Supporting Information

Four 3d-4f Heterometallic $Ln_{45}M_7$ Clusters Protected with Mixed Ligands

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Table S1. Crystal data and details of data collection and refinement for complexes **1**−**4**

Complex	**$Gd_{45}Co_7$ (1)**	**$Gd_{45}Ni_7$ (2)**	**$Dy_{45}Co_7$ (3)**	**$Dy_{45}Ni_7$ (4)**
formula	$C_{82}H_{416}Cl_{25}Co_7Gd_{45}O_{388}$	$C_{82}H_{416}Cl_{25}Ni_7Gd_{45}O_{388}$	$C_{82}H_{416}Cl_{25}Co_7Dy_{45}O_{388}$	$C_{82}H_{416}Cl_{25}Dy_{45}Ni_7O_{388}$
FW	15987.13	15985.59	16223.38	16221.84
Temperature/ K	133(2)	173(2)	173(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a /Å	31.5773(5)	31.6894(10)	31.4199(9)	31.3304(13)
b /Å	36.4648(5)	36.6432(15)	36.1969(8)	35.9748(10)
c /Å	38.7297(9)	39.6432(15)	39.2591(13)	39.1007(15)
β/°	107.410(2)	107.229(3)	107.313(3)	107.174(4)
V/Å^3	42552.7	43798(3)	42627(2)	42106(3)
Z	4	4	4	4
Dc/g cm^{-3}	2.495	2.424	2.528	2.559
μ/mm^{-1}	7.448	7.272	8.322	8.462
Data/parameters	74720/3557	76952/3449	74915/3566	73949/3547
θ/°	3.336 – 25.00	2.96 – 25.00	2.866 – 25.00	3.321 – 25.00
Observed reflections	204461	187030	192701	251651
F (000)	30024.0	30052.0	30384.0	30412.0
GOF	1.031	1.053	1.023	0.971
$R_1[I> 2\sigma(I)]$[a]	0.0835	0.1240	0.0873	0.1043
wR_2(All data)[b]	0.2517	0.3184	0.2611	0.3065

[a] $R_1 = \sum | |Fo| - |Fc| | / \sum |Fo|$ [b] $wR_2 = \{\sum [w (Fo^2 - Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/2}$

Table S2. Selected bonds of **1**.

Co1-O142	2.063(9)	Co4-O30	2.124(8)
Co1-O67	2.095(7)	Co4-O18	2.141(7)
Co1-O45	2.107(6)	Co4-O30W	2.165(9)
Co1-O68	2.117(9)	Co5-O55	2.031(6)
Co1-O47W	2.164(10)	Co5-O167	2.062(7)
Co1-O89	2.190(7)	Co5-O19	2.070(7)
Co2-O124	1.941(8)	Co5-O98	2.082(6)
Co2-O60	2.047(8)	Co5-O16	2.097(7)
Co2-O112	2.062(8)	Co5-O168	2.133(9)
Co2-O31	2.091(7)	Co6-O42	2.066(6)
Co2-O12	2.101(7)	Co6-O164	2.086(7)
Co2-O74	2.123(7)	Co6-O11	2.104(7)
Co3-O109	2.038(8)	Co6-O21	2.111(7)
Co3-O61	2.054(7)	Co6-O70W	2.126(9)
Co3-O69	2.117(5)	Co6-O101	2.127(7)
Co3-O28	2.130(6)	Co7-O77	2.058(9)
Co3-O25	2.131(7)	Co7-O103	2.069(7)
Co3-O127	2.135(8)	Co7-O40	2.097(5)
Co4-O140	2.038(6)	Co7-O43	2.099(7)
Co4-O46	2.055(6)	Co7-O32	2.106(6)
Co4-O78	2.112(6)	Co7-O92	2.107(7)
Gd1-O62	2.306(5)	Gd9-O52	2.370(6)
Gd2-O62	2.341(5)	Gd10-O82	2.440(6)
Gd3-O54	2.340(6)	Gd11-O22	2.344(6)
Gd4-O54	2.410(5)	Gd12-O64	2.314(6)
Gd5-O62	2.313(7)	Gd13-O54	2.481(7)
Gd6-O64	2.337(6)	Gd14-O84	2.399(6)
Gd7-O82	2.299(6)	Gd15-O66	2.443(8)
Gd8-O64	2.417(6)	Gd16-O48	2.344(5)

Table S3. Selected bonds of **2**.

Ni1-O142	2.040(18)	Ni4-O78	2.139(12)
Ni1-O67	2.082(15)	Ni5-O168	1.974(19)
Ni1-O45	2.105(13)	Ni5-O167	2.021(15)
Ni1-O89	2.138(13)	Ni5-O16	2.056(14)
Ni1-O47W	2.20(3)	Ni5-O55	2.060(11)
Ni1-O68	2.198(15)	Ni5-O98	2.089(13)
Ni2-O112	1.93(3)	Ni5-O19	2.125(14)
Ni2-O12	2.014(18)	Ni6-O164	2.076(17)
Ni2-O60	2.082(17)	Ni6-O101	2.079(15)
Ni2-O74	2.128(15)	Ni6-O21	2.090(16)
Ni2-O31	2.157(14)	Ni6-O11	2.094(13)
Ni2-Ni’	1.057(6)	Ni6-O5W	2.116(19)
Ni3-O25	1.970(13)	Ni6-O42	2.140(11)
Ni3-O61	1.974(12)	Ni7-O40	2.029(11)
Ni3-O127	2.018(11)	Ni7-O32	2.029(13)
Ni3-O109	2.05(2)	Ni7-O43	2.050(11)
Ni3-O69	2.143(14)	Ni7-O103	2.061(12)
Ni3-O28	2.154(14)	Ni7-O77	2.135(14)
Ni4-O140	2.006(14)	Ni7-O92	2.161(12)
Ni4-O46	2.020(11)	Ni’’-O127	1.452(13)
Ni4-O30	2.040(15)	Ni’’-O109	1.74(2)
Ni4-O18	2.129(13)	Ni’’-O69	2.229(14)
Ni4-O30W	2.139(17)	Ni’’-O28	2.247(15)
Gd1-O62	2.289(10)	Gd9-O52	2.288(13)
Gd2-O62	2.280(10)	Gd10-O83	2.384(14)
Gd3-O42	2.380(11)	Gd11-O44	2.417(12)
Gd4-O54	2.432(10)	Gd12-O64	2.271(11)
Gd5-O62	2.308(12)	Gd13-O54	2.437(12)
Gd6-O64	2.374(11)	Gd14-O49	2.453(13)

Table S4. Selected bonds of **3**.

Co1-O142	2.030(10)	Co4-O30	2.118(8)
Co1-O45	2.049(8)	Co4-O78	2.125(8)
Co1-O68	2.071(9)	Co4-O30W	2.174(9)
Co1-O89	2.124(9)	Co5-O167	2.037(9)
Co1-O67	2.143(9)	Co5-O55	2.065(8)
Co1-O47W	2.181(10)	Co5-O168	2.078(9)
Co2-O112	2.053(9)	Co5-O19	2.084(7)
Co2-O60	2.059(9)	Co5-O98	2.085(8)
Co2-O124	2.066(9)	Co5-O16	2.117(9)
Co2-O12	2.096(7)	Co6-O164	2.056(9)
Co2-O74	2.108(9)	Co6-O42	2.074(9)
Co2-O31	2.158(8)	Co6-O11	2.109(8)
Co3-O61	2.012(8)	Co6-O101	2.133(9)
Co3-O25	2.080(7)	Co6-O5W	2.139(10)
Co3-O109	2.096(9)	Co6-O21	2.148(9)
Co3-O69	2.101(8)	Co7-O32	2.051(7)
Co3-O127	2.136(9)	Co7-O40	2.055(6)
Co3-O28	2.141(8)	Co7-O103	2.074(8)
Co4-O46	2.032(8)	Co7-O43	2.076(8)
Co4-O140	2.037(9)	Co7-O92	2.078(9)
Co4-O18	2.107(8)	Co7-O77	2.094(9)
Dy1-O62	2.284(7)	Dy9-O52	2.287(8)
Dy2-O62	2.297(7)	Dy10-O82	2.396(8)
Dy3-O42	2.317(8)	Dy11-O44	2.406(7)
Dy4-O54	2.424(8)	Dy12-O84	2.301(8)
Dy5-O62	2.353(8)	Dy13-O44	2.321(8)
Dy6-O64	2.292(7)	Dy14-O84	2.392(8)
Dy7-O82	2.272(8)	Dy15-O66	2.392(8)
Dy8-O64	2.414(7)	Dy16-O48	2.309(8)

Table S5. Selected bonds of **4**.

Ni1-O142	2.013(11)	Ni4-O30	2.077(9)
Ni1-O45	2.017(8)	Ni4-O18	2.118(8)
Ni1-O68	2.036(9)	Ni4-O30W	2.118(11)
Ni1-67	2.055(8)	Ni5-O124	1.995(10)
Ni1-O47W	2.079(11)	Ni5-O112	2.031(9)
Ni1-O89	2.094(9)	Ni5-O12	2.047(8)
Ni2-O55	2.019(7)	Ni5-O60	2.052(8)
Ni2-O167	2.030(8)	Ni5-O31	2.082(8)
Ni2-O168	2.032(10)	Ni5-O74	2.084(9)
Ni2-O16	2.048(8)	Ni6-O32	2.004(7)
Ni2-O19	2.051(8)	Ni6-O40	2.028(7)
Ni2-O98	2.067(8)	Ni6-O77	2.055(11)
Ni3-O61	2.014(9)	Ni6-O92	2.059(9)
Ni3-O109	2.029(9)	Ni6-O43	2.059(9)
Ni3-O25	2.061(8)	Ni6-O103	2.090(8)
Ni3-O127	2.068(11)	Ni7-O42	2.032(9)
Ni3-O69	2.070(8)	Ni7-O169	2.057(10)
Ni3-O28	2.099(8)	Ni7-O11	2.061(9)
Ni4-O46	2.003(8)	Ni7-O164	2.077(10)
Ni4-O78	2.053(8)	Ni7-O21	2.097(9)
Ni4-O140	2.076(8)	Ni7-O101	2.122(9)
Dy1-O62	2.311(6)	Dy9-O52	2.290(8)
Dy2-O62	2.264(6)	Dy10-O82	2.411(8)
Dy3-O42	2.313(8)	Dy11-O44	2.395(8)
Dy4-O54	2.361(8)	Dy12-O64	2.276(8)
Dy5-O62	2.294(7)	Dy13-O44	2.315(8)
Dy6-O64	2.298(8)	Dy14-O84	2.392(8)
Dy7-O82	2.249(8)	Dy15-O18	2.377(8)
Dy8-O64	2.405(8)	Dy16-O48	2.336(7)

Table S5. Bond valence sum (BVS) calculations for Co ions in **1** and **3**.

	1	**3**
Co1	1.9269	2.0586
Co2	2.2934	2.1009
Co3	2.0426	2.0810
Co4	2.0188	2.0607
Co5	2.1610	2.1666
Co6	2.0206	1.9906
Co7	2.0977	2.2010

Table S6. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP–AES) for **1**-**4**.

Compounds	Ln : M	Ratio
1	Gd : Co	6.3
2	Gd : Ni	6.0
3	Dy : Co	6.2
4	Dy : Ni	6.1

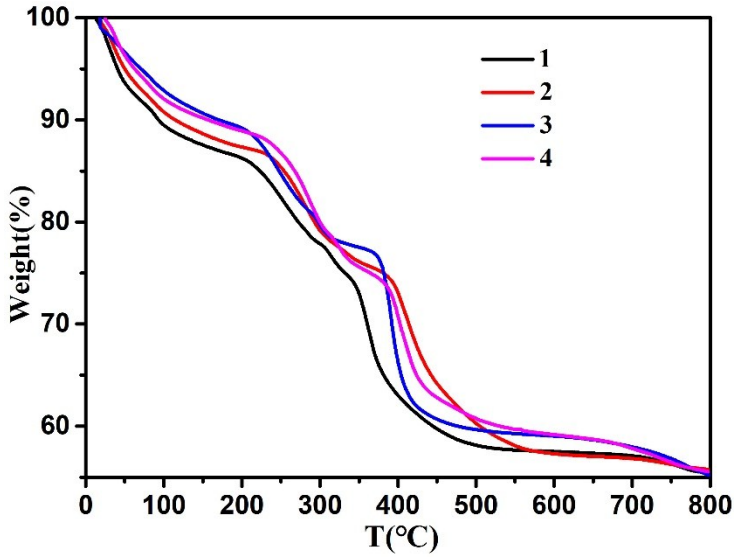

Figure S1. TG Curves for compounds **1-4**.

The TGA of compounds **1-4** were measured under atmosphere. As shown in Figure **S1**, the mass losses of **1-4** at about 210 °C are 13.8 %, 13.2 %, 12.1 % and 12.5 % respectively, which is close to the calculated value (13.3 – 13.5 %) to the removal of guest water molecular and coordination water molecular. When the temperature is higher than 220 °C, the metal frameworks of **1-4** are drastically collapsed. The final residues of **1-4** are about 55.6 %, which agree with calculated values (54.3 % – 55.4 %) based on Ln_2O_3 (Ln = Gd and Dy), NiO and Co_3O_4.

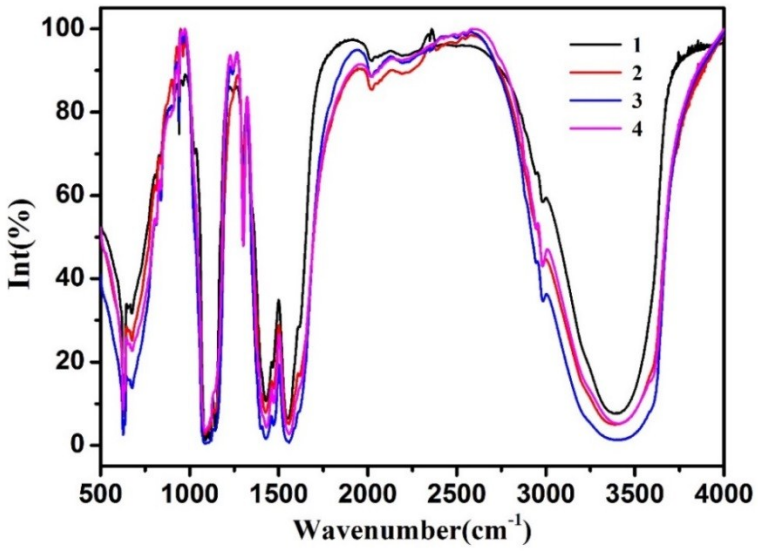

Figure S2. IR spectra in 500-4000 cm^{-1} for compounds **1-4**.