Supplementary Materials

Molecules

Heterometallic Zn^{II}–Ln^{III}–Zn^{II} Schiff base complexes with linear or bent conformation – synthesis, crystal structures, luminescent and magnetic characterization

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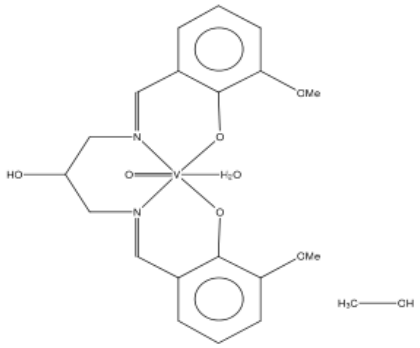
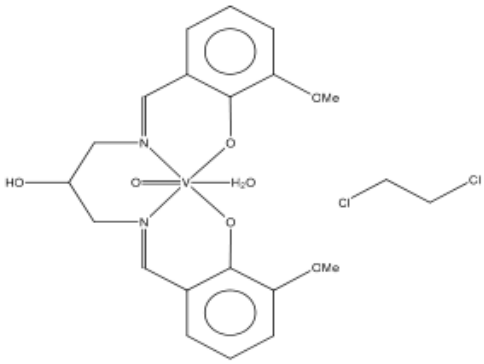
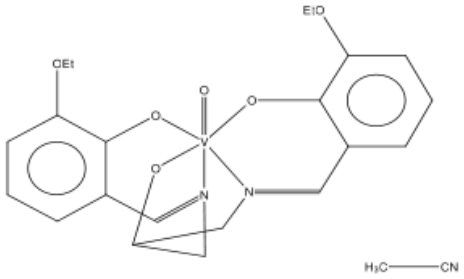
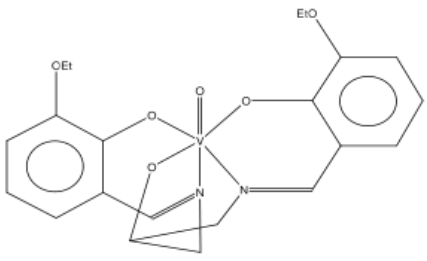
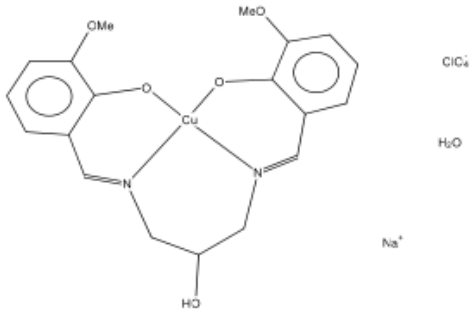
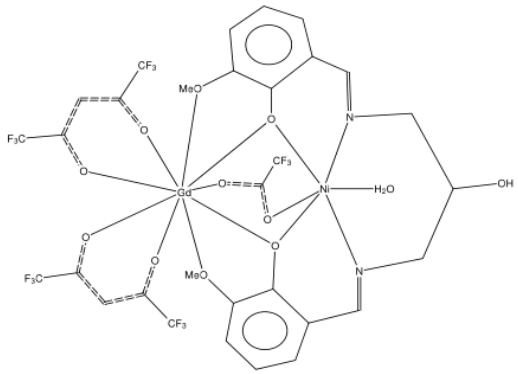
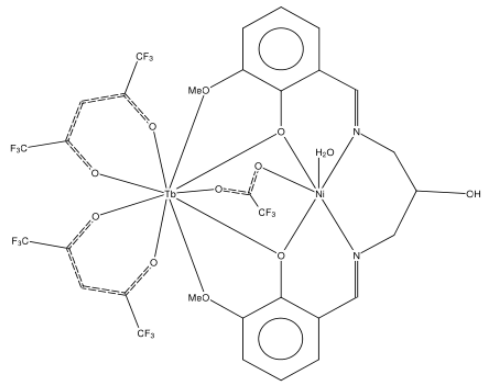
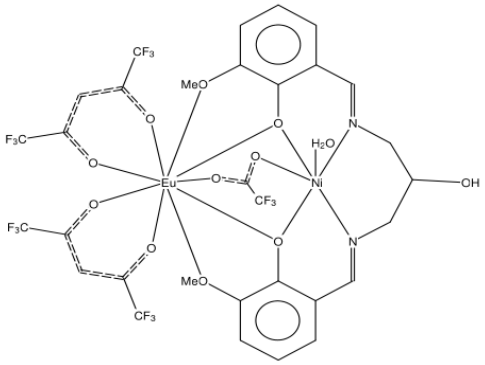
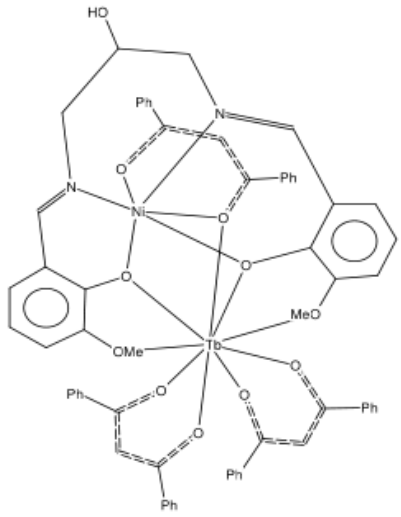
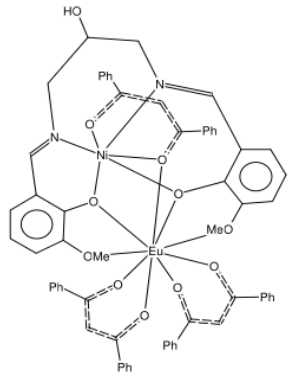
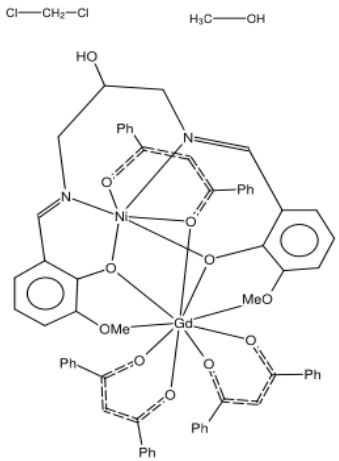
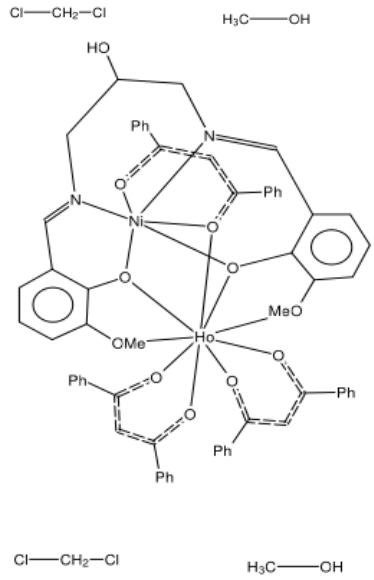
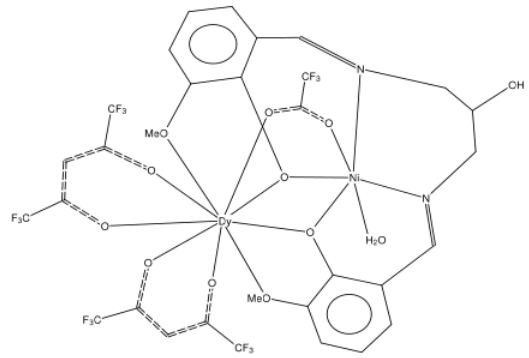
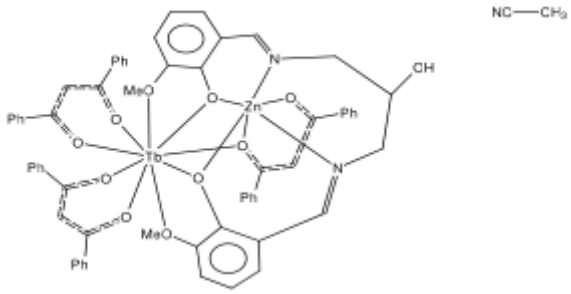
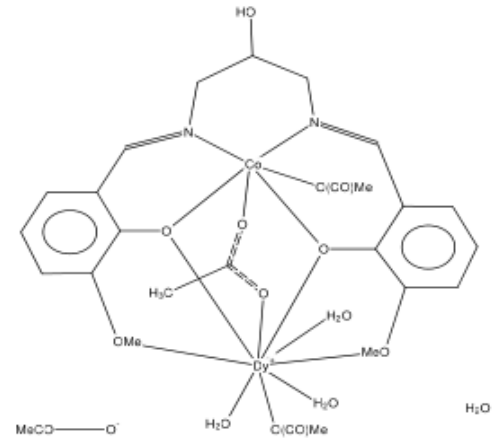
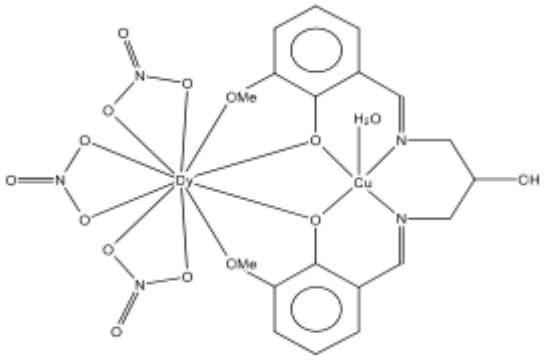
List of items:

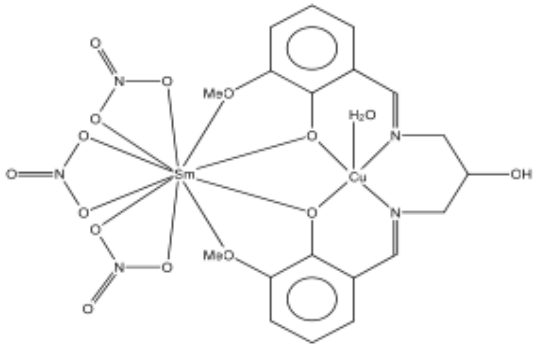
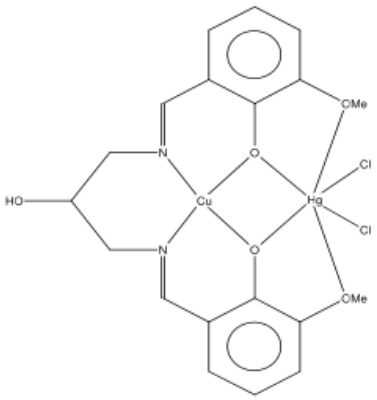
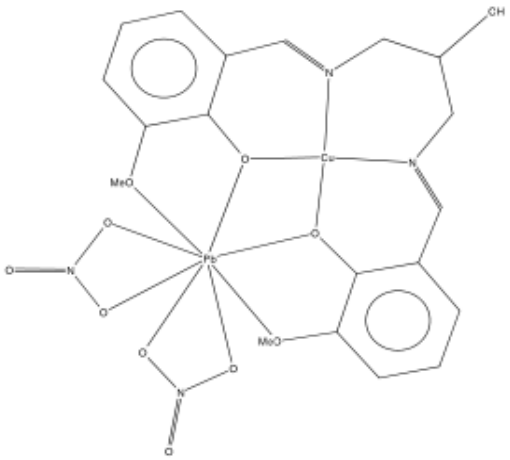
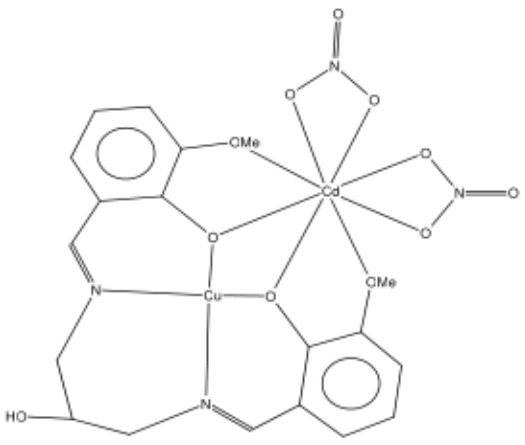
Table S1. Selected coordination compounds with Schiff base ligand having 2-hydroxypropyl bridge. [1]Involvement of the 2-hydroxypropyl bridge in the formation of coordination bond.

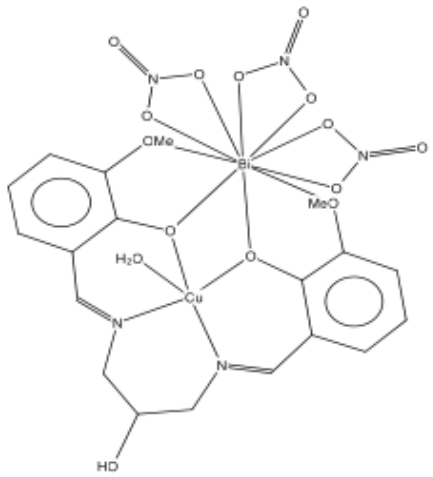
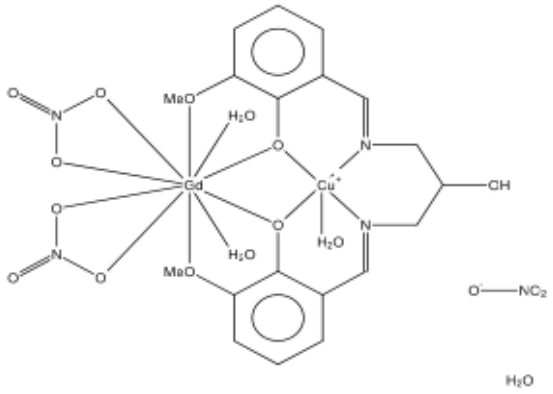
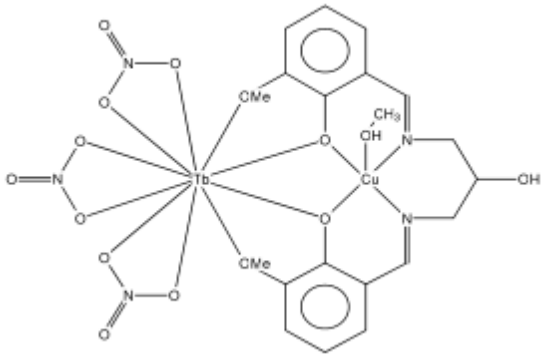
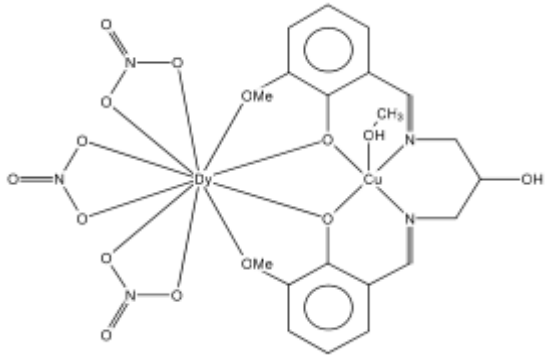
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	ABOZUP	1	V	No	[1]
	BEGHEB	1	V	No	[2]
	FEKHEJ	1	V	Yes	[3]
	FEKHIN	1	V	Yes	[3]
	TIYYUX	2	CuNa	No	[4]

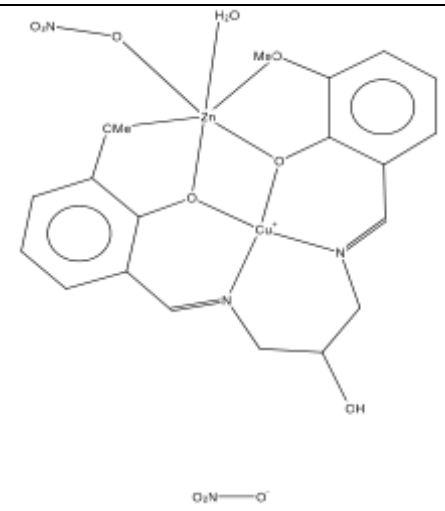
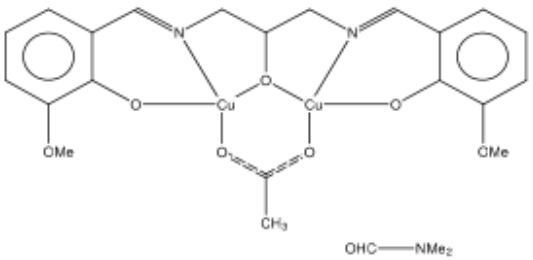
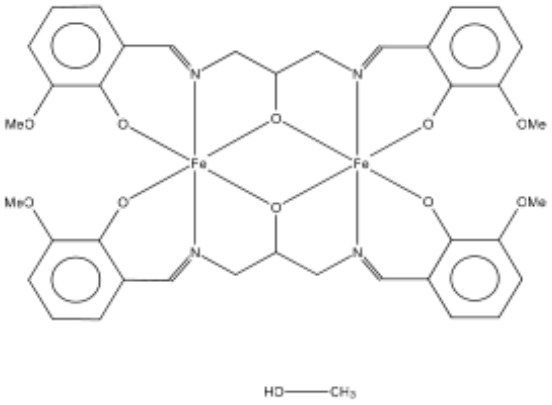
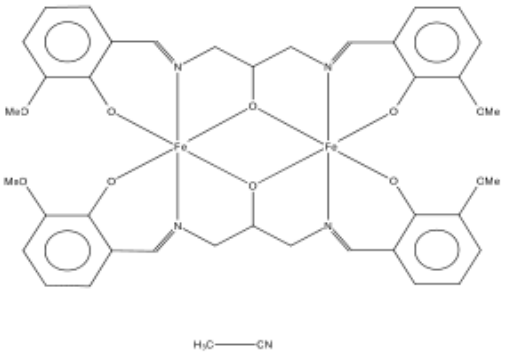
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	JAZFOI01	2	NiGd	No	[5]
	JAZFUO01	2	NiTb	No	[5]
	JAZGAV01	2	NiEu	No	[5]
	YECKOJ	2	NiTb	No	[5]

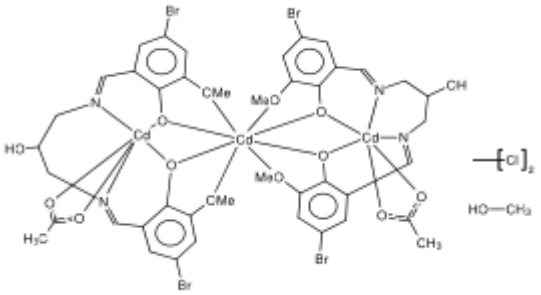
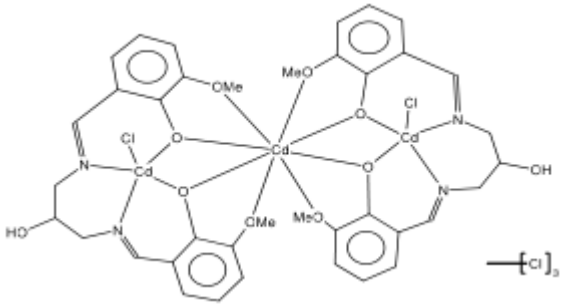
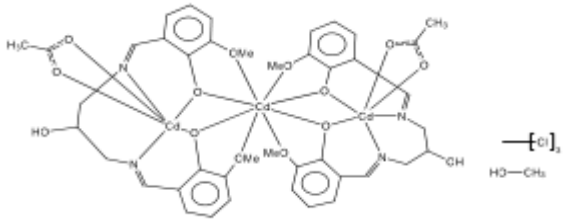
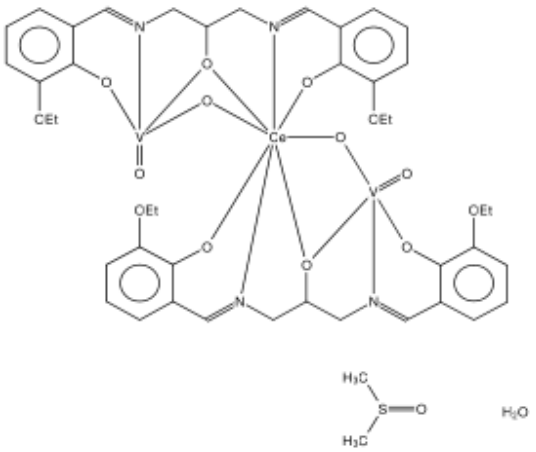
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	YECKUP	2	NiEu	No	[5]
	YECLAW	2	NiGd	No	[5]
	YECLEA	2	NiHo	No	[5]

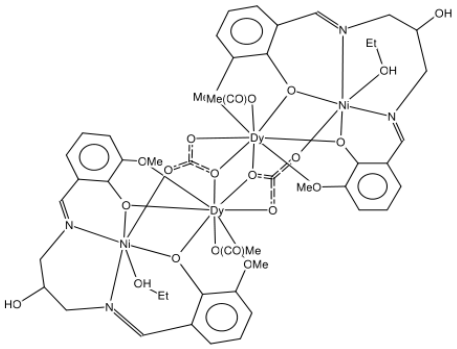
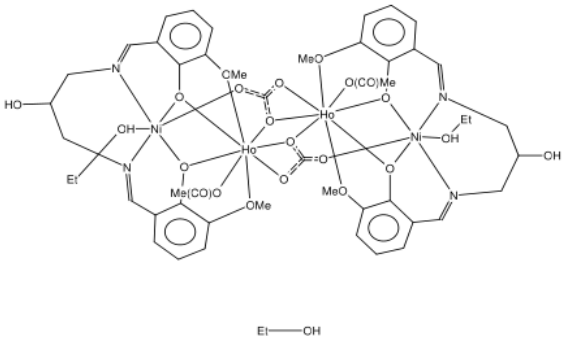
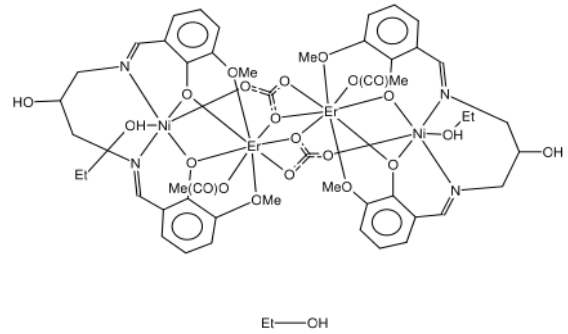
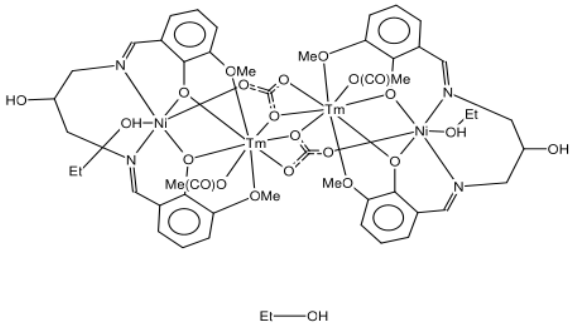
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	YECLIE	2	NiDy	No	[5]
	CANDUT	2	ZnTb	No	[6]
	YUFKUH	2	CoDy	Yes	[7]
	YUFWIH	2	CuDy	No	[7]

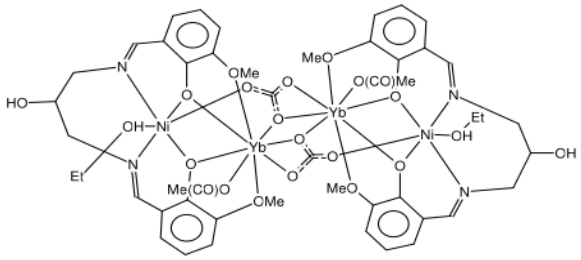
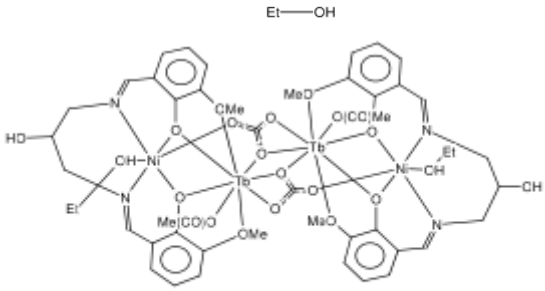
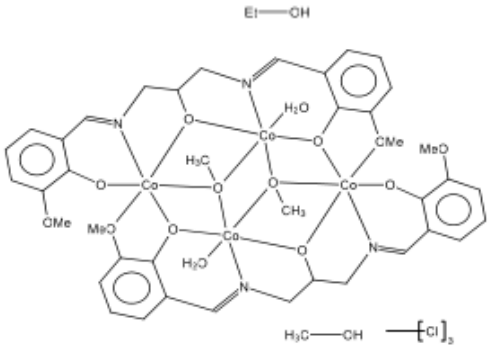
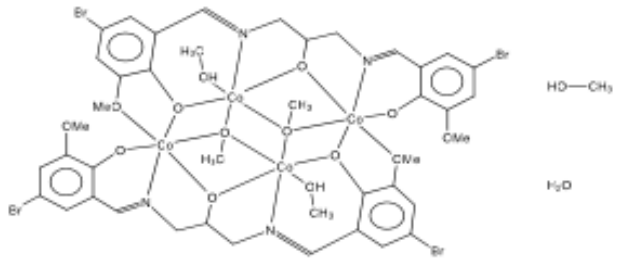
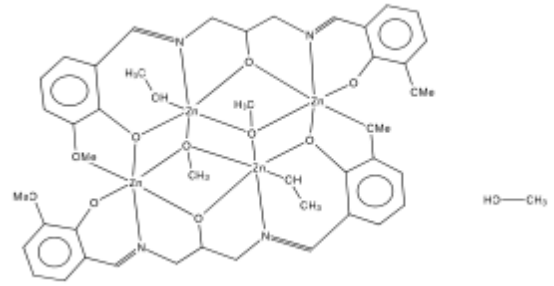
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	KEZYIZ	2	CuSm	No	[8]
	KEZYOF	2	CuHg	No	[8]
	KEZYUL	2	CuPb	No	[8]
	KEZZAS	2	CuCd	No	[8]

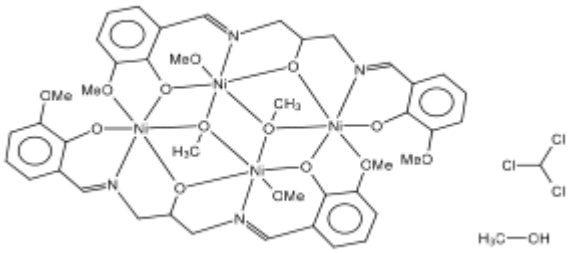
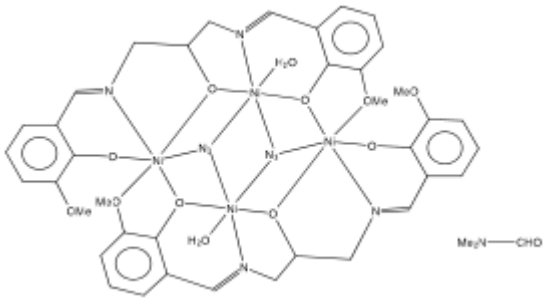
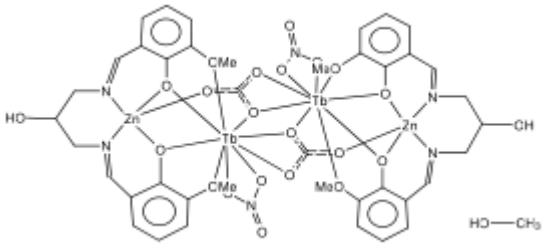
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	KEZZEW	2	CuBi	No	[8]
	LUXBOX	2	CuGd	No	[9]
	LUXBUD	2	CuTb	No	[9]
	LUXCAK	2	CuDy	No	[9]

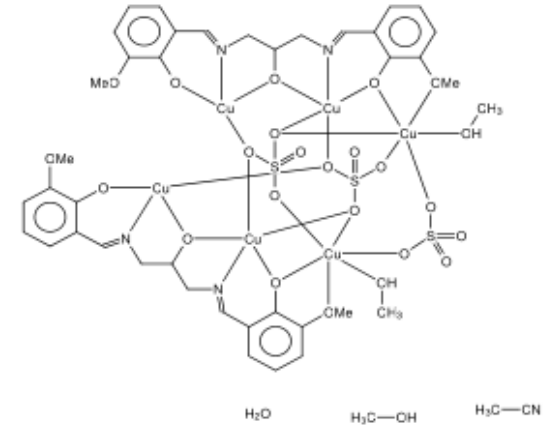
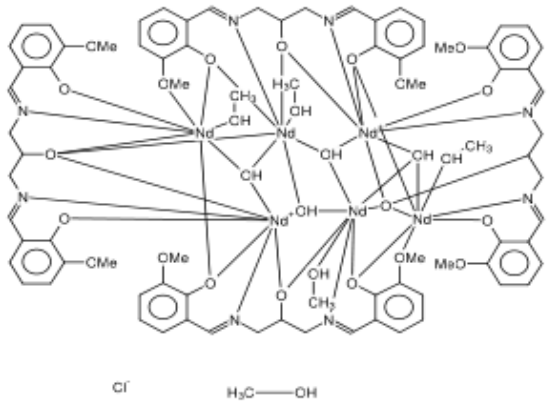
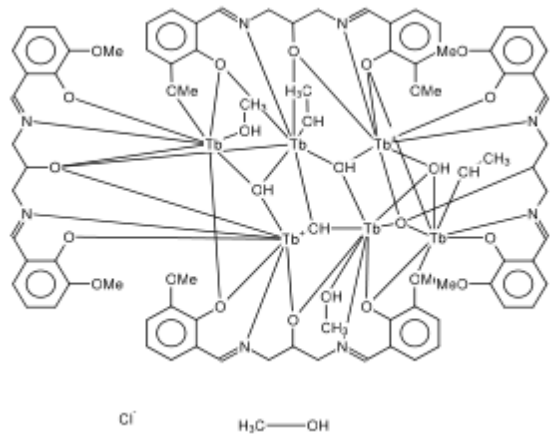
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	VEYLES	2	CuZn	No	[8]
	IWIHEB	2	Cu_2	Yes	[10]
	BOQLOJ	2	Fe_2	Yes	[11]
	RINXUJ	2	Fe_2	Yes	[12]

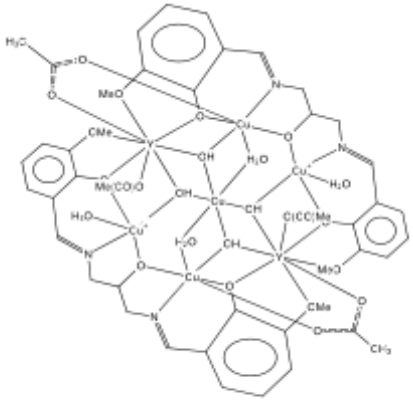
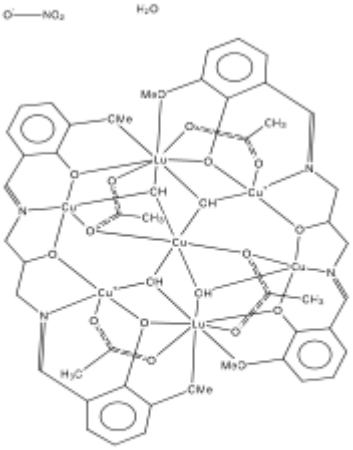
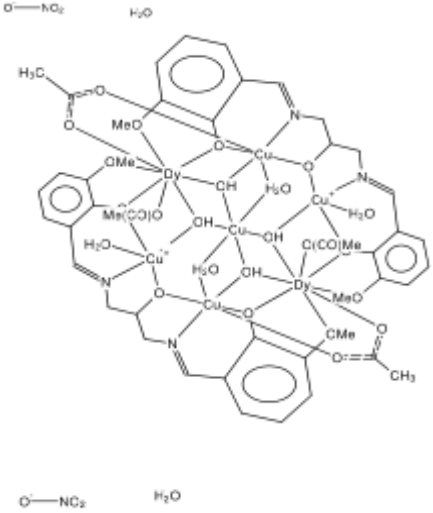
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	VEYLAO	2	CuNa	No	[8]
	ENICAH	3	Cd_3	No	[13]
	ENICEL	3	Cd_3	No	[13]
	ENICIP	3	Cd_3	No	[13]
	KEPQIG	3	V_2Ce	Yes	[14]

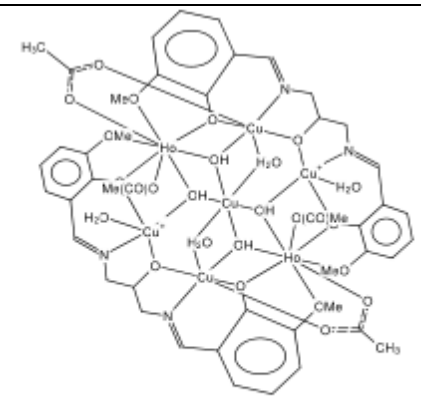
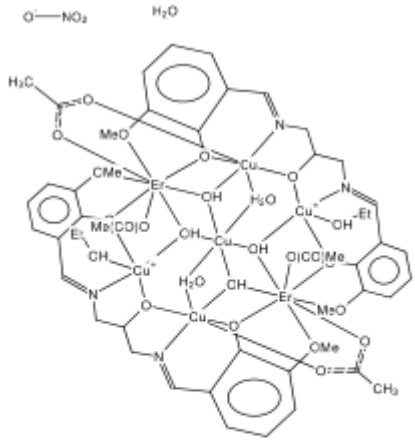
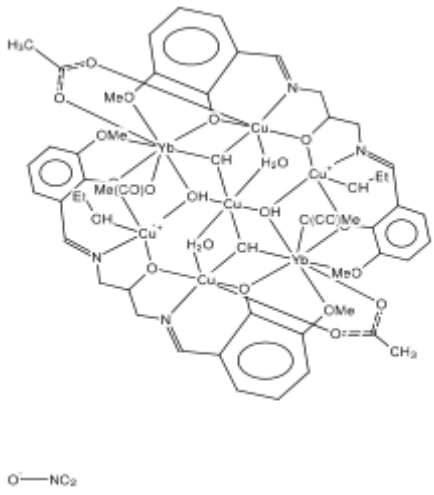
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	JASTUV01	4	Ni_2Dy_2	No	[5]
	YECJUO	4	Ni_2Ho_2	No	[5]
	YECKAV	4	Ni_2Er_2	No	[5]
	YECKEZ	4	Ni_2Tm_2	No	[5]

Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	YECKID	4	Ni_2Yb_2	No	[5]
	YECLOK	4	Ni_2Tb_2	No	[5]
	ENEZEE	4	Co_4	Yes	[13]
	ENEZOO	4	Co_4	Yes	[13]
	ENEZUU	4	Zn_4	Yes	[13]

Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	ENEZII	4	Ni_4	Yes	[13]
	ENICOV	4	Ni_4	Yes	[13]
	ENICUB	4	Ni_4	Yes	[13]
	XASDAZ	4	Zn_2Dy_2	No	[15]
	XASDED	4	Zn_2Tb_2	No	[15]
	XASDIH	4	Zn_2Eu_2	No	[15]

Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	BOQMEA	6	Cu_6	Yes	[11]
	DAVZOR	6	Nd_6	Yes	[16]
	DAVZUX	6	Tb_6	Yes	[16]

Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	CONZAI	7	Cu_5V_2	Yes	[17]
	CONZEM	7	Cu_5Lu_2	Yes	[17]
	CONZIQ	7	Cu_5Dy_2	Yes	[17]

Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	CONZOW	7	Cu_5Ho_2	Yes	[17]
	CONZUC	7	Cu_5Er_2	Yes	[17]
	COPBAM	7	Cu_5Yb_2	Yes	[17]

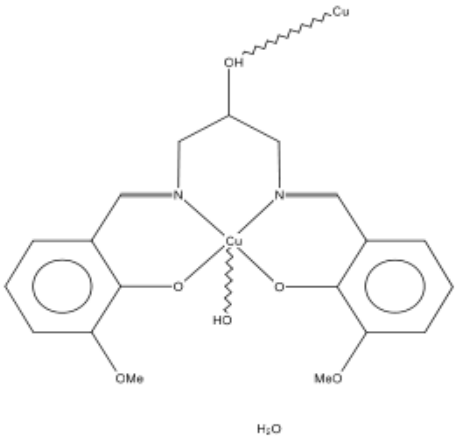
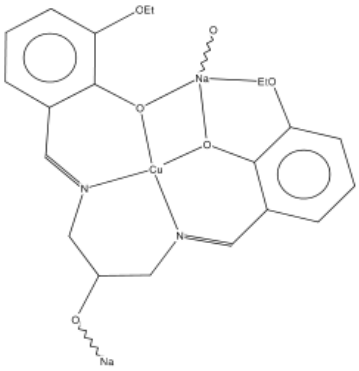
Structure	Refcode	Nuclearity	Metals	OH group[1]	Ref.
	REFJIX	Polymer	{Cu}$_n$	Yes	[18]
	CIKPAP	polymer	{CuNa}$_n$	Yes	[19]

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Table S2. Crystallographic data for complexes **1-5**.

Identification code	1	2	3	4	5
Empirical formula	$C_{42}H_{48}N_5O_{20}Br_4Zn_2Nd$	$C_{45}H_{54.67}N_5O_{20.33}Br_4Zn_2Sm$	$C_{42}H_{52.67}N_5O_{22.33}Br_4Zn_2Eu$	$C_{42}H_{52.67}N_5O_{22.33}Br_4Zn_2Tb$	$C_{42}H_{52.67}N_5O_{22.33}$ Br_4Zn_2Dy
Formula weight	1537.47	1591.07	1587.23	1594.19	1597.77
Temperature/K	293.0	120(1)	120(1)	293.0	120(1)
Crystal system	monoclinic	monoclinic	trigonal	trigonal	trigonal
Space group	$P2_1/n$	$P2_1/n$	$R\text{-}3c$	$R\text{-}3c$	$R\text{-}3c$
a/Å	9.9805(4)	10.2675(2)	19.8962(4)	20.0572(5)	19.8706(5)
b/Å	24.132(1)	23.8581(3)	19.8962(4)	20.0572(5)	19.8706(5)
c/Å	22.9091(7)	22.5353(3)	76.655(2)	76.388(3)	76.007(2)
α/°	90	90	90	90	90
β/°	91.55(1)	91.261(1)	90	90	90
γ/°	90	90	120	120	120
Volume/Å^3	5515.4(4)	5518.9(1)	26279.2(9)	26613(1)	25990(1)
Z	4	4	18	18	18
ρ_{calc}/ g/cm^3	1.852	1.915	1.7976	1.790	1.838
μ/mm^{-1}	4.763	12.967	12.414	4.765	11.701
F(000)	3020	3136.0	13720.0	14100.0	14118.0
Crystal size/mm^3	0.25 × 0.12 × 0.02	0.4 × 0.35 × 0.02	0.47 × 0.29 × 0.07	0.30 × 0.30 × 0.20	0.59 × 0.34 × 0.08
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range /°	5.3 to 50.48	7.42 to 152.88	8.88 to 135.34	4.8 to 50.48	8.9 to 135.36
Reflections collected	41616	38779	58409	70659	35163
Independent reflections	9953 [R_{int} = 0.0806, R_{sigma} = 0.0852]	11370 [R_{int} = 0.0548, R_{sigma} = 0.0444]	5291 [R_{int} = 0.1573, R_{sigma} = 0.0539]	5349 [R_{int} = 0.0860, R_{sigma} = 0.0376]	5229 [R_{int} = 0.0842, R_{sigma} = 0.0405]
Data/restr./parameters	9953/0/659	11370/0/699	5291/6/350	5349/6/352	5229/6/350
Goodness-of-fit on F^2	1.042	1.083	1.034	1.107	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0593, wR_2 = 0.1250	R_1 = 0.0481, wR_2 = 0.1314	R_1 = 0.0785, wR_2 = 0.2180	R_1 = 0.0561, wR_2 = 0.1505	R_1 = 0.0610, wR_2 = 0.1621
Final R indexes [all data]	R_1 = 0.1121, wR_2 = 0.1544	R_1 = 0.0540, wR_2 = 0.1384	R_1 = 0.0817, wR_2 = 0.2254	R_1 = 0.0789, wR_2 = 0.1704	R_1 = 0.0661, wR_2 = 0.1699
Larg. diff. peak/hole / e Å^{-3}	2.21/-1.72	2.29/-1.59	2.76/-1.73	2.08/-0.82	2.07/-1.24
CCDC No.	1849667	1849666	1849668	1849669	1849665

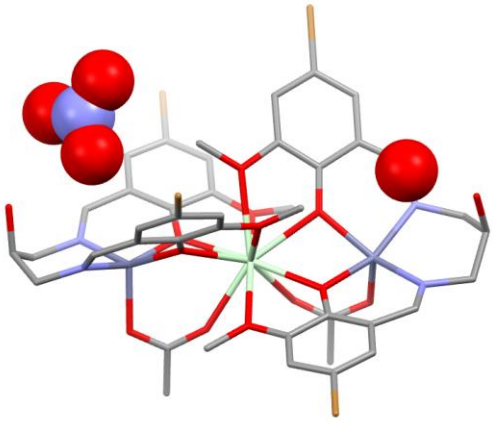

Figure S1. Location of hydrogen bonded NO_3^- anion and water molecule in pockets formed by 2-hydroxypropyl groups in complex Zn^{II}–Nd^{III}–Zn^{II} (**1**).

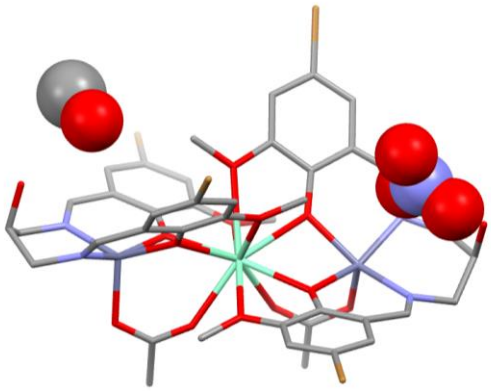

Figure S2. Location of hydrogen bonded NO_3^- anion and methanol molecule in pockets formed by 2-hydroxypropyl groups in complex Zn^{II}–Sm^{III}–Zn^{II} (**2**).

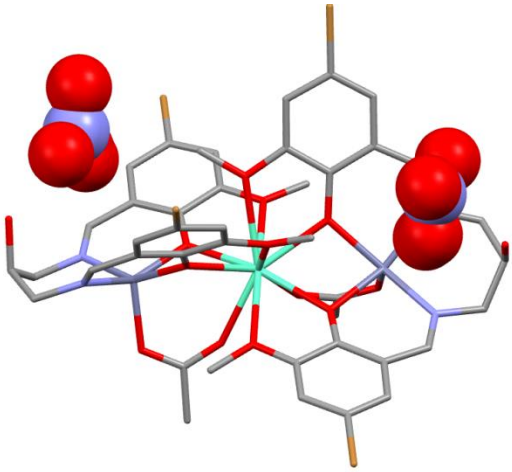

Figure S3. Location of disordered hydrogen bonded NO_3^- anion and water molecule in pockets formed by 2-hydroxypropyl groups in complex Zn^{II}–Eu^{III}–Zn^{II} (**3**).

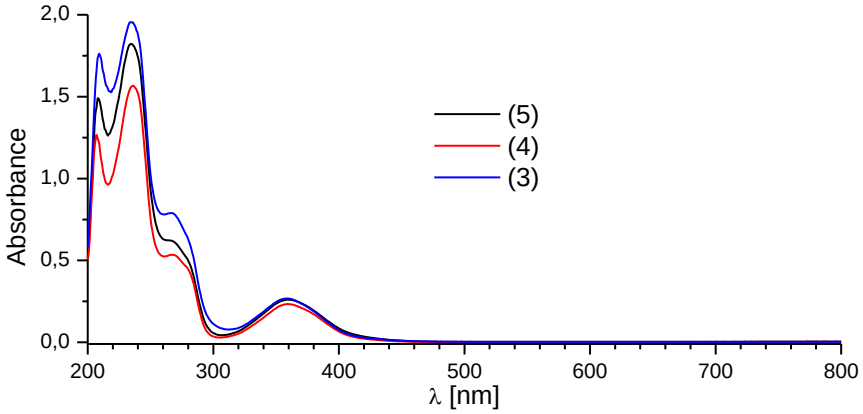

Figure S4. The absorbance spectra of compounds Zn^{II}–Eu^{III}–Zn^{II} (**3**), Zn^{II}–Tb^{III}–Zn^{II} (**4**) and Zn^{II}–Dy^{III}–Zn^{II} (**5**) in methanol solution (~$2 \cdot 10^{-5}$ M).

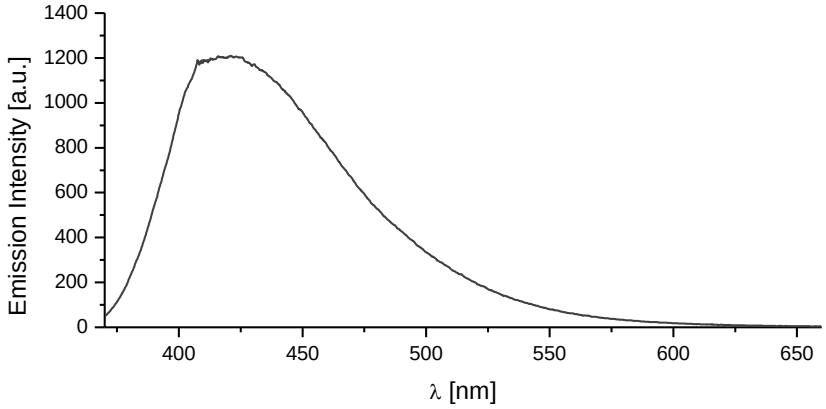

Figure S5. Luminescence spectrum of complex **1** (Zn^{II}–Nd^{III}–Zn^{II}) in methanol solution (~$2 \cdot 10^{-5}$ M).

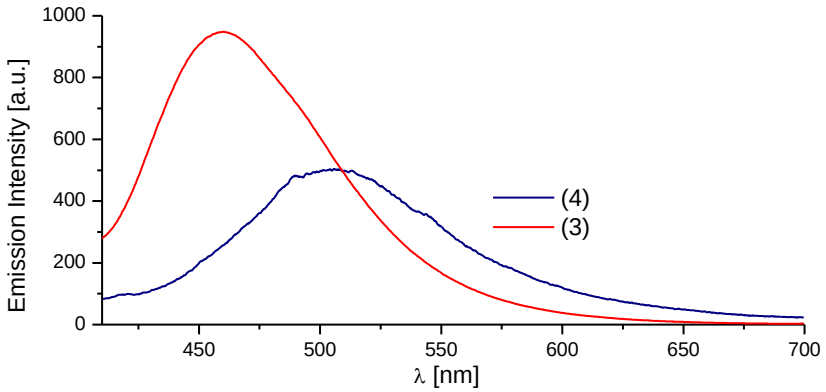

Figure S6. Solid state emission spectra of complexes **3** (Zn^{II}–Eu^{III}–Zn^{II}) and **4** (Zn^{II}–Tb^{III}–Zn^{II}).

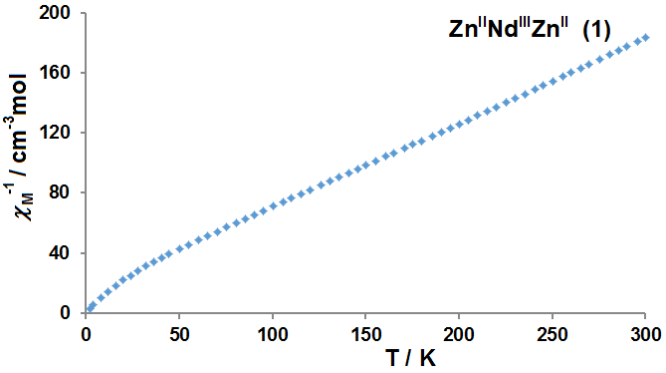

Figure S7. Temperature dependence of the experimental χ_M^{-1} versus T for Zn^{II}–Nd^{III}–Zn^{II} (**1**).

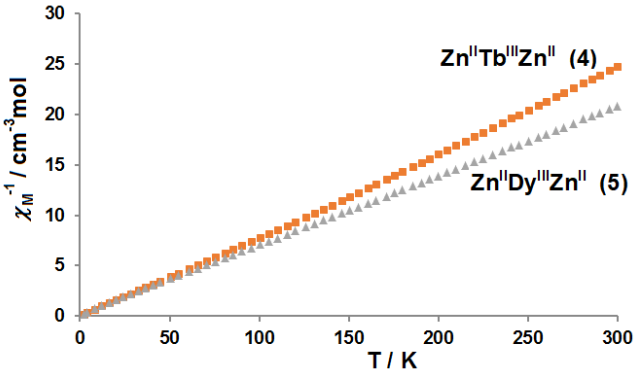

Figure S8. Temperature dependence of the experimental χ_M^{-1} versus T for Zn^{II}–Tb^{III}–Zn^{II} (**4**) and Zn^{II}–Dy^{III}–Zn^{II} (**5**).

Table S3. Theoretical and experimental values of the $\chi_M T$ product for compounds **1**, **4**, **5** at the room temperature.

Complex	**No. of *f* electrons**	**Ground state free ion symbol ($^{2S+1}L_J$)**	**g_{Ln}**	**$\chi_M T_{theor}$/ cm^{3}mol^{-1}K (Ln^{III})**	**$\chi_M T_{exp}$/ cm^{3}mol^{-1}K ($Zn^{II}_2Ln^{III}$)**
1 (Zn^{II}–Nd^{III}–Zn^{II})	3	$^4I_{9/2}$	8/11	1.64	1.62
4 (Zn^{II}–Tb^{III}–Zn^{II})	8	$^6F_6$	3/2	11.82	12.10
5 (Zn^{II}–Dy^{III}–Zn^{II})	9	$^4H_{15/2}$	4/3	14.17	14.39

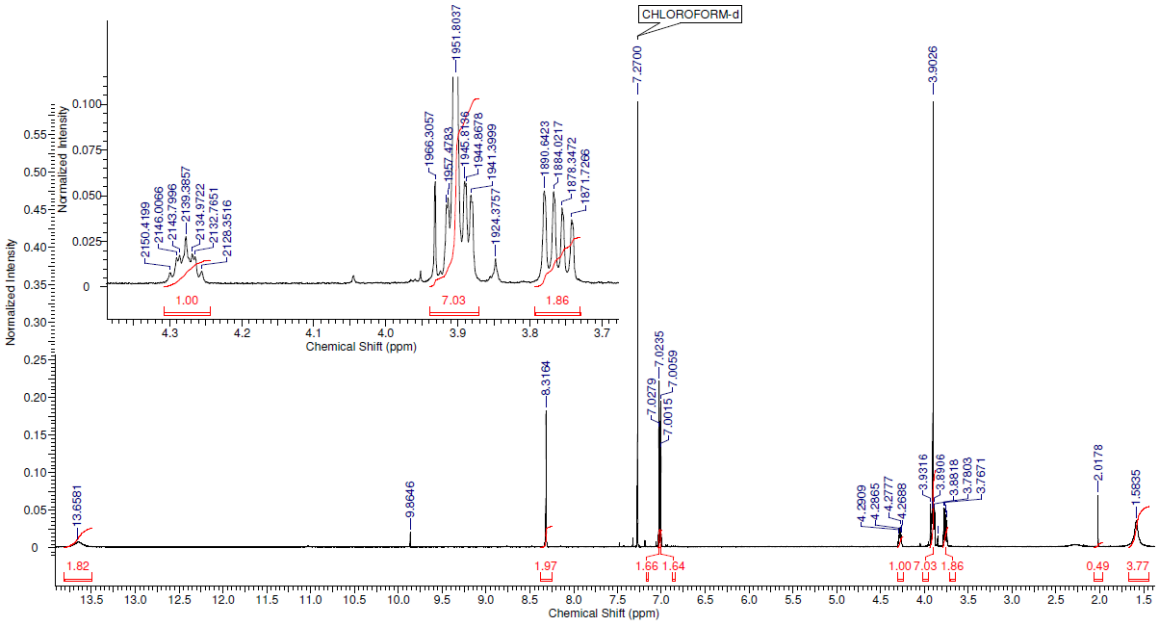

Figure S9. ^{1}H NMR spectrum of ligand **H$_3$L** in $CDCl_3$ solution.

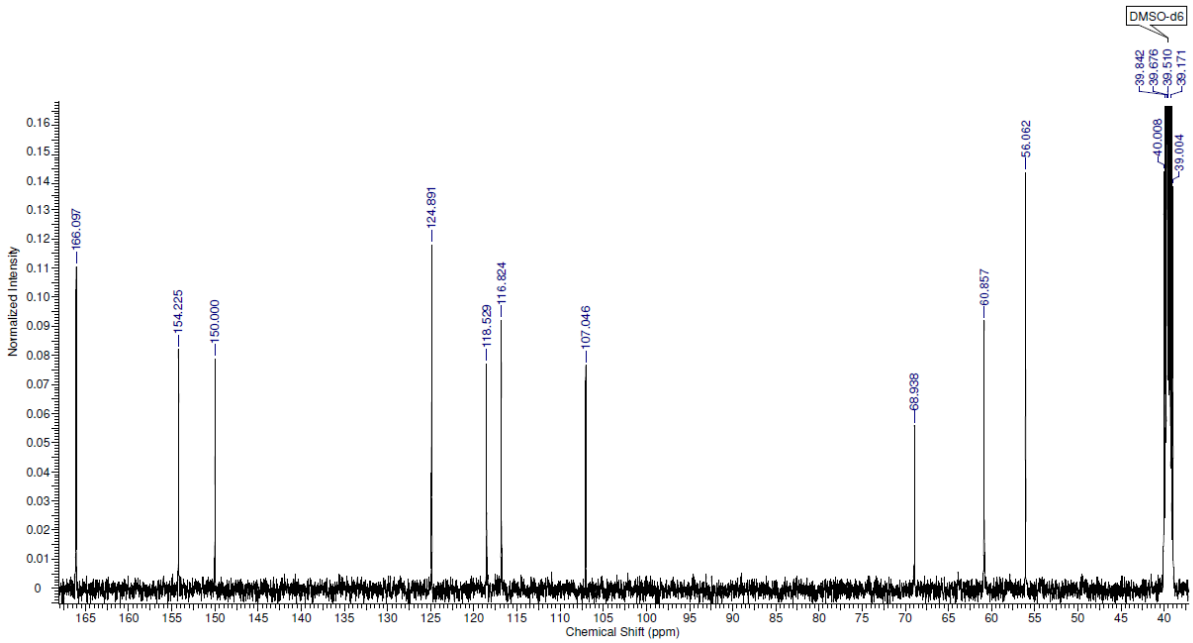

Figure S10. ^{13}C NMR spectrum of ligand **H$_3$L** in DMSO-d_6 solution.