

Supporting Information

Tune the coordination behavior of an unexplored asymmetric multidentate ligand for developing diverse heterometallic architectures with luminescent and magnetic properties

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1. Materials and General Methods.

All chemicals were obtained from commercial vendors without further purification.

Elemental analyses of carbon, hydrogen and nitrogen were conducted on an Elementar Vario EL III analyzer. Infrared spectra ($4000\sim 400\text{ cm}^{-1}$) were obtained with KBr discs on a Thermo Mattson FTIR spectrometer. Thermogravimetric and differential thermal analysis experiments were performed using a TGA/NETZSCH STA449C instrument heated from $25\sim 650\text{ }^{\circ}\text{C}$ (heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$, nitrogen stream). X-ray powder diffraction (XRPD) patterns of the samples were recorded on a X-ray diffractometer (Rigaku D/Max 2200PC) in the 2θ range from 5° to 50° at room temperature. Simulation of the PXRD pattern was carried out with the single-crystal X-ray diffraction data (SXRD) using Mercury software (version: 3.10). Emission and excitation spectra in visible region were recorded with a Hitachi F-7000 spectrophotometer equipped with quartz cuvettes of 1 cm path length. Luminescence measurements were performed using a $2.5\text{ nm} \times 2.5\text{ nm}$ slit width. Luminescence measurements of NIR emission as well as lifetime measurements were carried out on an Edinburgh FLS920 phosphorimeter equipped with a continuous Xe-900 xenon lamp. The absolute emission quantum yields of the compounds were measured at room temperature using a calibrated integrating sphere as a sample chamber, and specpure BaSO_4 was used as a reflecting standard. Direct-current (dc) magnetic susceptibility measurements were carried out on a Quantum Design SQUID MPMS-XL 7 magnetometer operating between 2 and 300 K for dc applied fields at 1000 Oe. Field dependence of the magnetization at 2~10K magnetic susceptibility measurements on the polycrystalline samples were performed with the same magnetometer at different magnetic fields. The data were corrected for the magnetization of the sample holder and the diamagnetism of the constituent atoms using Pascal constants. All crystalline samples characterized by PXRD, TG, EA, IR, photoluminescence and magnetic studies were obtained from the same batch.

2. Synthesis of H_3L .

The ligand H_3L was prepared according to the procedures outlined in the literature using 2-hydroxy-1,3-propylenediamine to replace ethaneamine.¹ Yield: 76%. Melting point: $192\sim 194\text{ }^{\circ}\text{C}$. Elem anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_6$: C, 60.95; H, 5.92; N, 7.48. Found: C, 61.28; H, 5.96; N, 7.50. ^1H NMR (500 MHz, DMSO-d_6) δ 13.79 (s, 1H), 12.70 (s, 1H), 8.73 (t, $J = 5.4\text{ Hz}$, 1H), 8.06 (s, 1H), 7.49 – 7.43 (m, 1H), 7.02 (d, $J = 8.0\text{ Hz}$, 1H), 6.95 (d, $J = 7.9\text{ Hz}$, 2H), 6.77 (dt, $J = 9.3, 8.2\text{ Hz}$,

2H), 4.03 (d, $J = 5.0$ Hz, 1H), 3.83 (d, $J = 2.3$ Hz, 7H), 3.77 (dd, $J = 12.4, 4.0$ Hz, 1H), 3.64 – 3.51 (m, 2H), 3.44 – 3.34 (m, 1H). IR(KBr, ν , cm^{-1}): 3452(w), 1636(s), 1543(s), 1470(s), 1374(m), 1253 (m), 1087(m), 734 (m).

3. Synthesis of Zn_8Ln_2 : 0.1 mmol (37 mg) H_3L and 0.20 mmol NEt_3 (27 μL) were dissolved in 21 mL CH_3CN to obtain a clear yellow CH_3CN solution, then 0.1 mmol (18 mg) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was added to afford a pale yellow suspension. After further stirring for 2 hours, 7 mL CH_3OH was added dropwise to result a clear solution in which 0.1 mmol $\text{Ln}(\text{OAc})_3 \cdot 6\text{H}_2\text{O}$ was added. The mixture was stirred overnight, filtered into a sealed 10–20 mL glass vial and set aside for slow evaporation. After about one month, pale yellow single crystals suitable for crystal analysis were obtained which were collected by filtration, washed with cold methanol, and dried in the air.

$[\text{Zn}_8\text{Nd}_2\text{L}_2(\text{OH})_4(\text{OAc})_{12}] \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (Zn_8Nd_2) Yield: 55 mg, 45% based on H_3L . Elemental analysis for $\text{C}_{64}\text{H}_{90}\text{N}_4\text{Nd}_2\text{O}_{44}\text{Zn}_8$: Calcd.: C 31.62; H 3.73; N 2.30. Found: C 31.72, H 3.75, N 2.28. IR (KBr, ν , cm^{-1}): 3451 (m), 1602 (s), 1554 (s), 1444 (s), 1219 (s), 1081 (m), 852 (m), 742 (m).

$[\text{Zn}_8\text{Tb}_2\text{L}_2(\text{OH})_4(\text{OAc})_{12}] \cdot \text{CH}_3\text{OH} \cdot \text{CH}_3\text{CN}$ (Zn_8Tb_2) Yield: 60 mg, 49% based on H_3L . Elemental analysis for $\text{C}_{65}\text{H}_{85}\text{N}_5\text{O}_{41}\text{Tb}_2\text{Zn}_8$: Calcd.: C 32.08; H 3.52; N 2.88. Found: C 32.48, H 3.54, N 2.85. IR (KBr, ν , cm^{-1}): 3449 (m), 1597 (s), 1553 (s), 1443(s), 1219 (s), 1078 (m), 852 (m), 742 (m).

$[\text{Zn}_8\text{Dy}_2\text{L}_2(\text{OH})_4(\text{OAc})_{12}] \cdot \text{CH}_3\text{OH} \cdot \text{CH}_3\text{CN}$ (Zn_8Dy_2) Yield: 64 mg, 53% based on H_3L . Elemental analysis for $\text{C}_{65}\text{H}_{85}\text{Dy}_2\text{N}_4\text{O}_{41}\text{Zn}_8$: Calcd.: C 38.76; H 3.43; N 8.48. Found: C 38.58, H 3.42, N 8.50. IR (KBr, ν , cm^{-1}): 3449 (m), 1598 (s), 1553 (s), 1445(s), 1221 (s), 1080 (m), 853 (m), 744 (m).

$[\text{Zn}_8\text{Er}_2\text{L}_2(\text{OH})_4(\text{OAc})_{12}] \cdot 2\text{CH}_3\text{CN}$ (Zn_8Er_2) Yield: 62 mg, 51% based on H_3L . Elemental analysis for $\text{C}_{66}\text{H}_{84}\text{Er}_2\text{N}_6\text{O}_{39}\text{Zn}_8$: Calcd.: C 32.45; H 3.47; N 3.44. Found: C 32.48, H 3.46, N 3.42. IR (KBr, ν , cm^{-1}): 3449 (m), 1601 (s), 1553 (s), 1443 (s), 1223 (s), 1080 (m), 852 (m), 742 (m).

4. Synthesis of Ni_3Tb_2 A similar procedure as that for preparation of Zn_8Tb_2 was employed by replacing of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with $\text{Ni}(\text{OAc}) \cdot 2\text{H}_2\text{O}$. $[\text{Ni}_3\text{Tb}_2(\text{HL})_2(\text{OH})_2(\text{OAc})_6] \cdot 3\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, Yield: 52 mg, 58% based on H_3L . Elemental analysis for $\text{C}_{56}\text{H}_{71}\text{N}_7\text{Ni}_3\text{O}_{27}\text{Tb}_2$: Calcd.: C 38.04; H 4.05; N 5.55. Found: C 38.29, H 4.03, N 5.59. IR (KBr, ν , cm^{-1}): 3419 (m), 1624 (s), 1559 (s), 1454 (s), 1409 (s), 1313 (m), 1220 (m), 1073 (m), 853 (m), 744 (m).

5. Synthesis of Ni₂Tb₂: A similar procedure as that for preparation of Ni₃Tb₂ was adopted by using Tb(NO₃)₃·6H₂O as a lanthanide source. [Ni₂Tb₂(HL)₂(OAc)₄(NO₃)₂(H₂O)₂]₄·4CH₃CN·3H₂O, Yield: 40 mg, 45% based on H₃L. Elemental analysis for C₅₄H₇₄N₁₀Ni₂O₃₁Tb₂: calcd.: C 36.14, H 4.16, N 7.81, found: C 36.19, H 4.15, N 7.78. IR (KBr, ν, cm⁻¹): 3424 (m), 1627 (s), 1575 (s), 1476 (s), 1454 (s), 1409 (s), 1217 (s), 1070 (m), 1028 (m), 852 (m), 744 (m).

6. Details of Single Crystal X-ray Diffraction

X-ray Data Collection and Reduction. Suitable block crystals of Zn₈Nd₂, Zn₈Tb₂, Zn₈Dy₂, Zn₈Er₂, Ni₃Tb₂ and Ni₂Tb₂ were coated with perfluoropolyether oil before mounting. Intensity data for the aligned crystals of Zn₈Tb₂, Zn₈Dy₂, Zn₈Er₂, Ni₃Tb₂ and Ni₂Tb₂ were recorded at 293(2) K and that of Zn₈Nd₂ and Ni₃Tb₂ were recorded at 173 (2) K by employing a Bruker SMART APEX II CCD diffractometer. Mo Kα radiation (λ= 0.71073 Å) source were adopted for Zn₈Nd₂, Zn₈Tb₂, Zn₈Dy₂ and Ni₂Tb₂ and Cu Kα radiation (λ= 1.54184 Å) were used for Zn₈Er₂ and Ni₃Tb₂. No crystal decay was observed during the data collections. The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).²

Structure Solution and Refinement. The structures were solved by direct methods and refined on *F*² by a full-matrix least-squares procedure. SHELXL-2014/2016 was used for both structure solutions and refinements.³ The locations of the heaviest atoms were determined easily. The O, N, and C atoms were subsequently determined from the difference Fourier maps and refined anisotropically. The H atoms were incorporated at calculated positions and refined with fixed geometry and riding thermal parameters with respect to their carrier atoms. Crystallographic diagrams were drawn using the DIAMOND software package.⁴ Also severely disordered solvents molecules in Zn₈Tb₂, Zn₈Dy₂, Ni₃Tb₂ and Ni₂Tb₂ were removed by SQUEEZE during the structural refinements.⁵ For details about the squeezed material, see cif data in Supporting Information. Therefore, solvent molecules which were determined on the basis of elemental microanalysis, thermal analysis and the data treated with the SQUEEZE routine within PLATON were added to the molecular formula of Zn₈Tb₂, Zn₈Dy₂, Ni₃Tb₂ and Ni₂Tb₂ respectively.

Table S1. Selected bond lengths (Å) for **Zn₈Nd₂**, **Zn₈Tb₂**, **Zn₈Dy₂**, **Zn₈Er₂**, **Ni₃Tb₂** and **Ni₂Tb₂**.

[Zn₈Nd₂L₂(OH)₄(OAc)₁₂]·CH₃OH·H₂O (Zn₈Nd₂)									
Nd1–O1	2.714(4)	Nd1–O2	2.401(4)	Nd1–O4	2.431(4)	Nd1–O5	2.432(4)	Nd1–O7	2.515(3)
Nd1–O8	2.505(3)	Nd1–O13	1.595(4)	Nd1–O15	2.418(4)	Nd1–O17	2.419(3)	Zn1–O3	1.936(3)
Zn1–O7	1.940(3)	Zn1–O16	1.954(3)	Zn1–O19	2.024(3)	Zn2–N1	2.048(4)	Zn2–O2	2.034(3)
Zn2–O3	2.058(3)	Zn2–O7	2.018(3)	Zn2–O20	2.033(4)	Zn3–O5	2.023(4)	Zn3–O6	2.219(4)
Zn3–O8	2.040(3)	Zn3–O9	1.982(4)	Zn3–O14	1.962(4)	Zn4–O8	1.940(3)	Zn4–O10	1.986(4)
Zn4–O12	1.920(4)	Zn4–O18	1.939(4)						
[Zn₈Tb₂L₂(OH)₄(OAc)₁₂]·CH₃OH·CH₃CN (Zn₈Tb₂)									
Tb1–O1	2.715(6)	Tb1–O2	2.451(6)	Tb1–O4	2.470(5)	Tb1–O5	2.481(6)	Tb1–O10	2.474(6)
Tb1–O12	2.602(6)	Tb1–O17	2.469(6)	Tb1–O19	2.551(5)	Tb1–O20	2.572(5)	Zn1–O3	1.923(5)
Zn1–O7	2.012(5)	Zn1–O9	1.953(6)	Zn1–O20	1.937(5)	Zn2–N1	2.037(7)	Zn2–O2	2.032(5)
Zn2–O3	2.058(5)	Zn2–O8	2.027(6)	Zn2–O20	2.010(5)	Zn3–O5	2.012(5)	Zn3–O6	2.212(6)
Zn3–O11	1.960(6)	Zn3–O13	1.973(6)	Zn3–O19	2.030(5)	Zn4–O14	1.982(7)	Zn4–O16	1.917(6)
Zn4–O18	1.941(6)	Zn4–O19	1.929(6)						
[Zn₈Dy₂L₂(OH)₄(OAc)₁₂]·CH₃OH·CH₃CN (Zn₈Dy₂)									
Dy1–O1	2.715(5)	Dy1–O2	2.415(5)	Dy1–O4	2.444(5)	Dy1–O5	2.433(5)	Dy1–O10	2.438(5)
Dy1–O11	2.531(4)	Dy1–O13	2.632(5)	Dy1–O19	2.440(4)	Dy1–O20	2.527(4)	Zn1–O3	1.941(4)
Zn1–O8	2.017(5)	Zn1–O9	1.958(4)	Zn1–O11	1.950(4)	Zn2–N1	2.041(6)	Zn2–O2	2.041(4)
Zn2–O3	2.056(4)	Zn2–O7	2.036(5)	Zn2–O11	2.014(4)	Zn3–O5	2.032(5)	Zn3–O6	2.203(6)
Zn3–O12	1.964(6)	Zn3–O14	1.979(5)	Zn3–O20	2.030(5)	Zn4–O15	1.994(5)	Zn4–O16	1.933(5)
Zn4–O18	1.949(5)	Zn4–O20	1.947(4)						
[Zn₈Er₂L₂(OH)₄(OAc)₁₂]·2CH₃CN (Zn₈Er₂)									
Er1–O2	2.343(6)	Er1–O3	2.387(5)	Er1–O5	2.300(5)	Er1–O6	2.711(5)	Er1–O8	2.349(5)
Er1–O9	2.590(6)	Er1–O16	2.323(5)	Er1–O19	2.411(5)	Er1–O20	2.432(4)	Zn1–O1	2.247(7)
Zn1–O2	2.033(5)	Zn1–O10	1.953(6)	Zn1–O11	2.000(6)	Zn1–O19	2.062(5)	Zn2–N2	2.034(6)
Zn2–O4	2.057(4)	Zn2–O5	2.047(4)	Zn2–O7	2.053(5)	Zn2–O20	2.010(4)	Zn3–O12	1.990(8)
Zn3–O13	1.941(7)	Zn3–O15	1.954(7)	Zn3–O19	1.931(5)	Zn4–O4	1.923(4)	Zn4–O17	2.028(5)
Zn4–O18	1.965(5)	Zn4–O20	1.939(4)						
[Ni₃Tb₂(HL)₂(OH)₂(OAc)₆]·3CH₃CN·H₂O (Ni₃Tb₂)									
Tb1–O1	2.533(3)	Tb1–O2	2.292(3)	Tb1–O7	2.659(3)	Tb1–O8	2.309(3)	Tb1–O13	2.319(3)
Tb1–O15	2.311(3)	Tb1–O24	2.381(3)	Tb1–O25	2.357(3)	Tb2–O5	2.321(3)	Tb2–O6	2.648(3)
Tb2–O11	2.289(3)	Tb2–O12	2.616(3)	Tb2–O18	2.386(3)	Tb2–O20	2.286(3)	Tb2–O22	2.300(3)
Tb2–O26	2.348(3)	Ni1–N2	2.008(4)	Ni1–O4	2.103(3)	Ni1–O5	2.000(3)	Ni1–O19	2.108(3)
Ni1–O23	2.091(3)	Ni1–O26	2.018(3)	Ni2–O16	2.065(3)	Ni2–O18	2.115(3)	Ni2–O21	2.071(3)
Ni2–O24	2.125(3)	Ni2–O25	2.008(3)	Ni2–O26	2.001(3)	Ni3–N3	2.007(4)	Ni3–O8	2.004(3)
Ni3–O9	2.121(3)	Ni3–O14	2.104(3)	Ni3–O17	2.091(3)	Ni3–O25	2.010(3)		
[Ni₂Tb₂(HL)₂(OAc)₄(NO₃)₂(H₂O)₂]·4CH₃CN·3H₂O (Ni₂Tb₂)									
Tb1–O1	2.638(4)	Tb1–O2	2.297(4)	Tb1–O5	2.347(4)	Tb1–O6	2.498(4)	Tb1–O7	2.426(4)
Tb1–O8	2.402(4)	Tb1–O9	2.361(4)	Tb1–O11	2.456(5)	Tb1–O12	2.500(5)	Ni1–N1	2.042(5)
Ni1–O2	2.010(4)	Ni1–O4	2.030(4)	Ni1–O5	2.020(4)	Ni1–O10	2.101(4)	Ni1–O14	2.080(5)

Table S2 Shape calculation of Ln^{III} in **Zn₈Nd₂**, **Zn₈Tb₂**, **Zn₈Dy₂**, **Zn₈Er₂**, **Ni₃Tb₂** and **Ni₂Tb₂**.

	Zn₈Nd₂	Zn₈Tb₂	Zn₈Dy₂	Zn₈Er₂	Ni₃Tb₂	Ni₂Tb₂	
Enneagon (EP-9)	0.2010	0.1973	0.2007	0.2558	–	–	0.2203
Octagonal pyramid (OPY-9)	0.1318	0.1341	0.1329	0.1387	–	–	0.2112
Heptagonal bipyramid (HBPY-9)	0.2222	0.2273	0.2260	0.2146	–	–	0.2251
Johnson triangular cupola J3 (JTC-9)	0.1752	0.1727	0.1751	0.1771	–	–	0.1779
Capped cube J8 (JCCU-9)	0.1675	0.1669	0.1659	0.1628	–	–	0.1254
Spherical-relaxed capped cube (CCU-9)	0.1785	0.1786	0.1779	0.1641	–	–	0.1579
Capped square antiprism J10 (JCSAPR-9)	0.1138	0.1184	0.1168	0.0973	–	–	0.1427
Spherical capped square antiprism (CSAPR-9)	0.1074	0.1107	0.1096	0.0932	–	–	0.1675
Tricapped trigonal prism J51 (JTCTPR-9)	0.1098	0.1135	0.1104	0.0926	–	–	0.1496
Spherical tricapped trigonal prism (TCTPR-9)	0.1050	0.1079	0.1081	0.9790	–	–	0.1692
Tridiminished icosahedron J63 (JTDIC-9)	0.1762	0.1736	0.1760	0.1643	–	–	0.1899
Hula-hoop (HH-9)	0.1790	0.1806	0.1804	0.1686	–	–	0.1480
Muffin (MFF-9)	0.1007	0.1031	0.1024	0.0893	–	–	0.1534
Octagon (OP-8)	–	–	–	–	0.2259	0.2565	–
Heptagonal pyramid (HPY-8)	–	–	–	–	0.1882	0.2053	–
Hexagonal bipyramid (BPY-8)	–	–	–	–	0.1892	0.2016	–
Cube (CU-8)	–	–	–	–	0.1895	0.2004	–
Square antiprism (SAPR-8)	–	–	–	–	0.0778	0.0973	–
Triangular dodecahedron (TDD-8)	–	–	–	–	0.0793	0.0874	–
Johnson gyrobifastigium (JGBF-8)	–	–	–	–	0.1559	0.1774	–
Johnson elongated triangular bipyramid (JETBPY-8)	–	–	–	–	0.1947	0.2072	–
Biaugmented trigonal prism J50 (JBTPR-8)	–	–	–	–	0.0626	0.0693	–
Biaugmented trigonal prism (BTPR-8)	–	–	–	–	0.0764	0.0763	–
Snub diphenoid J84 (JSD-8)	–	–	–	–	0.0740	0.0886	–
Triakis tetrahedron (TT-8)	–	–	–	–	0.1907	0.2049	–
Elongated trigonal bipyramid (ETBPY-8)	–	–	–	–	0.1805	0.2260	–

Table S3. H-bond parameters in **Zn₈Nd₂**, **Ni₃Tb₂** and **Ni₂Tb₂**.

Complex	D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠D–H···A	Symmetry code
Zn₈Nd₂	N2–H2···O21	0.859(5)	2.008(1)	2.844(9)	164.43(2)	1-x, 2-y, 2-z
	O21–H21···O11	0.821(2)	1.909(3)	2.687(3)	157.70(6)	1-x, 1.5+y, 2.5-z
	O22–H22B···O11	0.875(3)	1.942(4)	2.799(2)	165.77(3)	1-x, 1.5+y, 2.5-z
	O22–H22B···O8	0.750(2)	2.006(7)	2.753(9)	173.97(0)	1-x, 1.5+y, 2.5-z
Ni₃Tb₂	O9–H9···O10	0.862(1)	1.948(3)	2.709(4)	146.49(4)	2-x, 1-y, 1-z
	O4–H4B···O3	0.887(8)	1.851(7)	2.696(2)	158.16(9)	1-x, -y, -z
	O27–H27B···O3	0.849(8)	2.237(4)	3.035(5)	156.45(9)	1-x, -y, -z
	O26–H26···O27	0.980(2)	2.044(3)	2.959(9)	154.69(4)	x, y, z
Ni₂Tb₂	N2–H2···O3	0.861(3)	2.068(8)	2.858(8)	152.20(2)	1-x, 1-y, 1-z
	O14–H14A···O15	0.855(3)	1.854(5)	2.687(6)	164.2(1)	1-x, 1-y, 1-z
	O15–H15A···O7	0.809(9)	1.996(1)	2.761(9)	157.50(6)	1-x, 1-y, 1-z
	O15–H15B···O8	0.819(6)	1.974(8)	2.787(2)	171.02(8)	-0.5+x, 1.5-y, 0.5+z

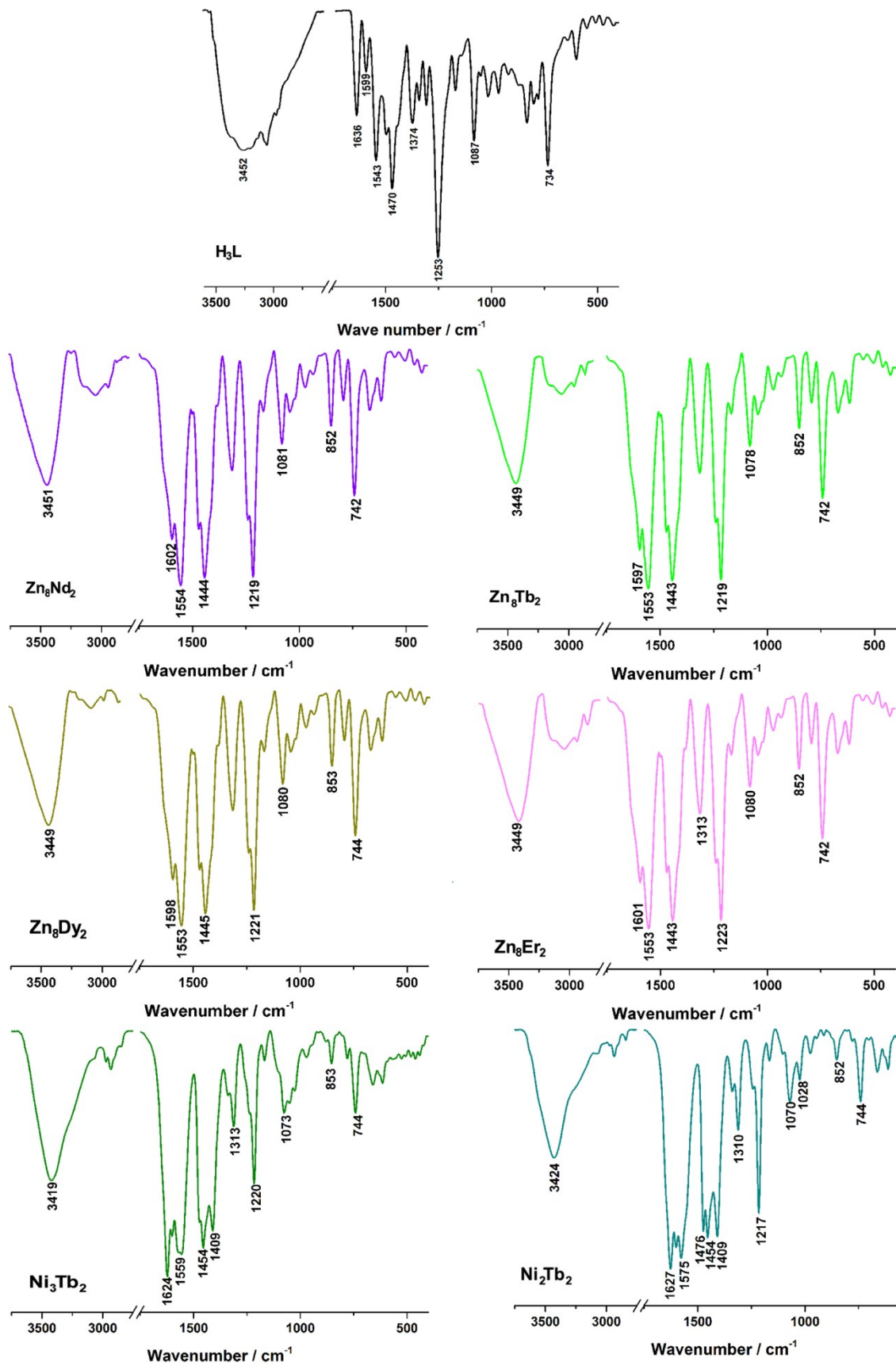


Figure S2. IR spectra of H_3L , Zn_8Nd_2 , Zn_8Tb_2 , Zn_8Dy_2 , Zn_8Er_2 , Ni_3Tb_2 and Ni_2Tb_2 in solid state.

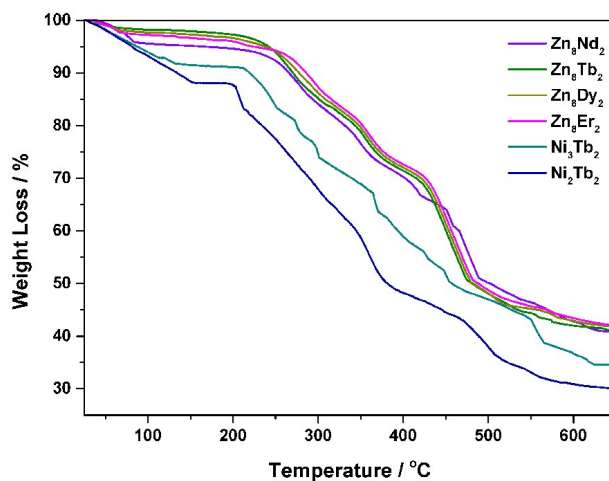


Figure S3. TGA curves of Zn_8Nd_2 , Zn_8Tb_2 , Zn_8Dy_2 , Zn_8Er_2 , Ni_3Tb_2 and Ni_2Tb_2 from 25 ~ 650 °C.

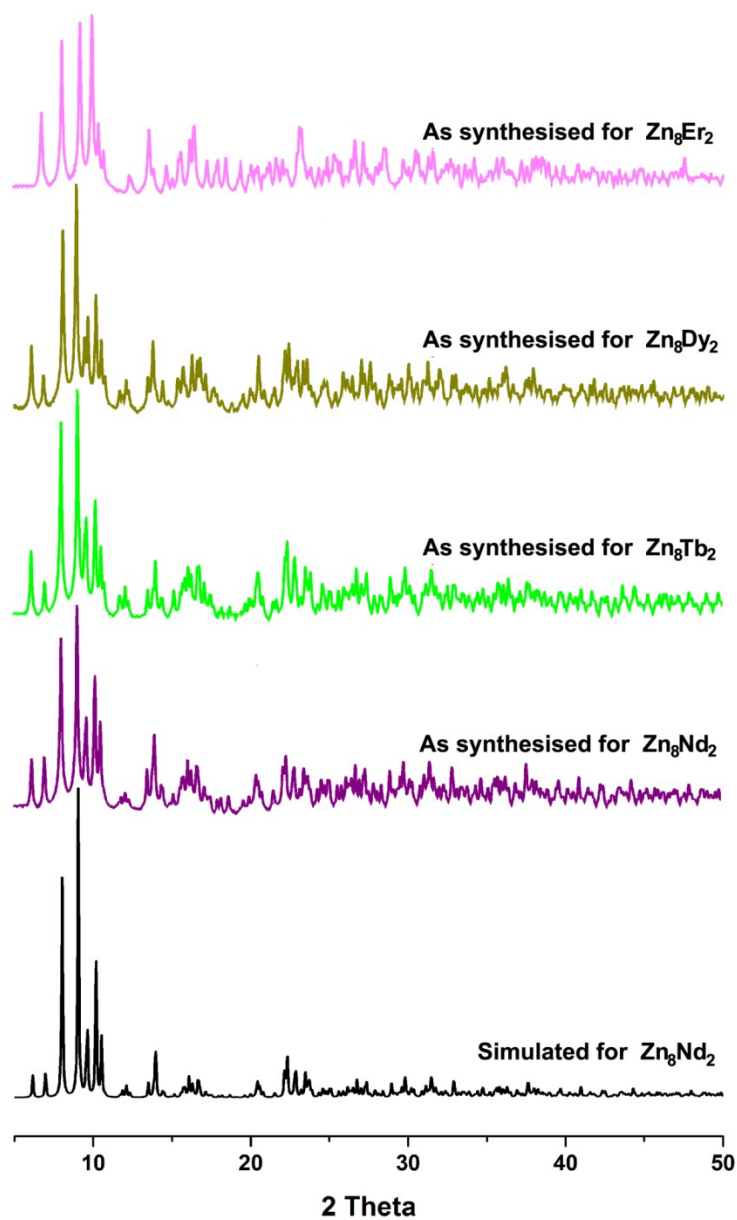


Figure S4. PXRD patterns of synthesized and simulated Zn_8Nd_2 , Zn_8Tb_2 , Zn_8Dy_2 and Zn_8Er_2 .

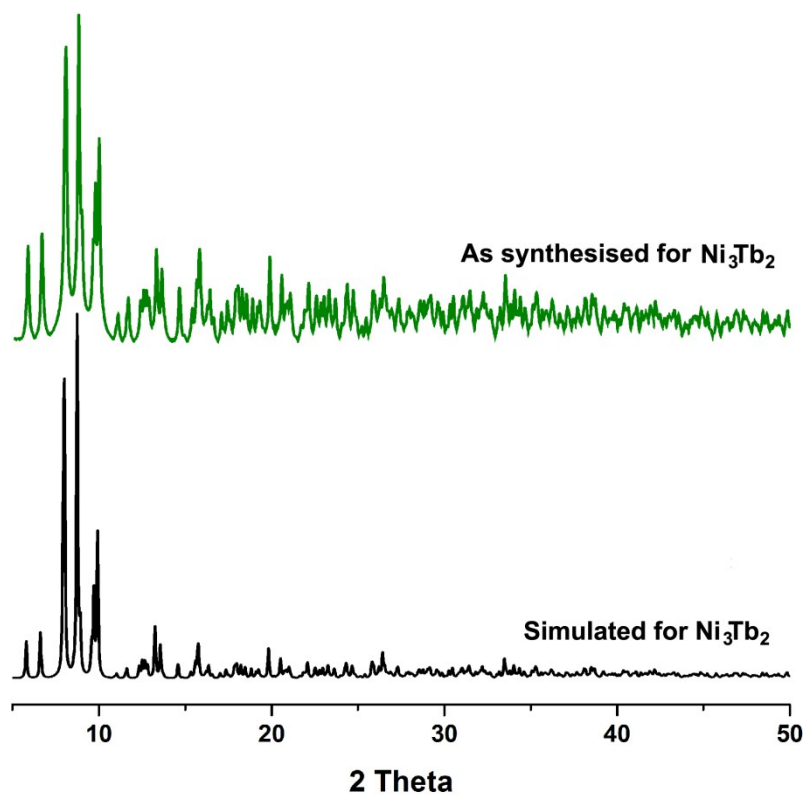


Figure S5. PXRD patterns of synthesized and simulated Ni_3Tb_2 .

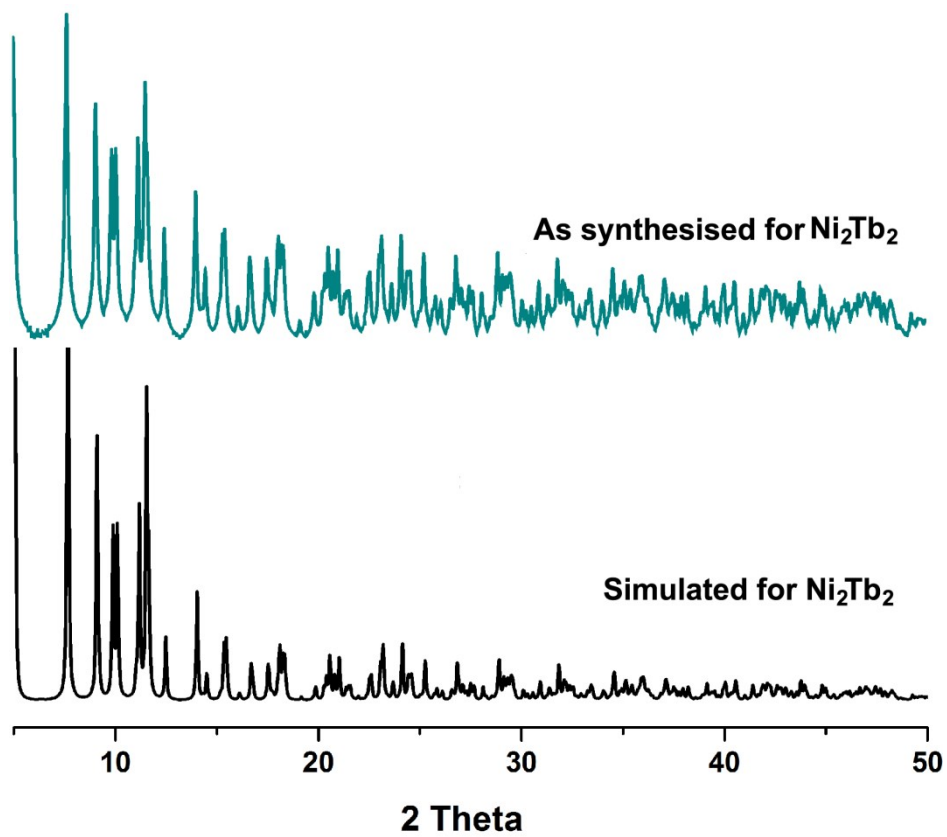


Figure S6. PXRD patterns of synthesized and simulated Ni_2Tb_2 .

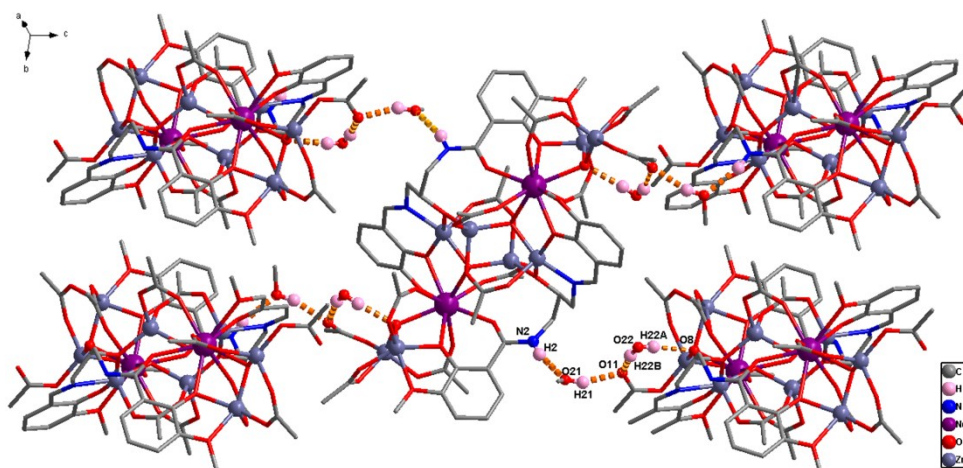


Figure S7 2D Supramolecular architecture of Zn_3Nd_2 constructed by intermolecular H-bond.

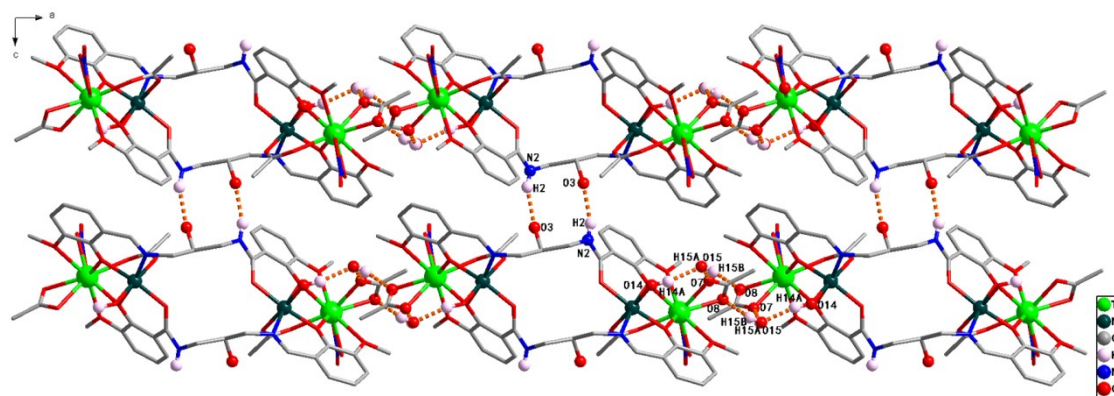


Figure S8 3D supramolecular network of Ni_2Tb_2 constructed by intermolecular H-bond viewing along b-axis.

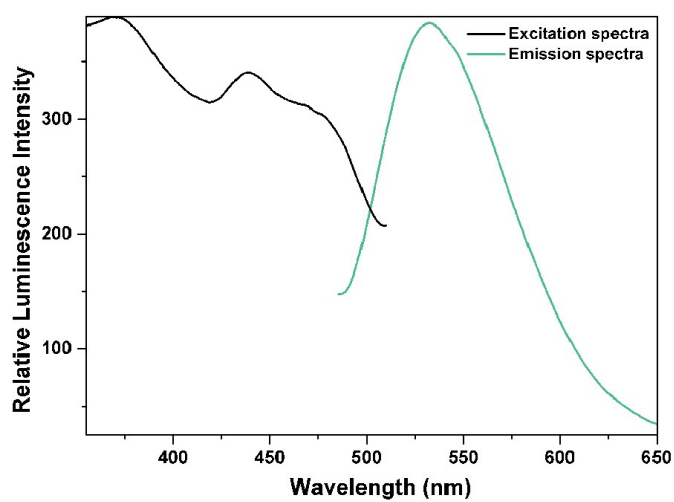


Figure S9 Excitation and emission spectra of H_3L in solid state.

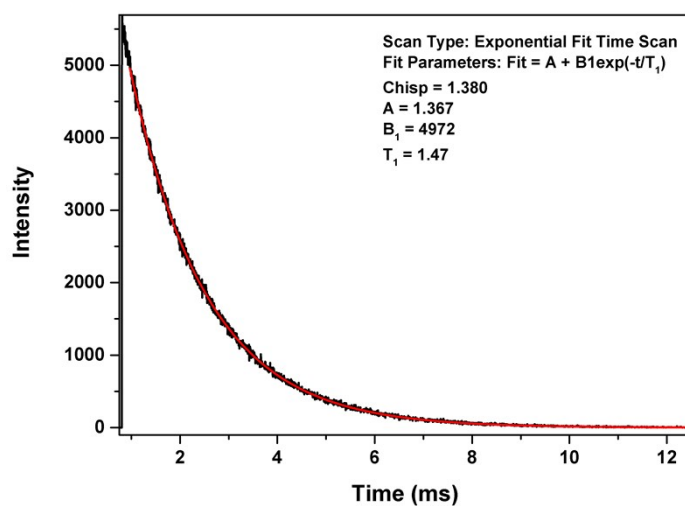


Figure S10 Emission intensity decay curves of Zn_8Tb_2 in solid state monitored at 546 nm.

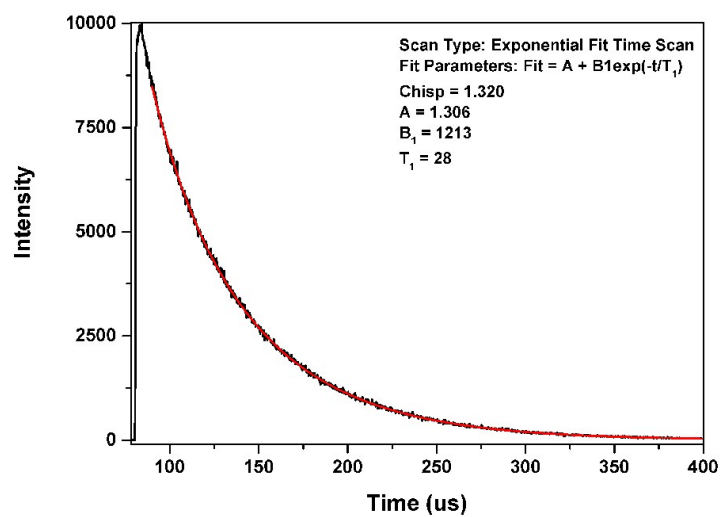


Figure S11 Emission intensity decay curves of Zn_8Dy_2 in solid state monitored at 484 nm.

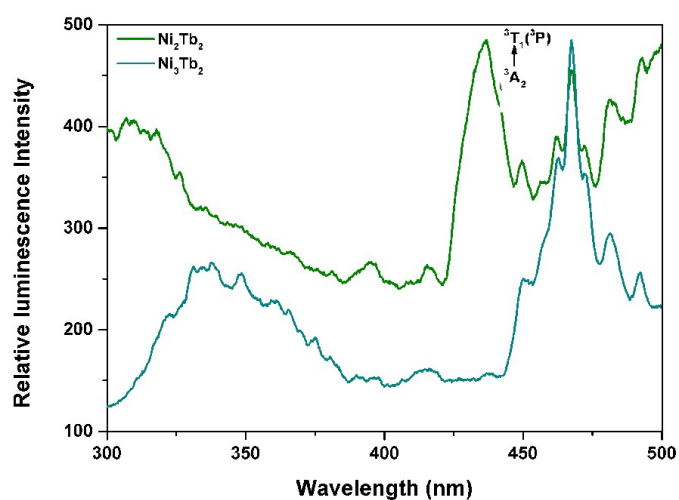


Figure S12 Excitation spectra of Ni_3Tb_2 and Ni_2Tb_2 monitored at 546 nm.

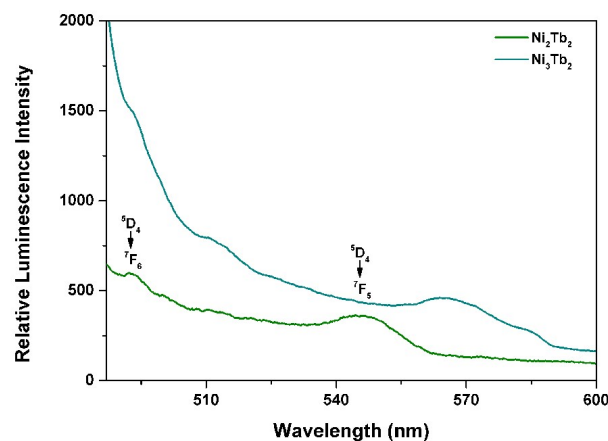


Figure S13 Emission spectra of Ni_3Tb_2 and Ni_2Tb_2 upon excited at 467nm.

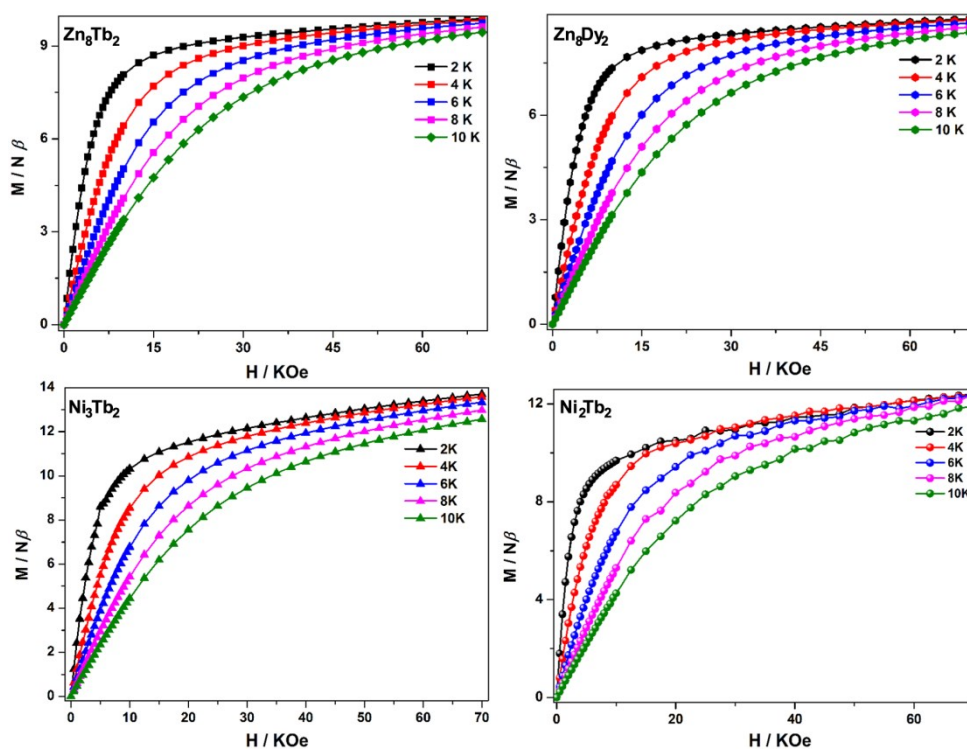


Figure S14 M-H curves of Zn_8Tb_2 , Zn_8Dy_2 , Ni_3Tb_2 and Ni_2Tb_2 .

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