Electronic Supplementary Material (ESI) for Dalton Transactions.

Lanthanide Clusters of Phenanthroline Containing Pyridine-Pyrazole Based Ligand: Magnetism & Cell Imaging

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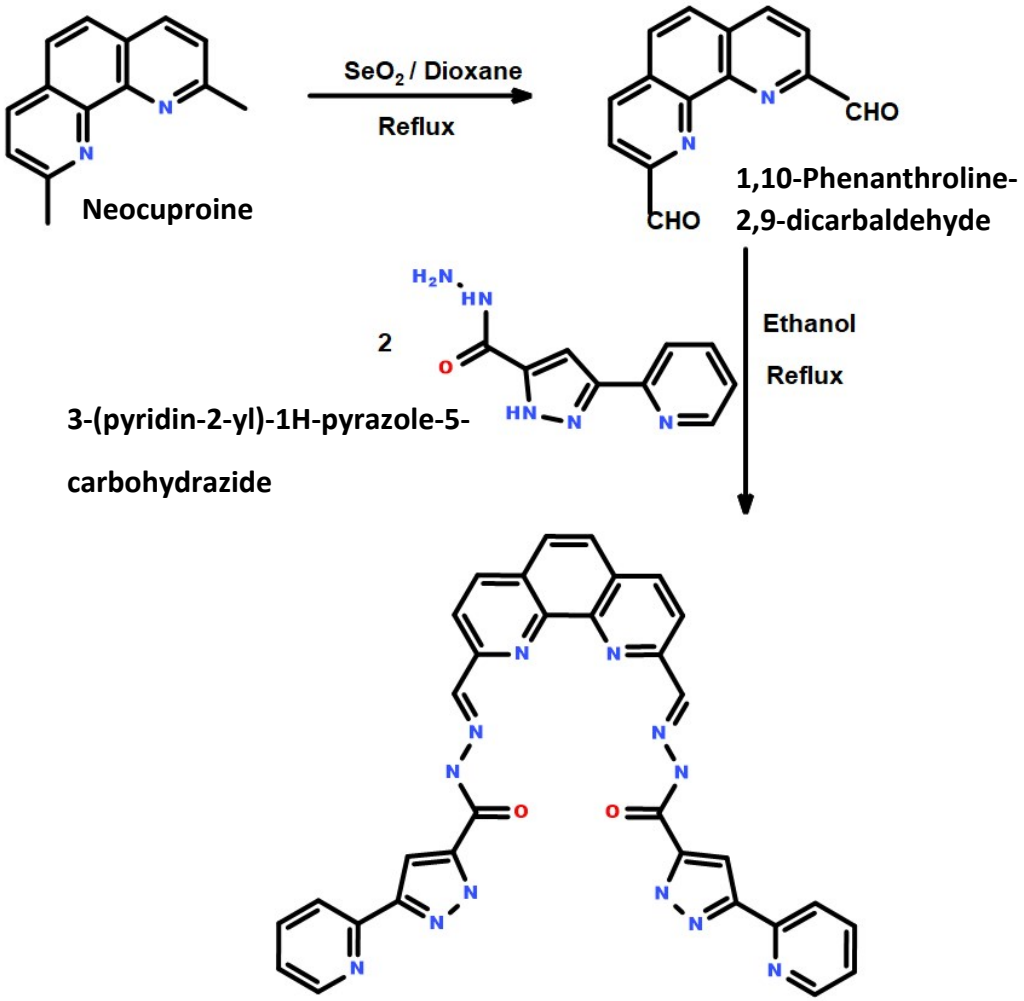

Scheme S1: Synthesis of ligand (**Phen**)

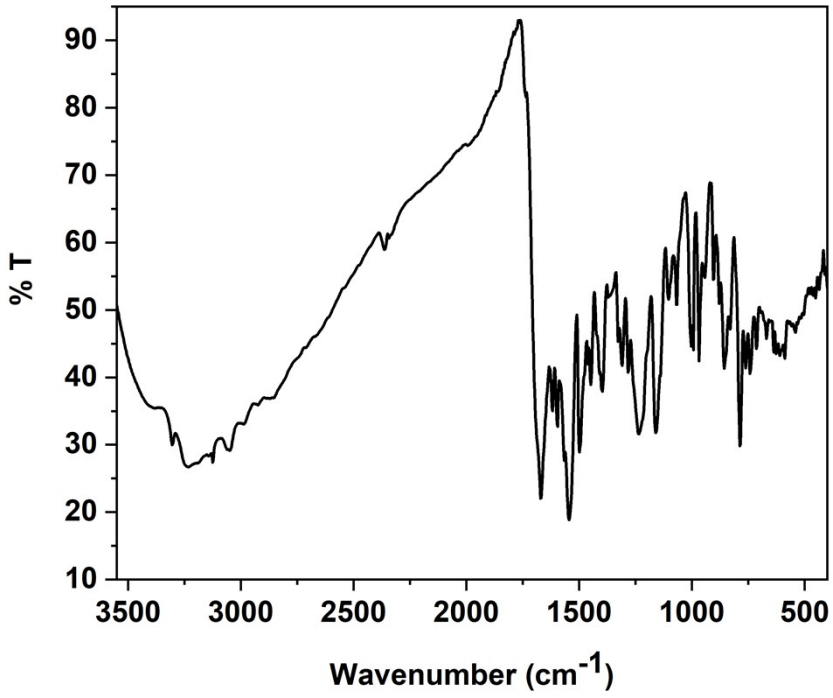

Fig. S1: IR spectra of **Phen**

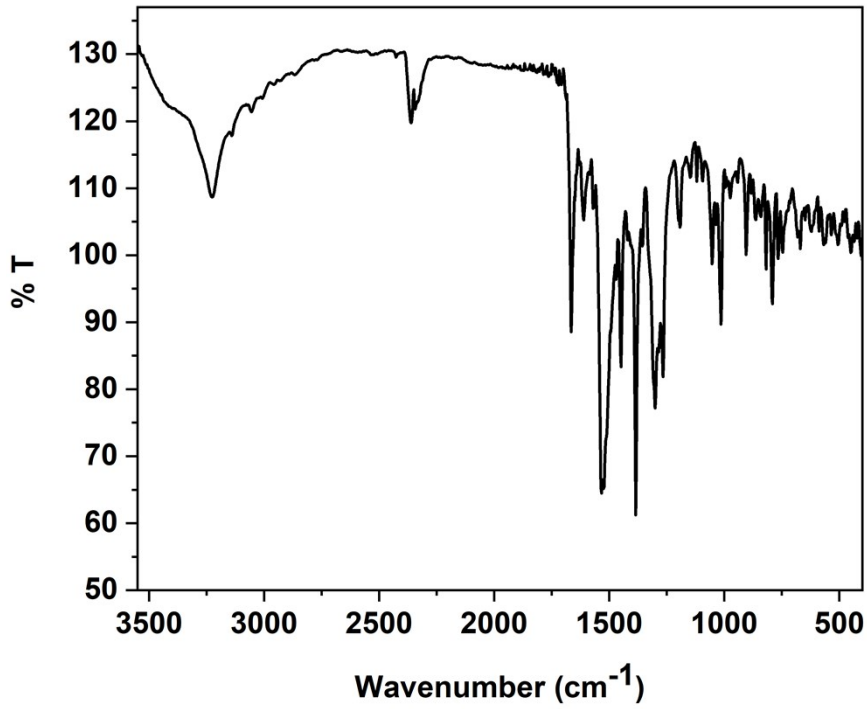

Fig. S2: IR spectra of **Phen-Gd**

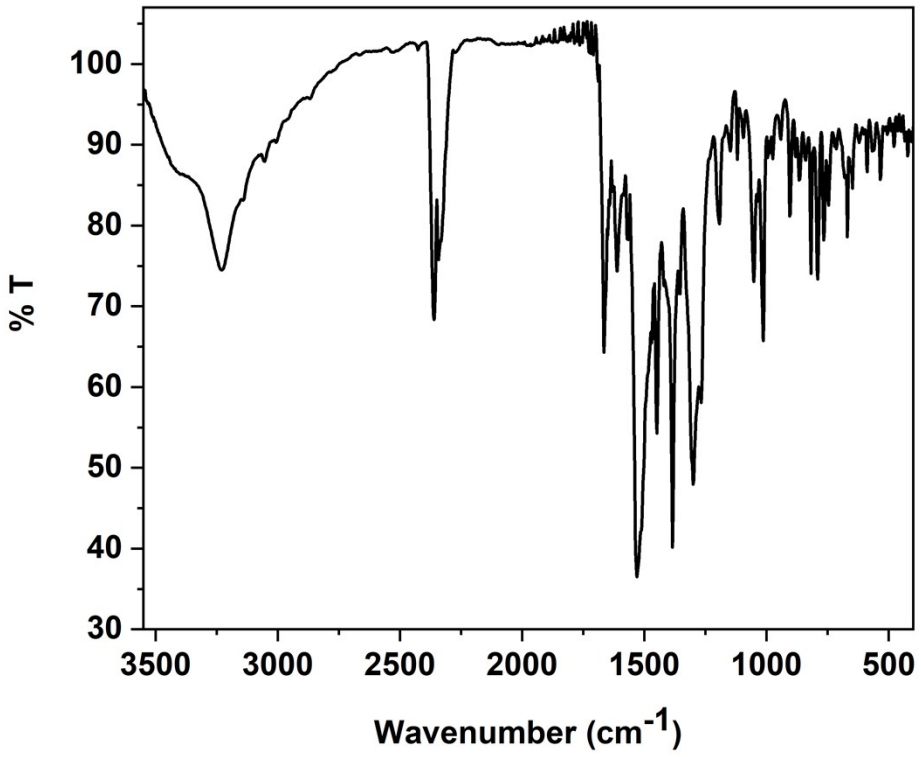

Fig. S3: IR spectra of **Phen-Eu**

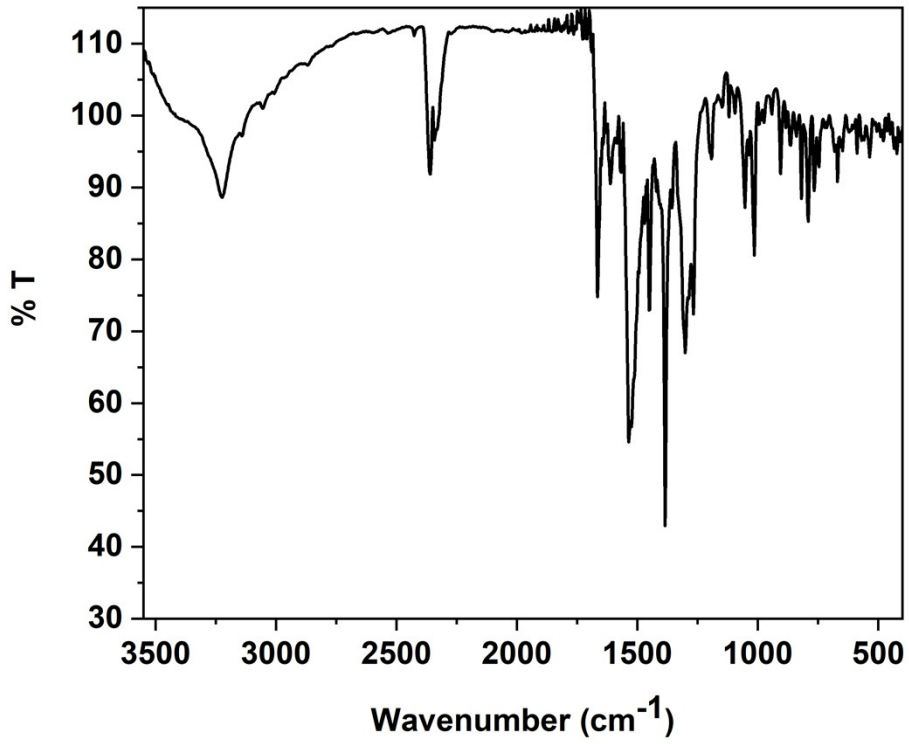

Fig. S4: IR spectra of **Phen-Tb**

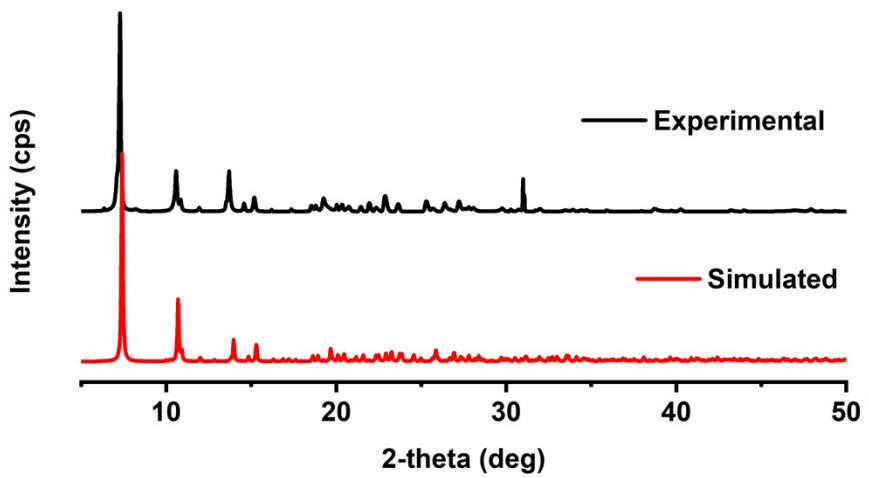

Fig. S5. Simulated & experimental powder x-ray diffraction data of **Phen-Gd**

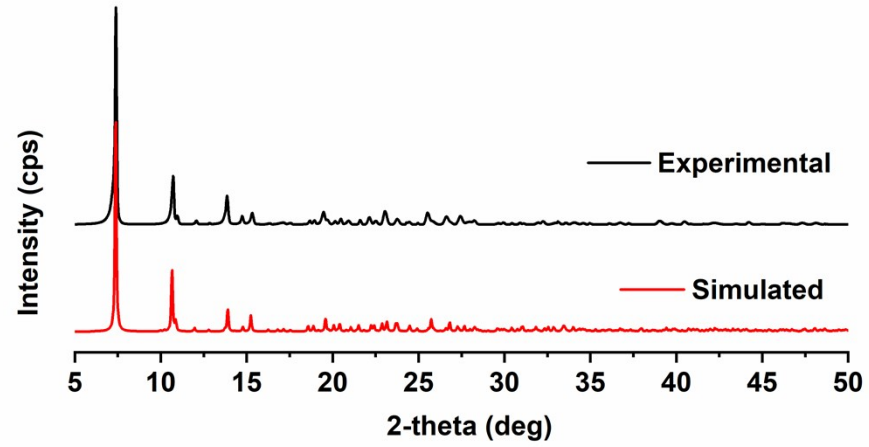

Fig. S6. Simulated & experimental powder x-ray diffraction data of**Phen-Eu**

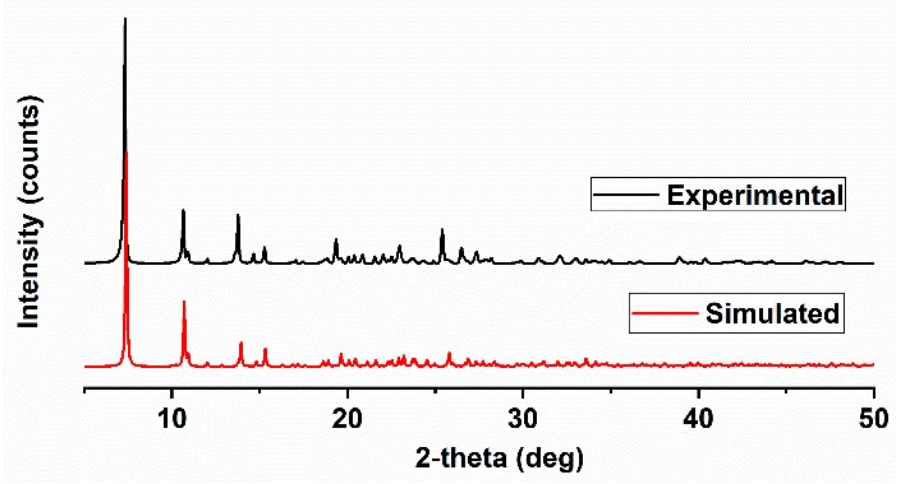

Fig. S7. Simulated & experimental powder x-ray diffraction data of**Phen-Tb**

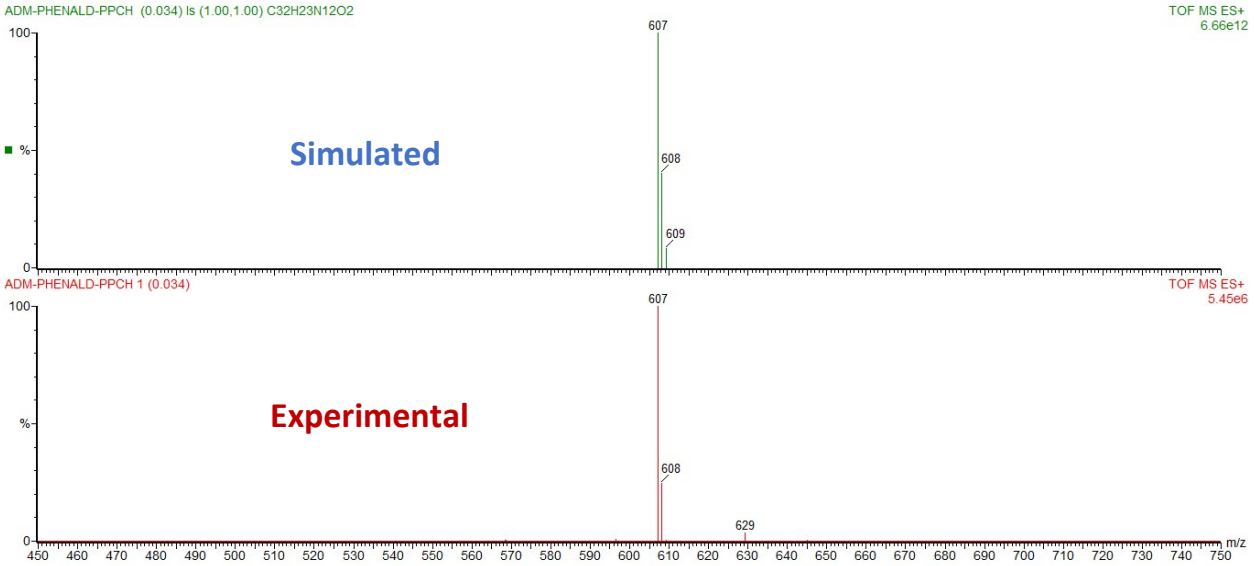

Fig. S8. Simulated & experimental mass data of **Phen**

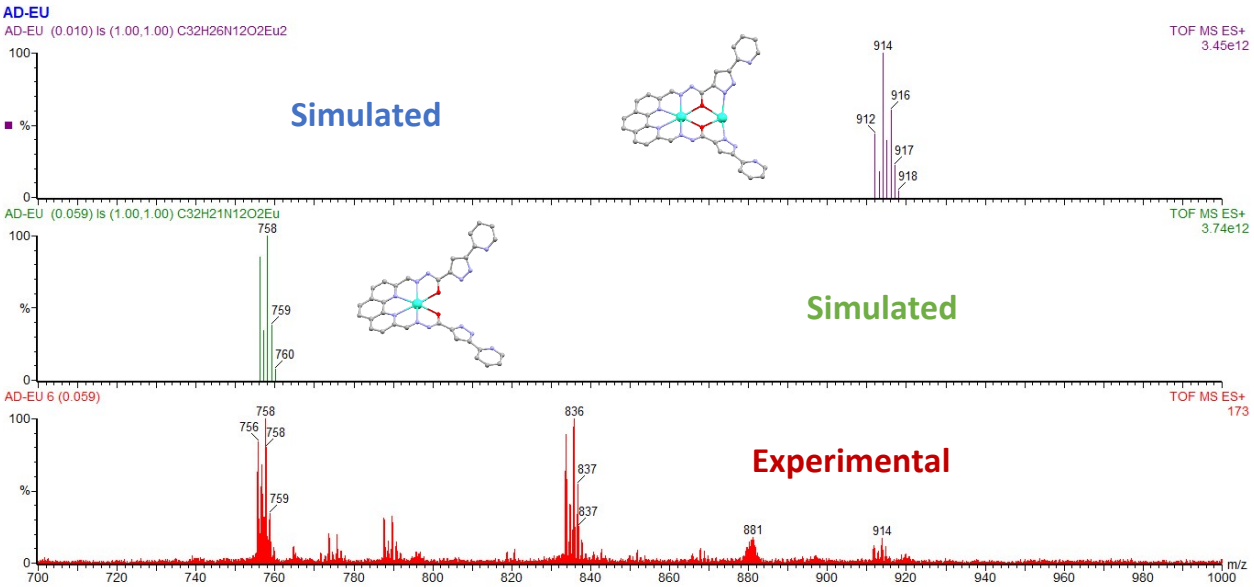

Fig. S9. Simulated & experimental mass data for fragments of **Phen-Eu**

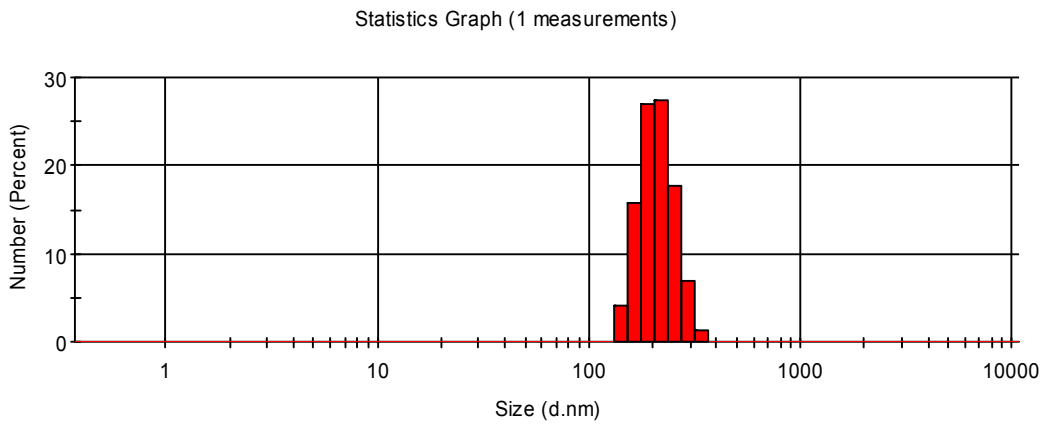

Fig. S10. DLS data for solution of **Phen-Eu**

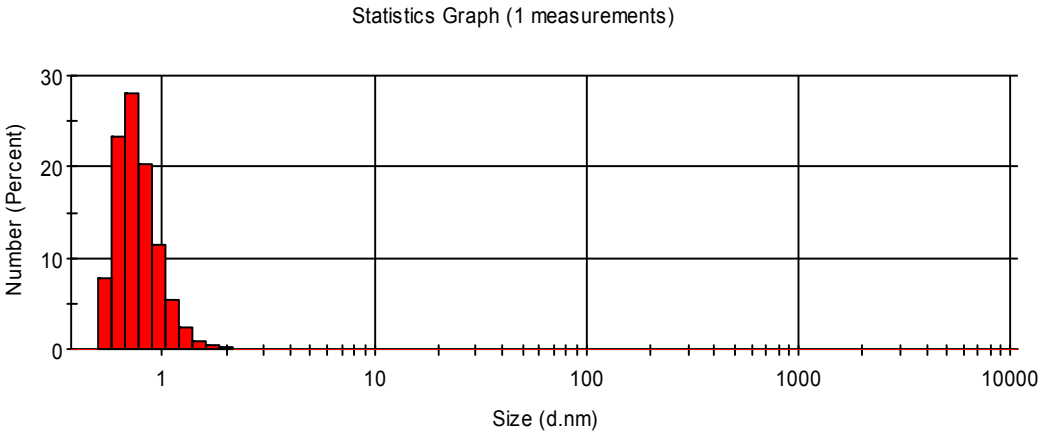

Fig. S11. DLS data for solution of **Phen-Tb**

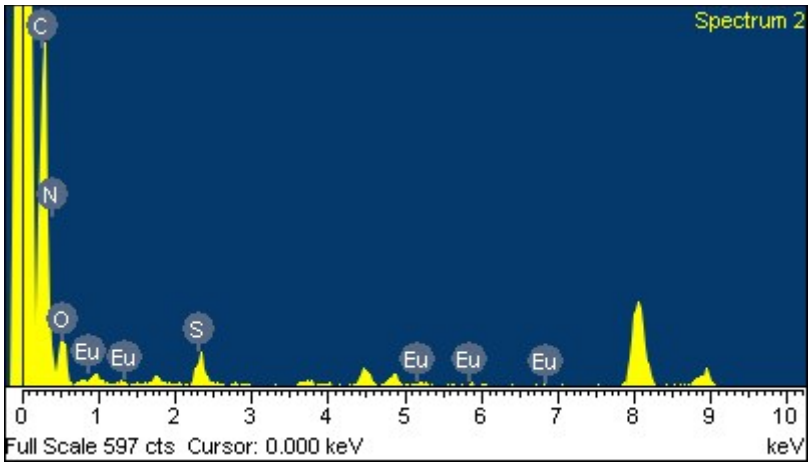

Fig. S12. TEM-EDX spectra for **Phen-Eu** solution

Table S1. Elemental analysis for **Phen-Eu** from TEM-EDX

Element	Weight%	Atomic%
C K	77.97	86.70
N K	0.61	0.58
O K	11.14	9.30
S K	7.64	3.18
Eu L	2.64	0.23
Totals	100.00	

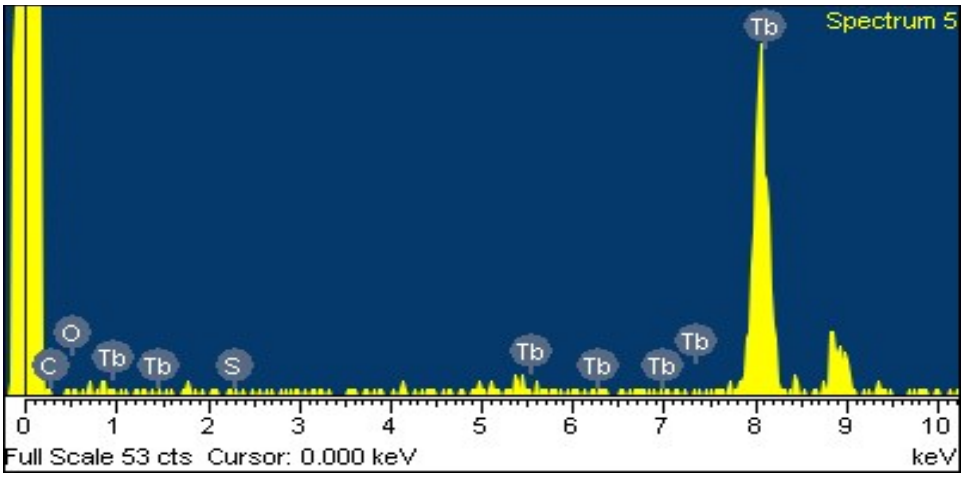

Fig. S13. TEM-EDX spectra for **Phen-Tb** solution

Table S2. Elemental analysis for **Phen-Tb** from TEM-EDX

Element	Weight%	Atomic%
C K	3.50	23.52
N K	3.37	19.44
O K	1.29	6.54
S K	1.89	4.76
Tb L	89.95	45.74
Totals	100.00	

Table S3. Some selected bond lengths (Å) and bond angles (°) for **Phen-Gd**.

Gd1-O2	2.402(5)	Gd1-N10	2.609(6)	Gd2-O1SA	2.456(6)	Gd2-N5	2.550(6)
Gd1-O1	2.505(5)	Gd2-O1	2.426(4)	Gd2-O2SA	2.487(7)	Gd2-N8	2.563(6)
Gd1-O1S	2.511(6)	Gd2-O2	2.460(5)	Gd2-O2SB	2.494(7)	Gd2-N6	2.647(6)
Gd1-N3	2.558(6)	Gd2-O1SB	2.502(6)	Gd2-N7	2.650(6)		
Gd2-O1-Gd1	116.08(17)	Gd1-O2-Gd2	118.79(19)				

Table S4. Some selected bond lengths (Å) and bond angles (°) for **Phen-Eu**.

Eu1-O2	2.413(5)	Eu2-O1	2.444(4)	Eu2-O1SA	2.515(7)	Eu2-N7	2.653(6)
Eu1-O1	2.502(4)	Eu2-O2	2.459(5)	Eu2-O2SA	2.519(6)	Eu2-N6	2.650(6)
Eu1-O1S	2.527(6)	Eu2-O2SB	2.472(6)	Eu1-N10	2.617(6)	Eu2-N5	2.557(6)
Eu1-N3	2.576(6)	Eu2-O3SB	2.492(7)	Eu2-N8	2.575(6)		
Eu2-O1-Eu1	115.75(17)	Eu1-O2-Eu2	118.62(19)				

Table S5. Some selected bond lengths (Å) and bond angles (°) for **Phen-Tb**.

Tb1-O2	2.384(9)	Tb2-O1	2.427(9)	Tb2-O2SB	2.473(13)	Tb2-N6	2.629(12)
Tb1-O1	2.491(10)	Tb2-O1SB	2.451(11)	Tb2-O2SA	2.491(12)	Tb2-N7	2.630(11)
Tb1-O1S	2.493(12)	Tb2-O2	2.459(10)	Tb1-N10	2.579(12)	Tb2-N5	2.536(11)
Tb1-N3	2.525(10)	Tb2-O1SA	2.472(15)	Tb2-N8	2.553(13)		
Tb2-O1-Tb1	116.5(3)	Tb1-O2-Tb2	119.4(4)				

Table S6. Crystallographic table

	Phen-Tb	Phen-Eu	Phen-Gd
Empirical formula	$C_{70}H_{54}N_{31}O_{21}Tb_3$	$C_{70}H_{54}Eu_3N_{31}O_{21}$	$C_{70}H_{54}Gd_3N_{31}O_{21}$
Formula weight	2142.20	2121.32	2137.19
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Fdd2	Fdd2	Fdd2
a/Å	32.353(5)	32.535(4)	32.418(2)
b/Å	35.316(6)	35.366(4)	35.298(3)
c/Å	13.8018(19)	13.8372(17)	13.7654(9)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	15769(4)	15922(3)	15751.9(19)
Reflections collected	39099	51745	54794
Unique reflections	8142	12624	12497
Observed reflections [I>2σ(I)]	6898	10989	10460
R1	0.0680	0.0426	0.0436
wR2	0.1633	0.0995	0.0960
CCDC No.	2047787	2047785	2047786

Table S7. Details of the 10-Coordinate Ln Centers and Their Geometry with SHAPE Values

Potential coordination polyhedra of the 10-coordinate metal centers	Abbreviation	Point group	Continuous Shape Measures (CShM) values					
			Phen-Gd		Phen-Tb		Phen-Eu	
			Gd1	Gd2	Tb1	Tb2	Eu1	Eu2
Decagon	DP-10	D10h	34.94136	36.58294	34.98092	36.54033	34.92095	36.62687
Enneagonal pyramid	EPY-10	C9v	23.42980	25.85713	23.44743	25.76090	23.20242	26.17997
Octagonal bipyramid	OBPY-10	D8h	15.50693	16.08311	15.48341	16.14831	15.64090	15.93891
Pentagonal prism	PPR-10	D5h	12.37035	10.59770	12.33972	10.70527	12.29455	10.50884
Pentagonal antiprism	PAPR-10	D5d	13.42812	10.60574	13.41715	10.65825	13.43726	10.29469
Bicapped cube J15	JBCCU-10	D4h	12.20037	8.66262	12.16177	8.70118	12.29332	8.95086
Bicapped square antiprism J17	JBCSAPR-10	D4d	**3.45375**	5.40785	**3.45684**	5.31676	**3.52737**	5.61596
Metabidiminished icosahedron J62	JMBIC-10	C2v	7.04667	6.12672	7.01704	6.15889	6.91859	6.26701
Augmented tridiminished icosahedron J64	JATDI-10	C3v	17.18286	18.00535	17.24957	17.99529	16.98412	18.17382
Sphenocorona J87	JSPC-10	C2v	3.83427	4.19373	3.79343	4.09988	3.86237	4.07924
Staggered Dodecahedron (2:6:2)	SDD-10	D2	5.85668	1.77812	5.86762	1.73678	5.99675	1.63713
Tetradecahedron (2:6:2)	TD-10	C2v	4.93495	**1.50029**	4.98436	**1.45976**	5.03629	**1.42902**
Hexadecahedron (2:6:2) or (1:4:4:1)	HD-10	D4h	9.70571	5.44468	9.67023	5.52479	9.75034	5.66662

The polyhedron with the CShM value in **bold** is the real coordination polyhedron of the corresponding lanthanide metal centre for each compound

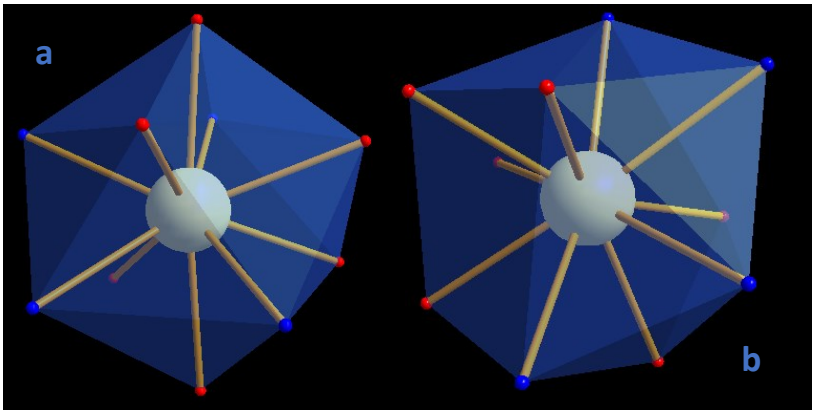

Fig. S14. Coordination geometry observed around metal centres in **Phen-Tb** (a)bicapped square antiprism (for Tb1) and (b) tetradecahedron (for Tb2)

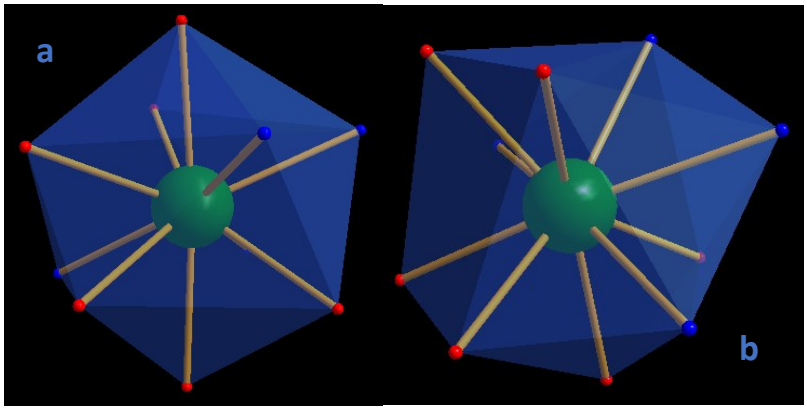

Fig. S15. Coordination geometry observed around metal centres in **Phen-Eu** (a)bicapped square antiprism (for Eu1) and (b) tetradecahedron (for Eu2)

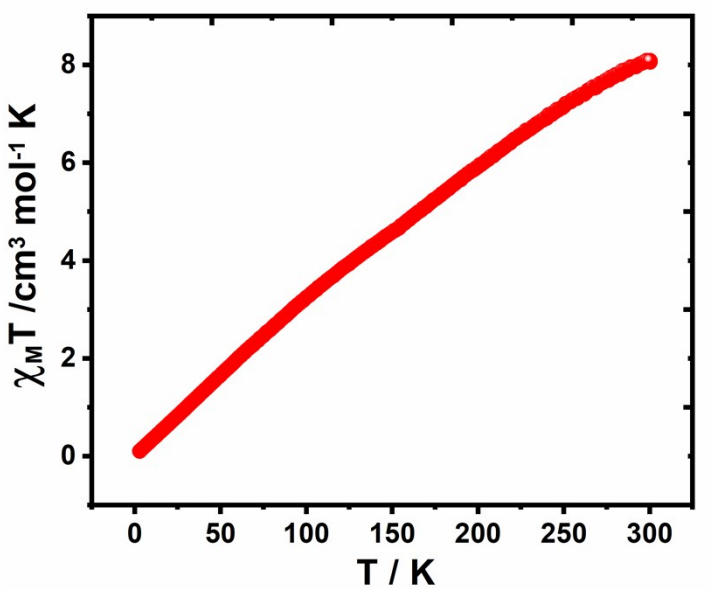

Fig. S16. χ_MT vs T plot for (a) **Phen-Eu**

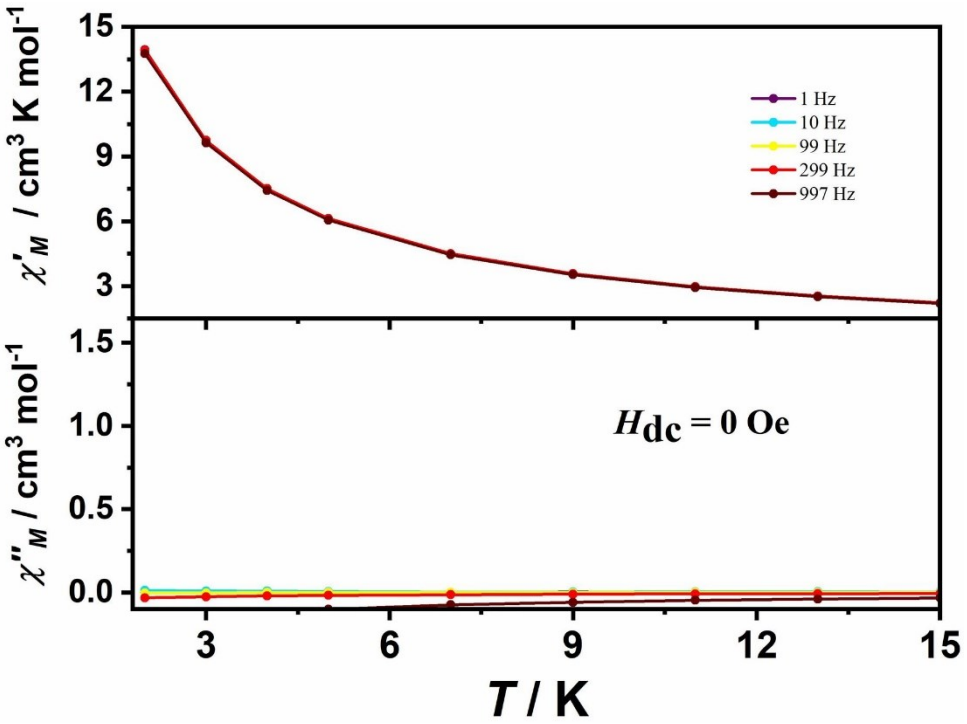

Fig. S17. Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility of **Phen-Tb** under zero dc field

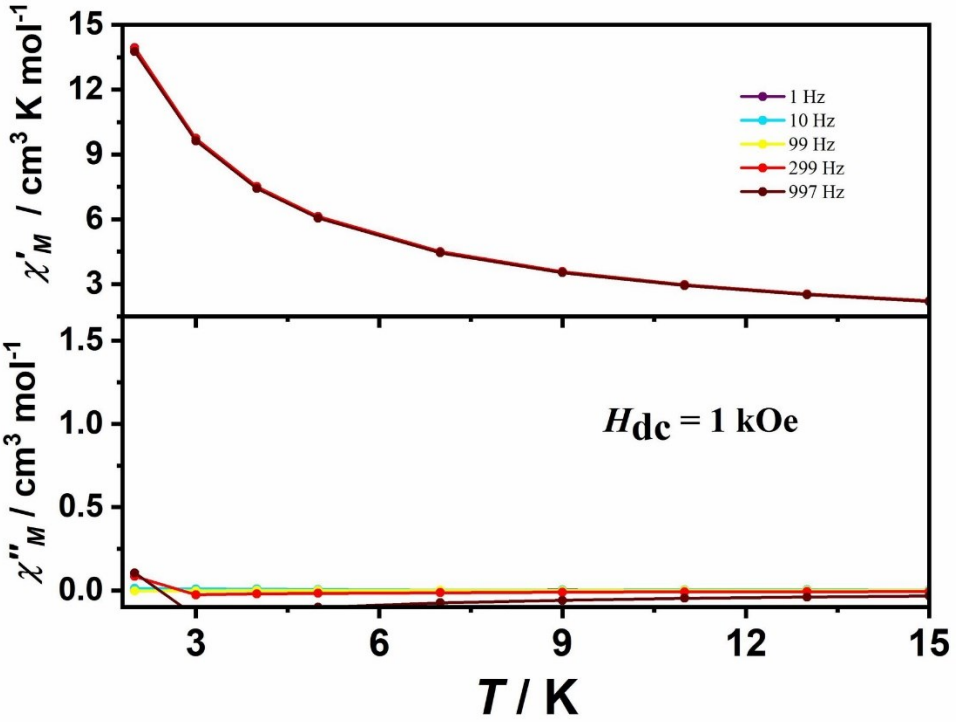

Fig. S18. Temperature dependence of the in-phase (χ′) and out-of-phase (χ″) ac susceptibility of **Phen-Tb** in presence of an applied dc field of 1kOe

Table S8. Comparison of the $-\Delta S_m$ values among **Phen-Gd** and recently reported Gd_3 clusters

Lanthanide core	$-\Delta S_m$ (J Kg^{-1} K^{-1})	Saturation magnetization value ($N\mu_B$)	Ref.
Linear Gd_3	23.42 J kg^{-1} K^{-1} at 2 K and 7T	20.96	This work
Triangular Shape Gd_3	10.65 J kg^{-1} K^{-1} at 7 K & 5 T	12.42	1
Triangular Shape Gd_3	30.22 J kg^{-1} K^{-1} at 3 K & 7T	20.86	2
Triangular Shape Gd_3	31.3 J kg^{-1} K^{-1} at 2 K and 7T	20.6	3
Nearly linear Gd_3	22.5 J kg^{-1} K^{-1} at 2 K and 7T	20.71	4
Non-linear Gd_3	20 J kg^{-1} K^{-1} at 2 K and 5T	21.2	5
Triangular Shape Gd_3	20.60 J kg^{-1} K^{-1} at 2 K and 7T	21.11	6

Reference

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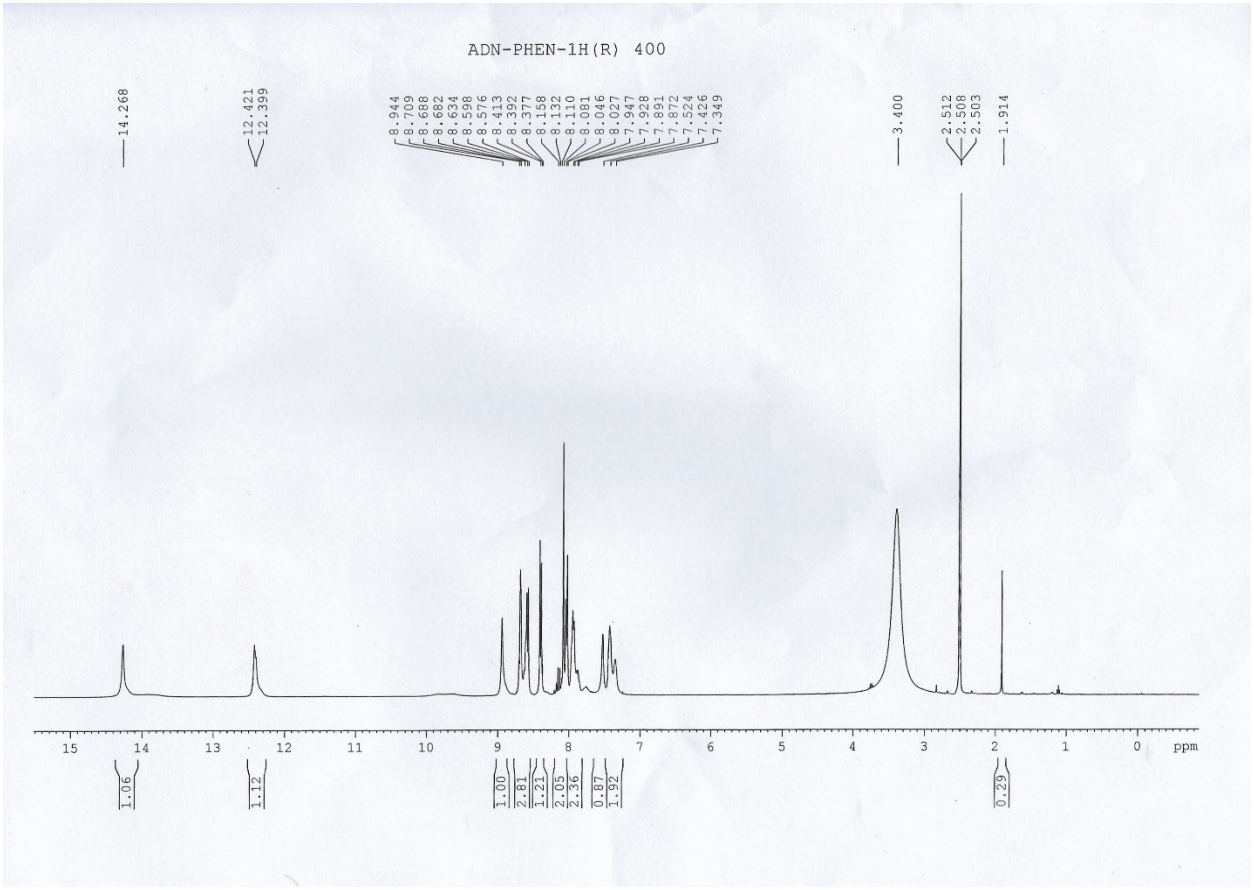

Fig. S19. NMR spectra of **Phen**