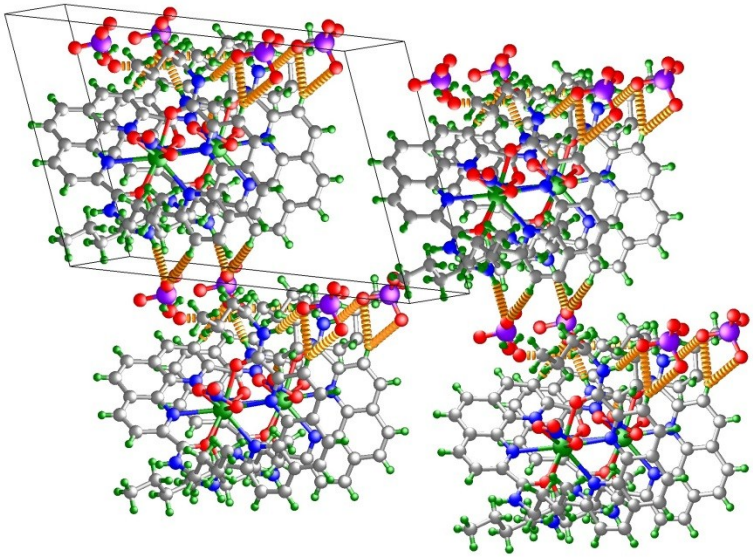

Figure S8. The H-bonding interactions in Dy^{3+} compound **6** and the closest Dy···Dy distance is 10.78 Å.

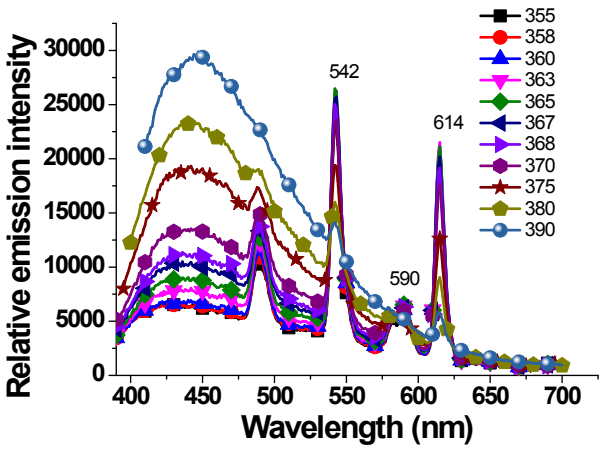

Figure S9. The solid state emission spectra of **2** upon different excitation wavelengths.

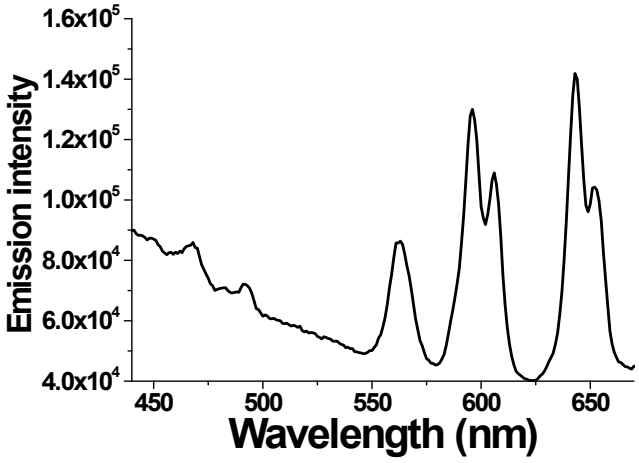

Figure S10. The solid state emission spectra of **4** upon excitation by λ_{ex} = 355 nm.

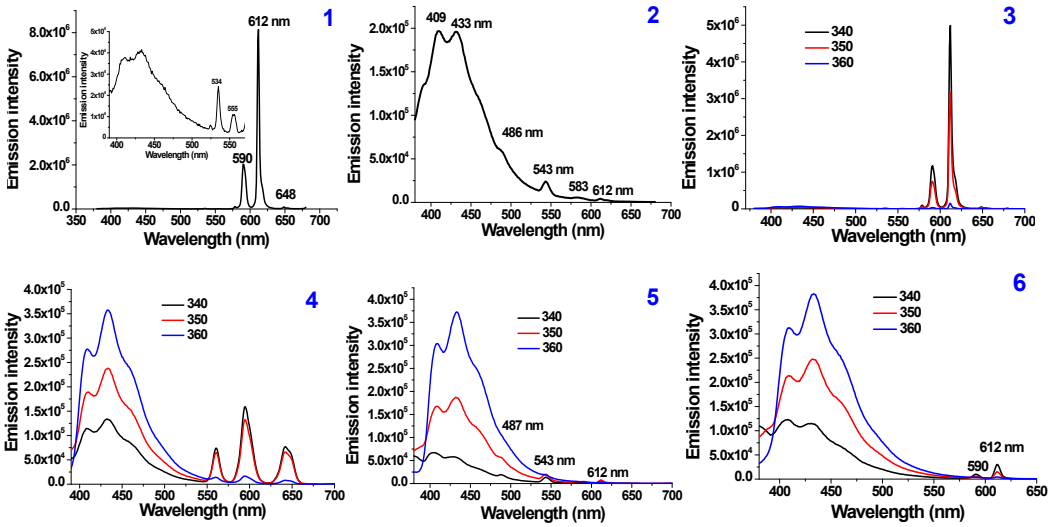

Figure S11. The emission spectra (λ_{ex} = 355 nm) in MeOH solutions for **1**-**6**.

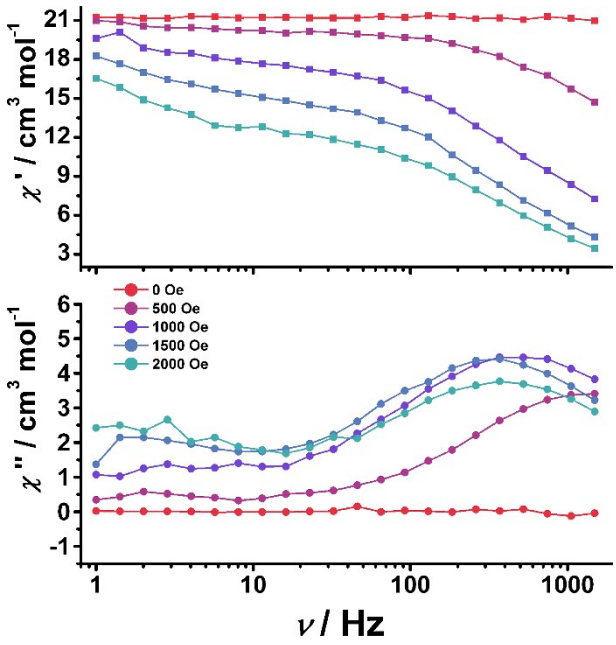

Figure S12. Frequency dependence of in phase (χ') and out-of-phase (χ'') ac magnetic susceptibility at 2 K under the applied static field from 0 to 2000 Oe for **5**. The solid lines are for eye guide.

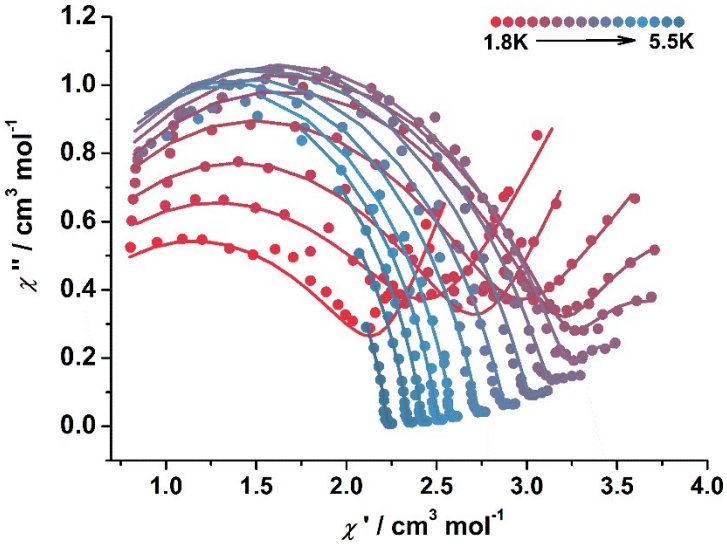

Figure S13. Cole-Cole plots for **5** under a *dc* field at indicated temperatures in the range of 1.8-5.5 K.

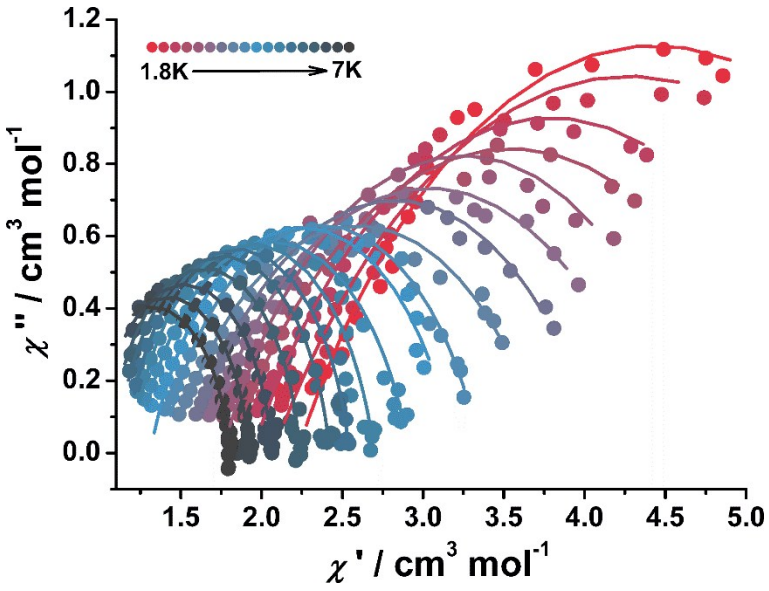

Figure S14. Cole-Cole plots for **6** under a *dc* field at indicated temperatures in the range of 1.8-7 K.