

## Electronic Supplementary Information

Structural evolution from preorganized  
mononuclear triazamacrocyclic metalloligands to polynuclear  
metallo cages and heterometallic 2D layers: modular  
architectures, assembly tracking and magnetic properties

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## Experimental Section

### Materials and methods

The reagents and solvents used in the experiment were analytically pure without further purification. The azamacrocyclic ligand 1,4,7-triazacyclononane-1,4,7-tripropionic acid (**tacntpH<sub>3</sub>**) was synthesized according to our previously published method.<sup>[1]</sup> The C, H, N elemental analyses were conducted with a Vario Micro Cube elemental analyzer. The infrared spectrum data was recorded on a Nicolet 360 FT-IR infrared spectrometer in the spectral range of 400–4000 cm<sup>-1</sup>. Electrospray ionization mass spectrometry (ESI-MS) was determined from a Thermo Exactive Plus mass spectrometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2500V/PC X-ray powder diffractometer equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in the  $2\theta$  range 5° to 60°. The magnetic properties of compounds were measured on a Quantum Design MMPS-XL-7 SQUID magnetometer. Diamagnetic corrections for the sample and the sample holder were applied using Pascal's constants. Images of the transmission electron microscopy (TEM) were taken on an FEI Tecnai G2 F20 instrument with a STEM aberration corrector. Thermogravimetric data were obtained by Perkin Elmer Diamond TG/DTA thermal analyzer at a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere in the temperature range of 30 to 1000 °C.

### Crystal data collection and refinement

The Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used to collect single crystal data of the reported compounds except that no good-quality single crystals of **1-NiLa**, **1-NiYb**, **6-CoLa**, **6-CoEu** and **6-CoDy** were obtained for X-ray structural analysis. The original diffraction intensities were empirically corrected for absorption using the SADABS program, and the SAINT program was used to integrate the diffraction profile.<sup>[2–3]</sup> All crystal structures were analyzed by the direct method included in the SHELXTL software package, and refined with the SHELXL program.<sup>[4]</sup> The coordinates of all non-hydrogen atoms were located by successive difference Fourier syntheses and anisotropic refinement was performed. C-bound hydrogen atoms were placed in

calculated positions as riding atoms, and O-bound hydrogen atoms were placed in calculated positions and refined isotropically with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ . Supplementary crystallographic data for compounds **1-NiCe**, **2-Co**, **3-NiLa**, **3-NiCe**, **4-Ni**, **5-NiYb** and **6-CoTb** can be found in CCDC 2165408–2165414, respectively. The crystallographic data and structure refinement parameters for the selected six compounds were listed in Table S1. Selected bond lengths and bond angles for these compounds and selected hydrogen bond parameters for compounds **2-Co**, **3-NiLa** and **4-Ni** were presented in Tables S2 and S3, respectively.

### Synthesis of compounds

**(H<sub>3</sub>O<sup>+</sup>)[Ln<sup>III</sup>(H<sub>2</sub>O)<sub>8</sub>][Ni<sup>II</sup>(tacntp)]<sub>4</sub> (1-NiLn, Ln = La, Ce, Yb).** Compounds **1-NiLn** were achieved by a similar synthetic method except that different Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was applied in the assay. A typical preparation procedure for **1-NiCe** was as follows: Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.15 mmol, 0.055 g) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.038 mmol, 0.017 g) were dissolved in 5 mL distilled water, followed by the addition of an aqueous solution (2 mL) of **tacntpH<sub>3</sub>** (0.15 mmol, 0.052 g) under stirring. Upon mixing, the solution with a pH of 3 was transferred to a 25-mL Teflon-lined stainless steel autoclave and then placed in an oven kept at 120 °C for three days. After cooling, the solution was filtered under reduced pressure to give a clear lilac filtrate. The filtrate was kept stand at room temperature for open-air evaporation. Massive rhombus-shaped purple single crystals suitable for X-ray structural analysis were obtained after two weeks. Yield: 0.058 g (81% based on **tacntpH<sub>3</sub>**). Anal. Calcd. for C<sub>60</sub>H<sub>115</sub>CeN<sub>12</sub>Ni<sub>4</sub>O<sub>33</sub> (Found)%: C, 37.78(37.76); H, 6.08(6.09); N, 8.81(8.80). FT-IR (cm<sup>-1</sup>, KBr): 3432(s), 2982(w), 2860(w), 1584(s), 1401(m), 1331(s), 1122(s), 1100(m), 895(w), 780(w), 624(m).

**[Co<sup>III</sup>(tacntp)]·4H<sub>2</sub>O (2-Co).** 0.037 g Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.10 mmol) was dissolved in 2 mL distilled water, then mixed with 2 mL aqueous solution of **tacntpH<sub>3</sub>** (0.10 mmol, 0.035 g) under stirring. Subsequently solid K<sub>2</sub>CO<sub>3</sub> was added to adjust the pH to 4–5. The mixture was then transferred to a 50 mL round-bottom flask and heated at

80 °C for 4 h to obtain a purplish red solution. Hexagonal plate-like purplish red single crystals were obtained after evaporating the solution for five days at room temperature. Yield: 0.031 g (67% based on **tacntpH<sub>3</sub>**). Anal. Calcd. for C<sub>15</sub>H<sub>32</sub>CoN<sub>3</sub>O<sub>10</sub> (Found)%: C, 38.06(38.45); H, 6.81(6.64); N, 8.88(9.19). FT-IR (cm<sup>-1</sup>, KBr): 3419(s), 2992(w), 1614(s), 1586(s), 1468(m), 1389(s), 1328(m), 1086(m), 901(w), 793(m), 630(m).

**[Ni<sup>II</sup><sub>5</sub>(tacntp)<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>][Ln<sup>III</sup>(NO<sub>3</sub>)<sub>6</sub>]Cl·2H<sub>2</sub>O (3-NiLn, Ln = La, Ce).** Two compounds were prepared by a similar procedure and only the preparation of **3-NiLa** was described: **1-NiLa** (0.020 mmol, 0.038 g) was dissolved in 2 mL distilled water, then aqueous solution (2 mL) of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.15 mmol, 0.065 g) was added slowly under stirring followed by the pH was adjusted to 2 using aqueous HCl (0.1 M). After a thorough mixing, the above solution was transferred to a stainless steel autoclave and kept at 160 °C for three days. A dark yellow filtrate was obtained after cooling and filtration, which was subject to evaporation at room temperature for two weeks to give a mass of regular hexagonal plate-like light purple single crystals. Yield: 0.026g (36% based on **1-NiLa**). Anal. Calcd. for C<sub>30</sub>H<sub>76</sub>ClLaN<sub>12</sub>Ni<sub>5</sub>O<sub>44</sub> (Found)%: C, 20.28(20.24); H, 4.31(4.30); N, 9.46(9.44). FT-IR (cm<sup>-1</sup>, KBr): 3439(s), 2866(w), 1632(w), 1563(s), 1440(s), 1385(m), 1322(s), 1098(m), 819(w), 698(m), 634(m).

**[Ni<sup>II</sup><sub>9</sub>(tacntp)<sub>4</sub>(H<sub>2</sub>O)<sub>18</sub>](ClO<sub>4</sub>)<sub>6</sub>·10H<sub>2</sub>O (4-Ni).** **1-NiCe** (0.020 mmol, 0.038 g) and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.15 mmol, 0.055 g) were mixed in 5 mL of distilled water under stirring and pH was maintained at 3. The mixture solution was then transferred to a stainless steel autoclave and then placed in an oven kept at 160 °C for five days. After cooling, a purple solid was filtered and the light purple filtrate was allowed to stand at ambient temperature to evaporate the solvent. Two weeks later, massive rectangular block-like purple single crystals were yielded and collected. Yield: 0.019 g (31% based on **1-NiCe**). Anal. Calcd. for C<sub>60</sub>H<sub>152</sub>Cl<sub>6</sub>N<sub>12</sub>Ni<sub>9</sub>O<sub>76</sub> (Found)%: C, 24.03(23.84); H, 5.11(5.12); N, 5.60(5.80). FT-IR (cm<sup>-1</sup>, KBr): 3438(s), 2925(w), 2849 (w), 1642(w), 1562(s), 1441(m), 1337(w), 1285(s), 1107(s), 838(w), 698(w), 628(m).

$(\text{H}_3\text{O}^+)[\text{Ni}^{\text{II}}_2\text{Yb}^{\text{III}}(\text{tacntp})_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$  (**5-NiYb**). **1-NiYb** (0.020 mmol, 0.038 g) was dissolved in 5 mL distilled water, followed by the addition of  $\text{Yb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (0.10 mmol, 0.045 g). Under violent stirring, the pH value of the mixture was adjusted to 5–6 by 0.1 M aqueous NaOH solution. After a further stirring for 10 minutes, the solution was transferred to a stainless steel autoclave and reacted at 160 °C for three days. After cooling and filtration, a brownish yellow filtrate was obtained and evaporated at room temperature for two weeks to yield regular hexagonal plate-like purple single crystals. Yield: 0.014 g (29% based on **1-NiYb**). Anal. Calcd. for  $\text{C}_{30}\text{H}_{57}\text{Cl}_2\text{N}_6\text{Ni}_2\text{O}_{24}\text{Yb}$  (Found)%: C, 28.89(28.90); H, 4.61(4.45); N, 6.74(6.73). FT-IR ( $\text{cm}^{-1}$ , KBr): 3446(s), 2933(w), 2861(w), 1632(m), 1562(m), 1444(m), 1333(w), 1292(w), 1092(s), 825(w), 702(w), 618(m).

During the preparation of **5-NiYb**, if  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was used to replace  $\text{Yb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ , an isomorphous compound

$(\text{H}_3\text{O}^+)[\text{Ni}^{\text{II}}_2\text{Yb}^{\text{III}}(\text{tacntp})_2](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (denoted as **5-NiYb-NO<sub>3</sub>**) was acquired.

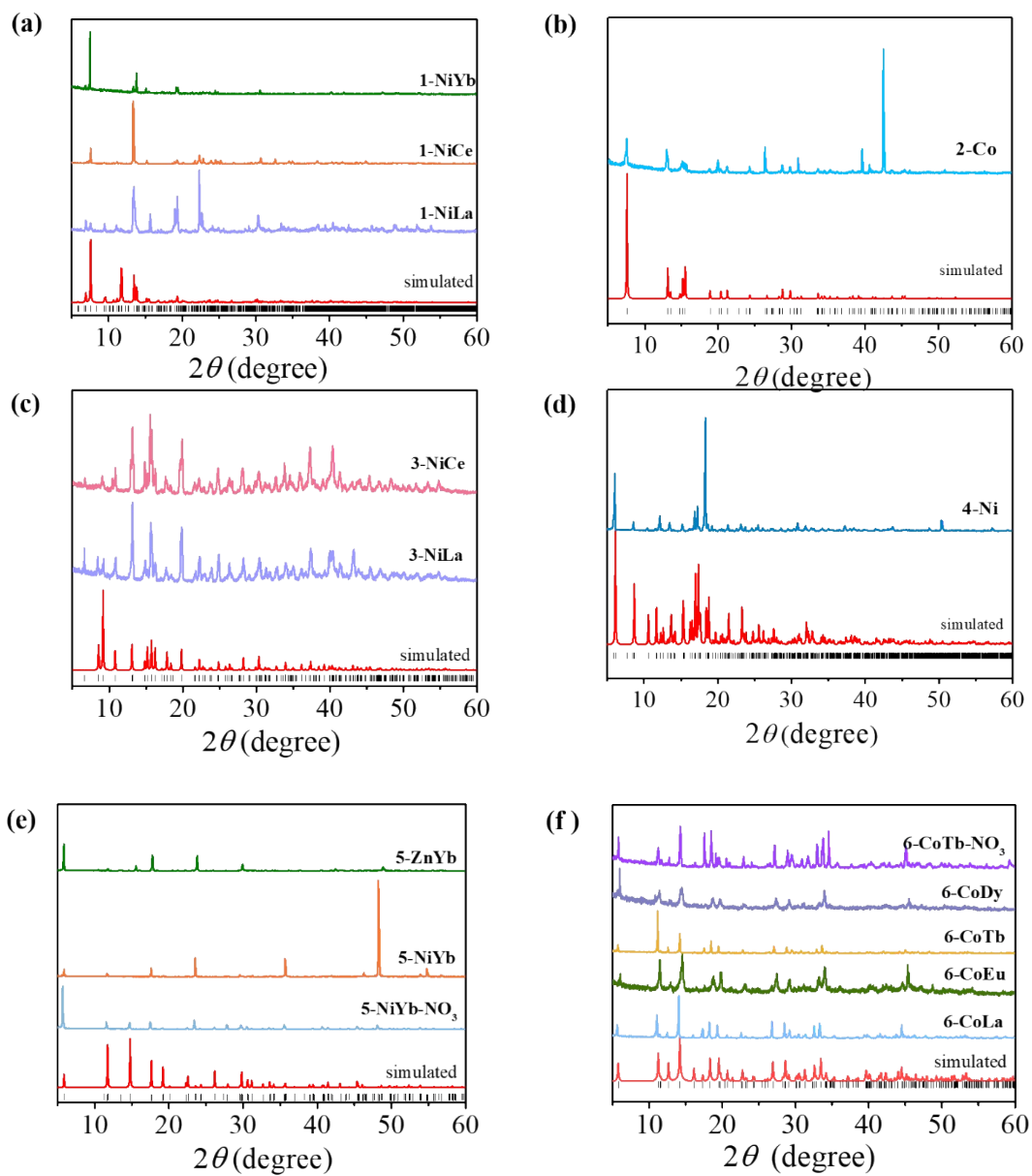
$[\text{Co}^{\text{III}}_2\text{Tb}^{\text{III}}(\text{tacntp})_2(\text{H}_2\text{O})_3](\text{ClO}_4) \cdot \text{Cl}_2 \cdot 5\text{H}_2\text{O}$  (**6-CoLn**, Ln = La, Eu, Tb, Dy). These compounds were prepared by a same procedure and only the preparation of **6-CoTb** was described: compound **2-Co** (0.070 mmol, 0.032 g) was dissolved in 2 mL of distilled water to give a clear deep purple solution. To this solution 3 mL aqueous solution of  $\text{Tb}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  (0.15 mmol, 0.085 g) was added with stirring, and then the pH was tuned to 4 by 0.1 M aqueous HCl. The well-blended mixture was transferred to a stainless steel autoclave with stirring for further ten minutes. Afterward, the reaction vessel was heated to 160 °C and maintained at this temperature for three days. On cooling and filtering, a purple filtrate was obtained. After evaporating the filtrate under room temperature for two weeks, hexagonal plate-like purple single crystals was obtained and collected. Yield: 0.012 g (27% based on **2-Co**). Anal. Calcd. for  $\text{C}_{30}\text{H}_{64}\text{Cl}_3\text{Co}_2\text{N}_6\text{O}_{24}\text{Tb}$  (Found)%: C, 28.24(28.25); H, 5.06(5.05); N, 6.59(6.62). FT-IR ( $\text{cm}^{-1}$ , KBr): 3487(s), 2981(w), 2885(w), 1571(s), 1411(s), 1083(m), 615(w).

Similar to the preparation of **6-CoLn**, the microcrystalline samples of  $[\text{Co}^{\text{III}}_2\text{Tb}^{\text{III}}(\text{tacntp})_2(\text{H}_2\text{O})_3](\text{NO}_3) \cdot \text{Cl}_2 \cdot x\text{H}_2\text{O}$  (denoted as **6-CoTb-NO<sub>3</sub>**) were yielded

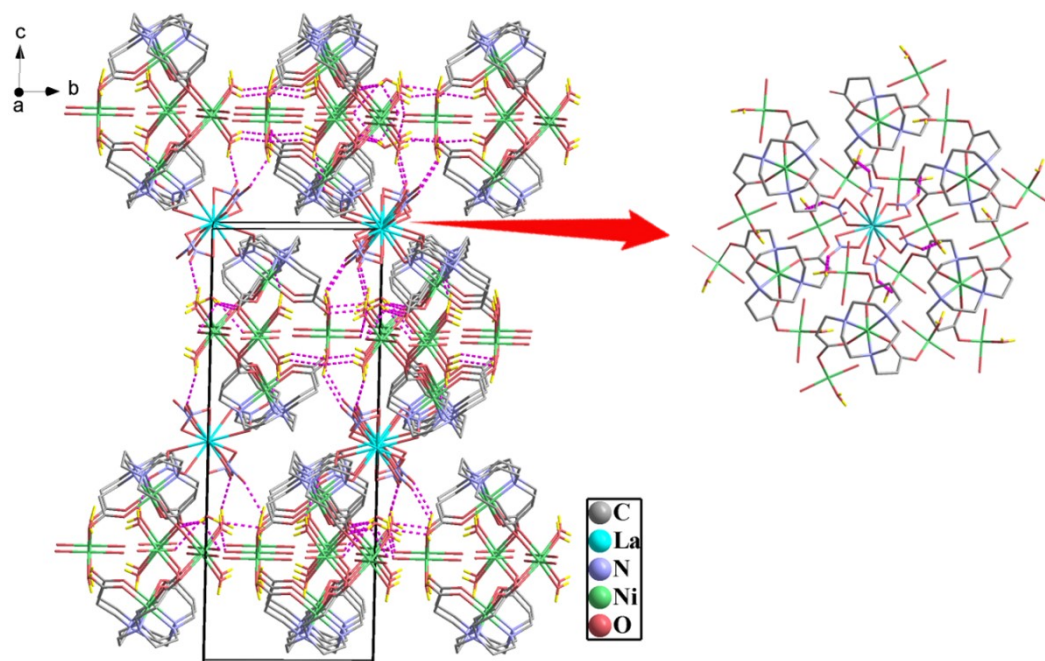
when  $\text{Ln}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$  was replaced by  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The anion of the added lanthanide salt may be a possible factor that influences the morphology of compounds

The phase purity of the as-prepared bulk samples of all compounds was examined by the experimental powder X-ray diffraction (PXRD) patterns which match well with the simulated patterns from the single-crystal X-ray data (Figure S1).

**Figure S1** PXRD patterns for the reported compounds.

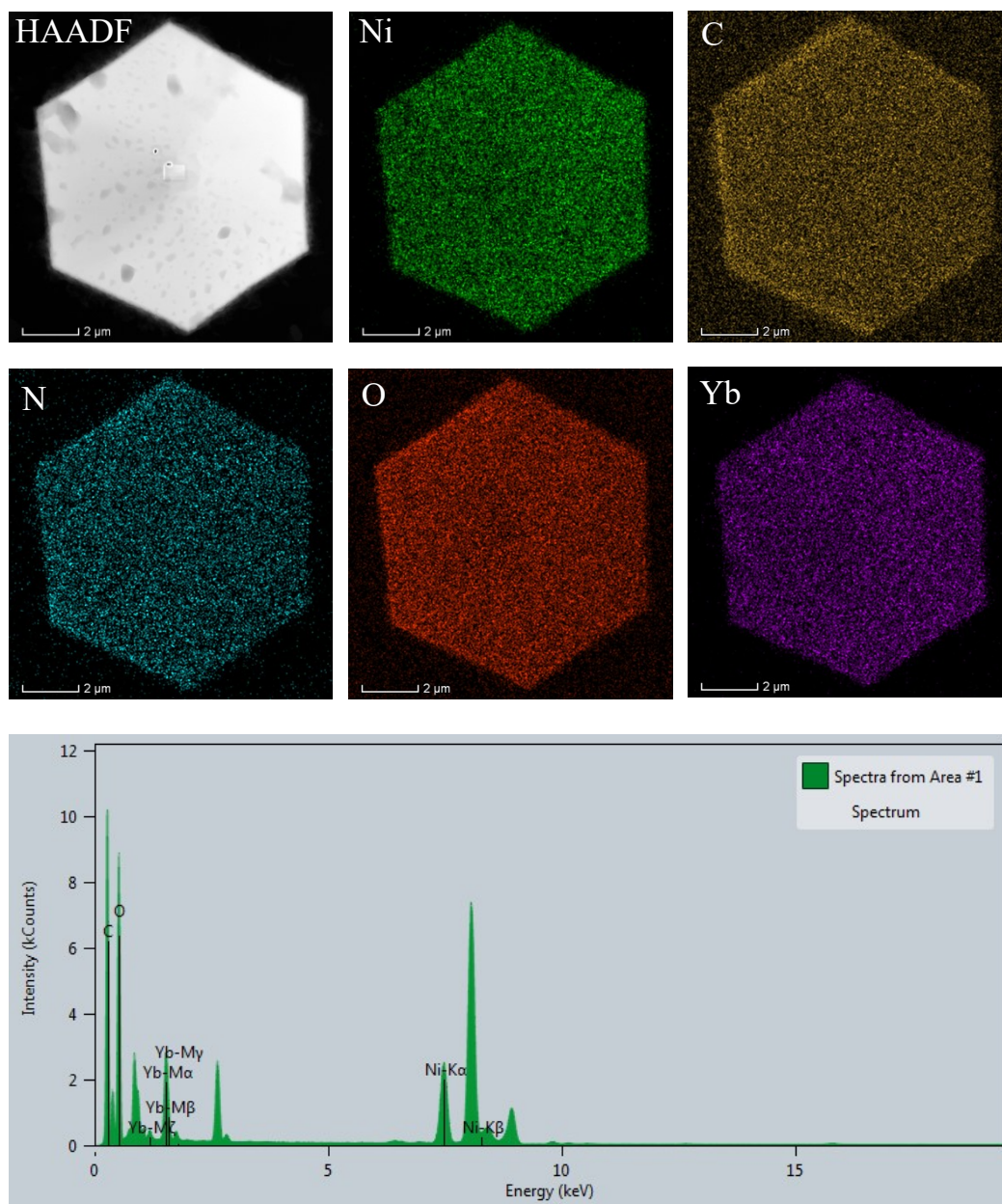


**Figure S2** Three-dimensional supramolecular network formed by hydrogen bonding in compound **3-NiLa** (dashed lines indicate hydrogen bonding).

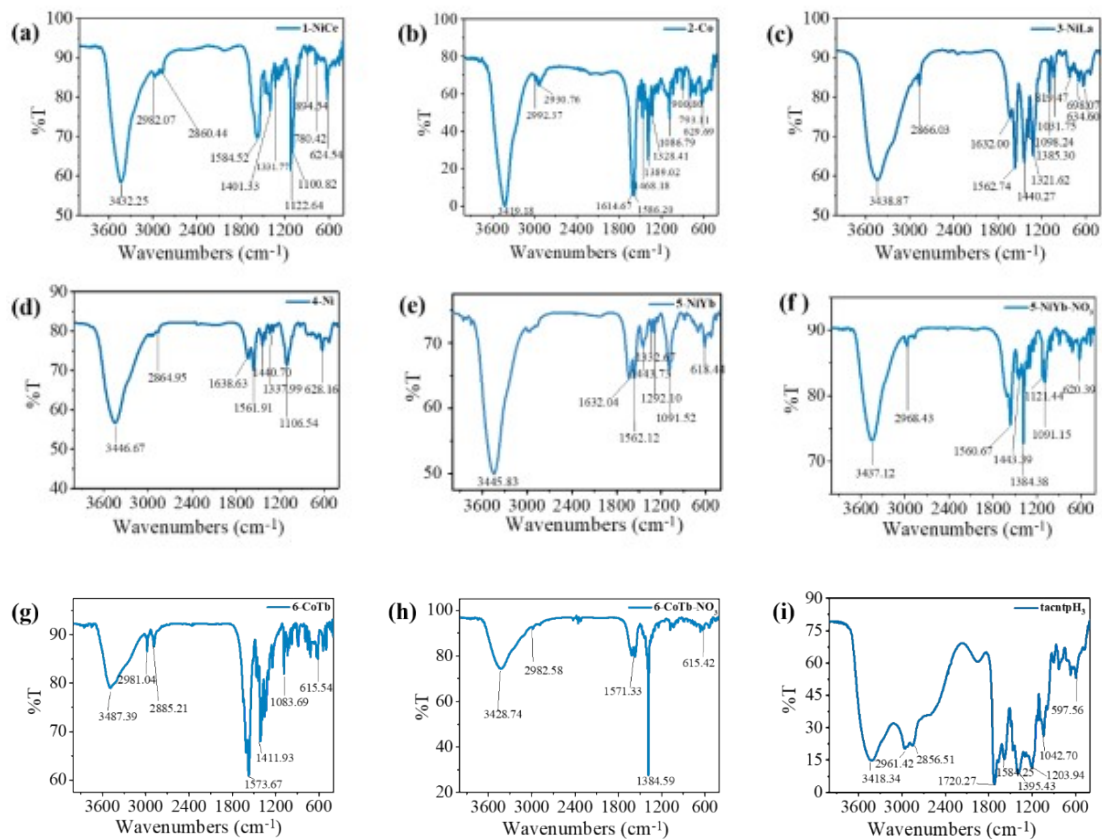




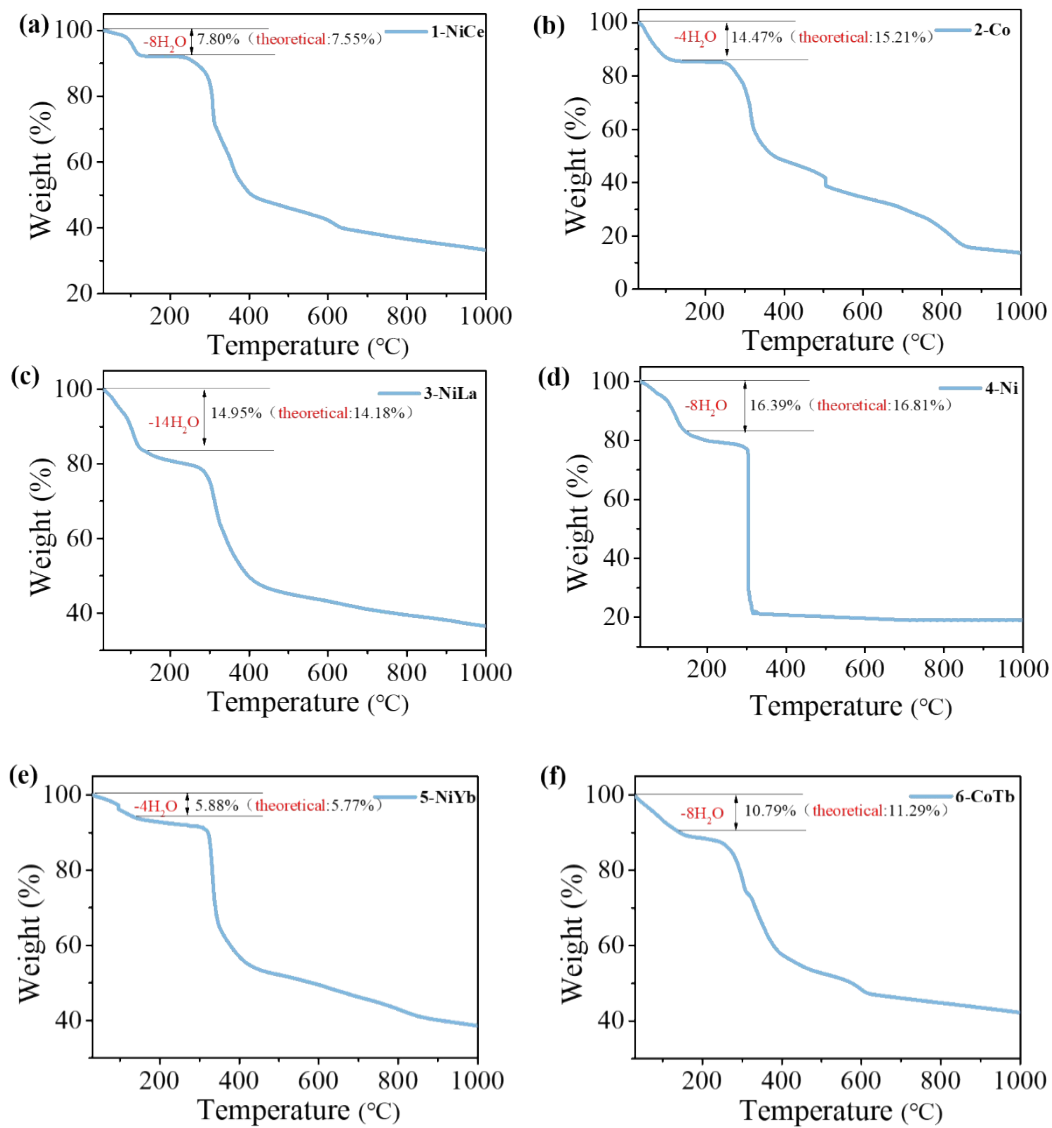
**Figure S3** TEM-EDX mapping for the sample of compound **5-NiYb**.



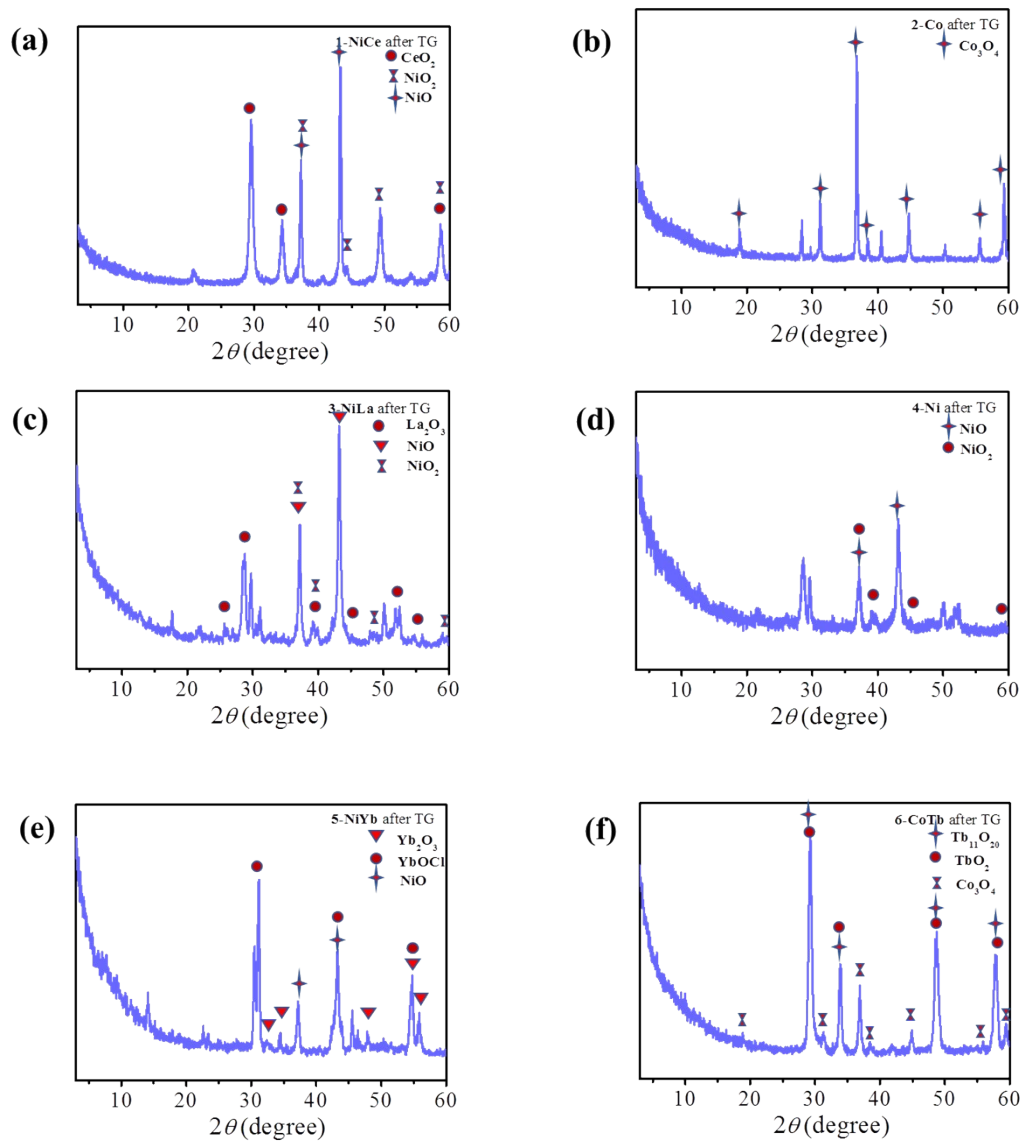
**Figure S4** The FT-IR spectra of (a) compound **1-NiCe**, (b) compound **2-Co**, (c) compound **3-NiLa**, (d) compound **4-Ni**, (e) compound **5-NiYb**, (f) compound **5-NiYb-NO<sub>3</sub>**, (g) compound **6-CoTb**, (h) compound **6-CoTb-NO<sub>3</sub>** and (i) ligand **tacntpH<sub>3</sub>**.



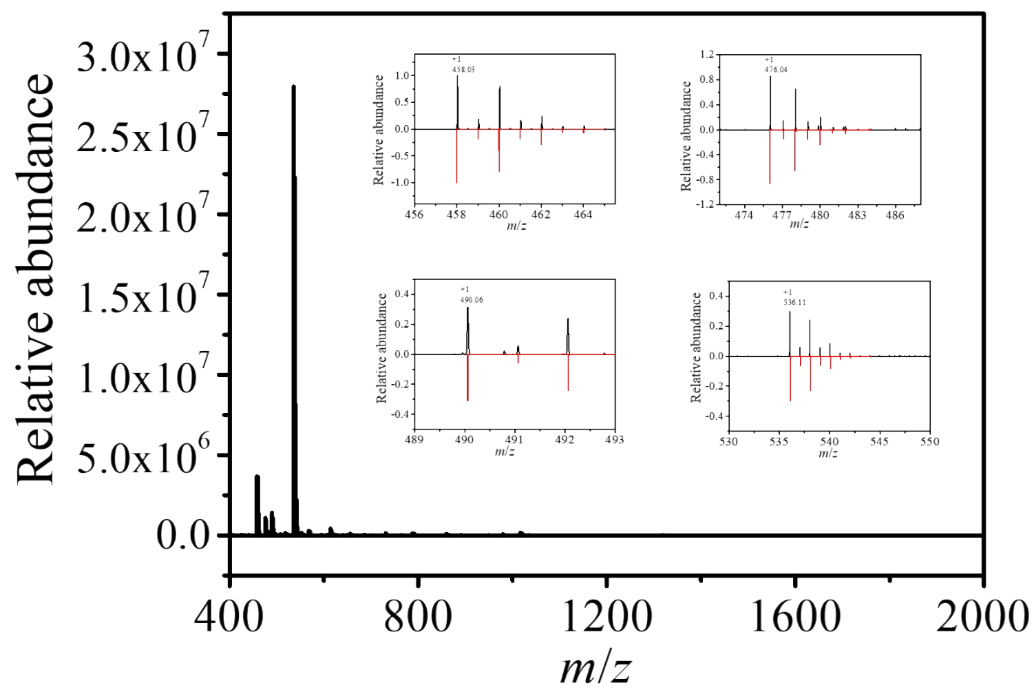
**Figure S5** The thermogravimetric curves of (a) compound **1-NiCe**, (b) compound **2-Co**, (c) compound **3-NiLa**, (d) compound **4-Ni**, (e) compound **5-NiYb** and (f) compound **6-CoTb**.



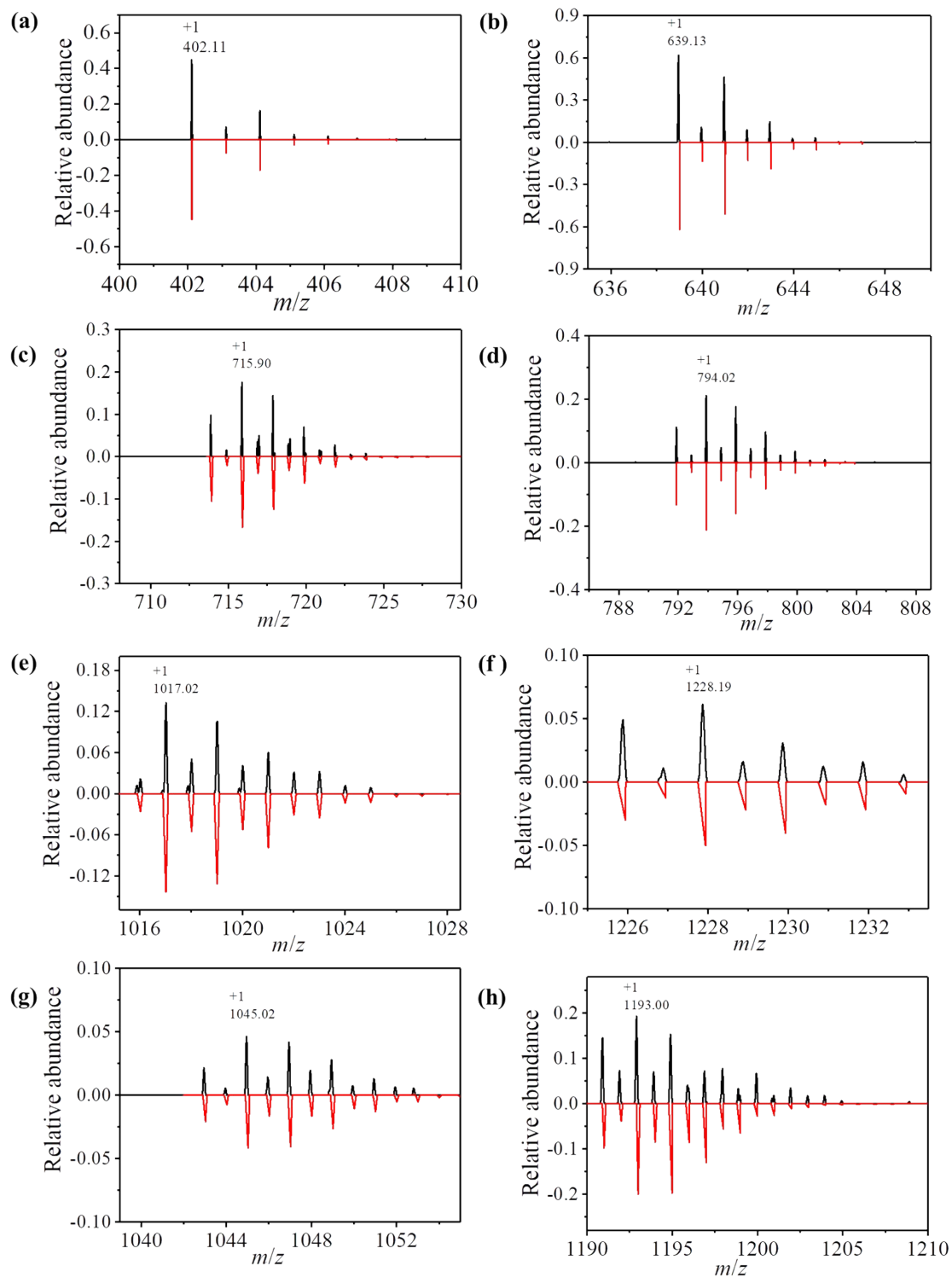
**Figure S6** The assignment of the pyrolysis products of the reported compounds through PXRD patterns.



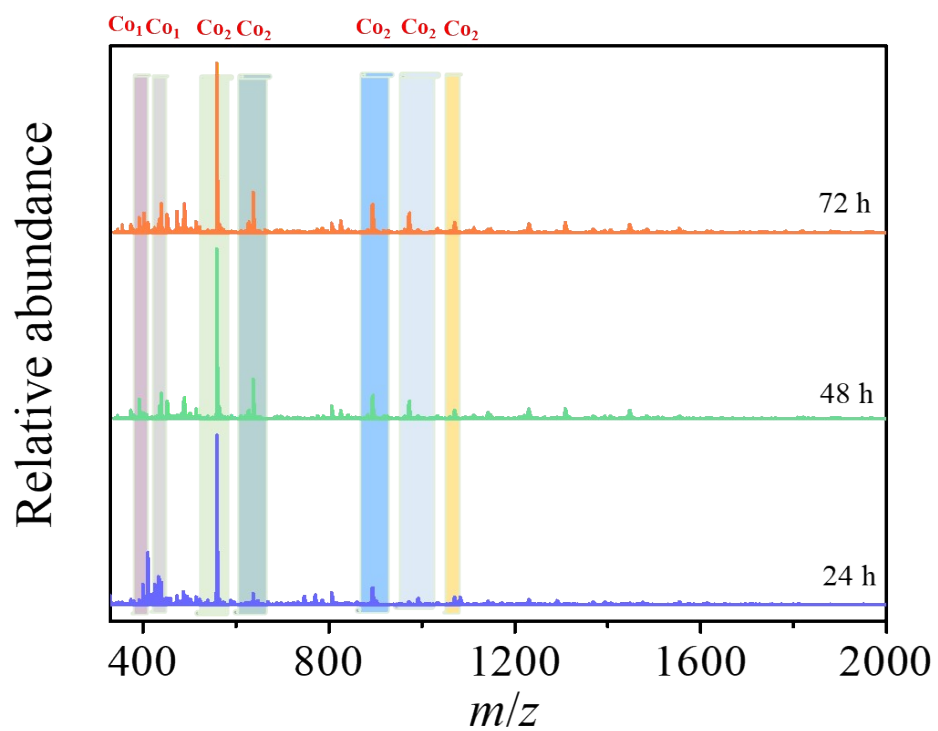
**Figure S7** Positive ion mode ESI-MS spectrum of compound **4-Ni** dissolved in DMSO (solid black line represents experimental pattern and solid red line represents simulated data).



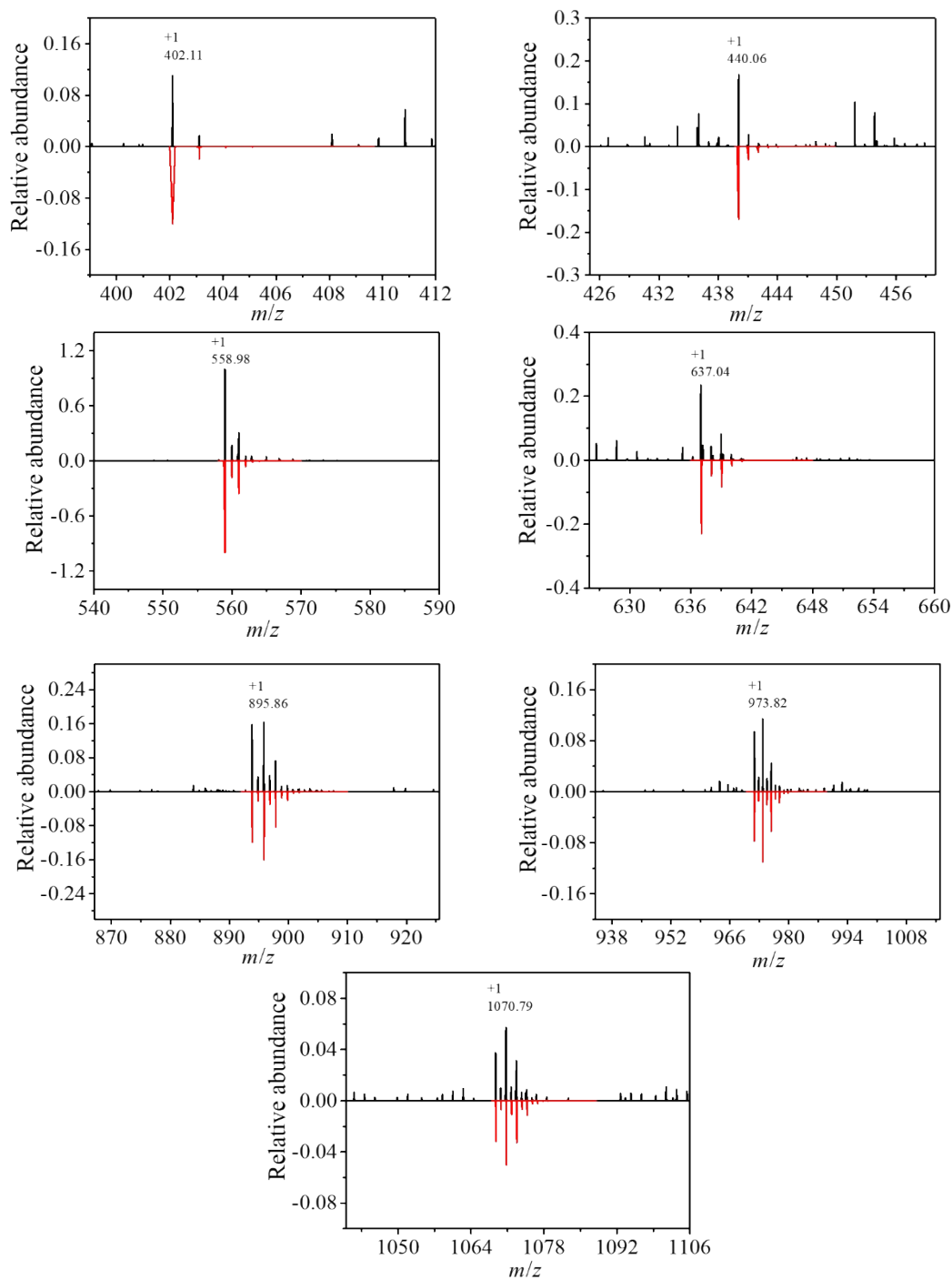
**Figure S8** The isotope distribution patterns for the major intermediates observed in the time-dependent ESI-MS spectra of the reaction solution during the assembly of compound **4-Ni** (solid black line represents experimental pattern and solid red line represents simulated data).



**Figure S9** The time-dependent ESI-MS spectra of the hydrothermal reaction mixture of **2-Co** and excess Co(II) salt.

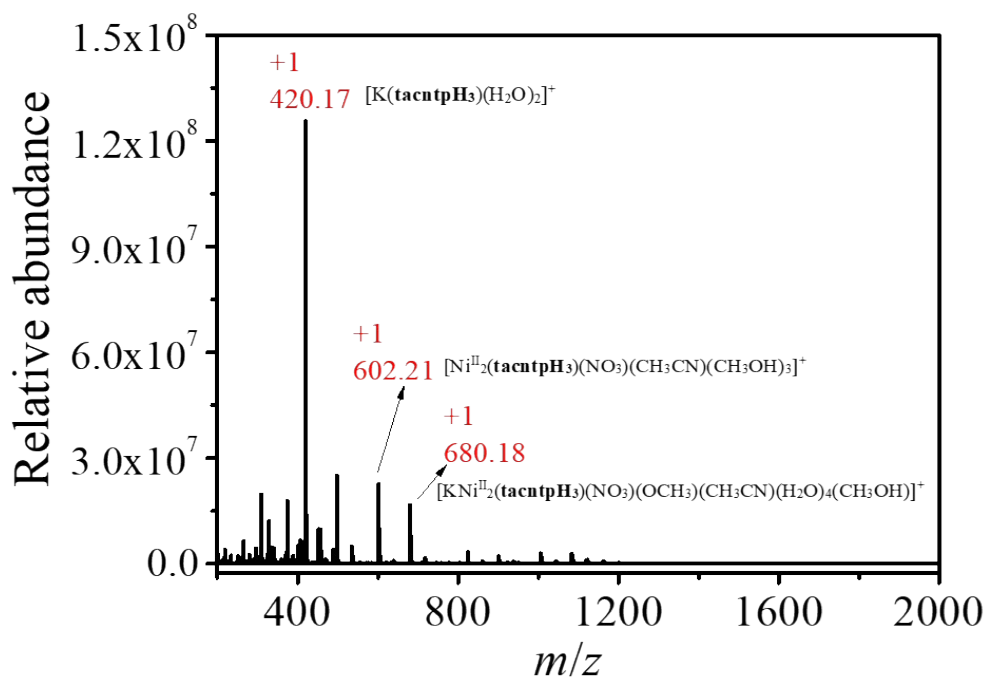


**Figure S10** The isotope distribution patterns for the major species observed in the time-dependent ESI-MS spectra of the hydrothermal reaction mixture of **2-Co** and excess Co(II) salt (solid black line represents experimental pattern and solid red line represents simulated data).

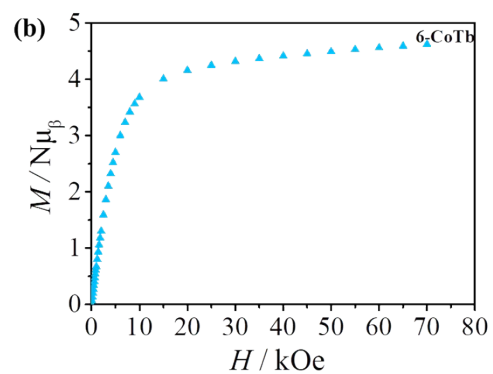
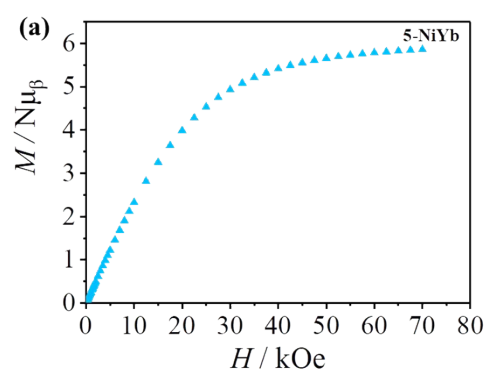




**Figure S11** Positive ion mode ESI-MS spectrum of the aqueous mixture of **1-NiLn** and Ln(III) salts.



**Figure S12** (a) Plot of  $M$  versus  $H$  for compound **5-NiYb** measured at 2.0 K. (b) Plot of  $M$  versus  $H$  for compound **6-CoTb** measured at 2.0 K.



**Table S1** Crystallographic data for compounds **1-NiCe**, **2-Co**, **3-NiLa**, **4-Ni**, **5-NiYb** and **6-CoTb**.

Compound	<b>1-NiCe</b>	<b>2-Co</b>	<b>3-NiLa</b>
Empirical formula	C <sub>60</sub> H <sub>115</sub> CeN <sub>12</sub> Ni <sub>4</sub> O <sub>33</sub>	C <sub>15</sub> H <sub>32</sub> CoN <sub>3</sub> O <sub>10</sub>	C <sub>30</sub> H <sub>76</sub> ClLaN <sub>12</sub> Ni <sub>5</sub> O <sub>44</sub>
Formula weight	1907.6	473.37	1776.94
Temperature (K)	293	296	291
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Trigonal	Hexagonal
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{3}$ <i>c</i> 1	<i>P</i> 6 <sub>3</sub> / <i>m</i>
<i>a</i> (Å)	18.4701(5)	13.4684(16)	11.9438(19)
<i>b</i> (Å)	18.7158(5)	13.4684(16)	11.9438(19)
<i>c</i> (Å)	25.6171(8)	13.0934(16)	26.820(9)
$\alpha$ (°)	90	90.000	90.000
$\beta$ (°)	90	90.000	90.000
$\gamma$ (°)	90	120.000	120.000
Volume (Å <sup>3</sup> )	8855.4(4)	2056.9(4)	3313.4(13)
<i>Z</i>	4	4	2
Calculated density (g/cm <sup>3</sup> )	1.431	1.529	1.781
Absorption coefficient (mm <sup>-1</sup> )	1.42	0.89	2.17
<i>F</i> (000)	3972	1000	1812
$\theta$ range for data collection	2.9 to 27.0	1.8 to 26.0	1.5 to 26.1
Crystal size (mm <sup>3</sup> )	0.32×0.27×0.16	0.28×0.27×0.14	0.26×0.24×0.22
	-23≤ <i>h</i> ≤23	-14≤ <i>h</i> ≤16	-14≤ <i>h</i> ≤14
Limiting indices	0≤ <i>k</i> ≤23	-13≤ <i>k</i> ≤16	-14≤ <i>k</i> ≤14
	0≤ <i>l</i> ≤32	-16≤ <i>l</i> ≤16	-33≤ <i>l</i> ≤31
Reflections collected	29575	6815	26532
Data / restraints / parameters	17223/0/1019	1350/1/87	2251/0/147
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.03	1.01	1.06
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.0470	<i>R</i> <sub>1</sub> =0.0357	<i>R</i> <sub>1</sub> =0.0489
	<i>wR</i> <sub>2</sub> =0.1317	<i>wR</i> <sub>2</sub> =0.0754	<i>wR</i> <sub>2</sub> =0.1316
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.0567	<i>R</i> <sub>1</sub> =0.0656	<i>R</i> <sub>1</sub> =0.0549
	<i>wR</i> <sub>2</sub> =0.1338	<i>wR</i> <sub>2</sub> =0.0824	<i>wR</i> <sub>2</sub> =0.1327
Largest diff. peak and hole (e Å <sup>-3</sup> )	1.209 and -1.040	0.316 and -0.282	1.172 to -0.751

Compound	4-Ni	5-NiYb	6-CoTb
Empirical formula	C <sub>60</sub> H <sub>152</sub> Cl <sub>6</sub> N <sub>12</sub> Ni <sub>9</sub> O <sub>76</sub>	C <sub>30</sub> H <sub>37</sub> Cl <sub>2</sub> N <sub>6</sub> Ni <sub>2</sub> O <sub>24</sub> Yb	C <sub>30</sub> H <sub>64</sub> Co <sub>2</sub> TbN <sub>6</sub> O <sub>24</sub> Cl <sub>3</sub>
Formula weight	2999.03	1247.18	1276.00
Temperature (K)	294	296	296
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Trigonal	Hexagonal
Space group	<i>C2/m</i>	<i>R<sup>3</sup>m</i>	<i>P6<sub>3</sub>/mmc</i>
<i>a</i> (Å)	12.7937(5)	9.241(2)	9.0019(13)
<i>b</i> (Å)	28.8770(11)	9.241(2)	9.0019(13)
<i>c</i> (Å)	15.5362(6)	45.210(2)	30.036(5)
<i>α</i> (°)	90.000	90.000	90.00
<i>β</i> (°)	102.944(4)	90.000	90.00
<i>γ</i> (°)	90.000	120.000	120.00
Volume (Å <sup>3</sup> )	5593.9(4)	3344(2)	2107.9(6)
<i>Z</i>	2	3	2
Calculated density (g/cm <sup>3</sup> )	1.781	1.858	2.001
Absorption coefficient (mm <sup>-1</sup> )	1.74	3.13	2.73
<i>F</i> (000)	3116	1884	1284
<i>θ</i> range for data collection	3.0 to 26.0	2.6 to 26.0	2.6 to 26.0
Crystal size (mm <sup>3</sup> )	0.29×0.27×0.24	0.20×0.17×0.11	0.33×0.29×0.19
	-15 ≤ <i>h</i> ≤ 13	-11 ≤ <i>h</i> ≤ 11	-11 ≤ <i>h</i> ≤ 11
Limiting indices	-20 ≤ <i>k</i> ≤ 35	-11 ≤ <i>k</i> ≤ 11	-11 ≤ <i>k</i> ≤ 11
	-19 ≤ <i>l</i> ≤ 19	-39 ≤ <i>l</i> ≤ 55	-37 ≤ <i>l</i> ≤ 37
Reflections collected	11567	6306	23690
Data / restraints / parameters	5613/20/392	874/12/82	852/26/82
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.03	1.03	1.03
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0476 <i>wR</i> <sub>2</sub> = 0.1384	<i>R</i> <sub>1</sub> = 0.0458 <i>wR</i> <sub>2</sub> = 0.1447	<i>R</i> <sub>1</sub> = 0.0688 <i>wR</i> <sub>2</sub> = 0.1809
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0632 <i>wR</i> <sub>2</sub> = 0.1499	<i>R</i> <sub>1</sub> = 0.0472 <i>wR</i> <sub>2</sub> = 0.1488	<i>R</i> <sub>1</sub> = 0.0715 <i>wR</i> <sub>2</sub> = 0.1819
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.760 and -0.652	1.614 and -0.913	2.510 to -1.921

**Table S2** Selected bond lengths / Å and bond angles / ° for compounds **1-NiCe**, **2-Co**, **3-NiLa**, **4-Ni**, **5-NiYb** and **6-CoTb**.

Compound 1-NiCe			
Ni1–O3	2.120(4)	Ni1–N1	2.056(5)
Ni1–O1	2.132(4)	Ni1–N2	2.065(5)
Ni1–O5	2.134(4)	Ni1–N3	2.056(5)
Ni2–O9	2.059(4)	Ni2–N4	2.046(5)
Ni2–O7	2.129(4)	Ni2–N5	2.069(5)
Ni2–O11	2.400(4)	Ni2–N6	2.050(4)
Ni3–O13	2.050(4)	Ni3–N7	2.061(5)
Ni3–O17	2.057(4)	Ni3–N8	2.071(5)
Ni3–O15	2.065(4)	Ni3–N9	2.064(4)
Ni4–O21	2.050(4)	Ni4–N10	2.062(5)
Ni4–O19	2.056(4)	Ni4–N11	2.053(5)
Ni4–O23	2.150(4)	Ni4–N12	2.082(5)
Ce1–O4W	2.352(4)	Ce1–O7W	2.635(4)
Ce1–O8W	2.382(4)	Ce1–O1W	2.644(4)
Ce1–O2W	2.450(4)	Ce1–O3W	2.664(4)
Ce1–O6W	2.534(4)	Ce1–O5W	2.677(4)
N1–Ni1–N3	86.38(19)	O4W–Ce1–O8W	121.91(13)
N1–Ni1–N2	86.2(2)	O4W–Ce1–O2W	83.47(14)
N3–Ni1–N2	85.2(2)	O8W–Ce1–O2W	73.71(13)
N1–Ni1–O3	170.61(17)	O4W–Ce1–O6W	77.14(13)
N3–Ni1–O3	102.60(17)	O8W–Ce1–O6W	69.29(12)
N2–Ni1–O3	91.78(17)	O2W–Ce1–O6W	118.70(14)
N1–Ni1–O1	90.89(17)	O4W–Ce1–O7W	147.66(13)
N3–Ni1–O1	170.03(18)	O8W–Ce1–O7W	77.42(13)
N2–Ni1–O1	104.16(18)	O2W–Ce1–O7W	128.63(13)
O3–Ni1–O1	80.72(15)	O6W–Ce1–O7W	88.12(13)
N1–Ni1–O5	85.27(18)	O4W–Ce1–O1W	142.24(13)
N3–Ni1–O5	89.97(18)	O8W–Ce1–O1W	78.96(13)
N2–Ni1–O5	170.43(17)	O2W–Ce1–O1W	72.29(13)
O3–Ni1–O5	97.36(16)	O6W–Ce1–O1W	139.98(13)
O1–Ni1–O5	80.24(15)	O7W–Ce1–O1W	60.99(13)

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N4–Ni2–N6	85.18(19)	O4W–Ce1–O3W	79.26(13)
N4–Ni2–O9	176.09(18)	O8W–Ce1–O3W	139.92(13)
N6–Ni2–O9	97.32(17)	O2W–Ce1–O3W	75.96(13)
N4–Ni2–N5	85.7(2)	O6W–Ce1–O3W	150.19(13)
N6–Ni2–N5	85.14(19)	O7W–Ce1–O3W	102.63(13)
O9–Ni2–N5	91.50(18)	O1W–Ce1–O3W	67.20(12)
N4–Ni2–O7	90.23(17)	O4W–Ce1–O5W	75.46(13)
N6–Ni2–O7	169.13(18)	O8W–Ce1–O5W	146.65(12)
O9–Ni2–O7	86.79(15)	O2W–Ce1–O5W	139.44(13)
N5–Ni2–O7	84.69(17)	O6W–Ce1–O5W	90.08(13)
N4–Ni2–O11	105.85(18)	O7W–Ce1–O5W	75.94(11)
N6–Ni2–O11	92.89(17)	O1W–Ce1–O5W	104.75(12)
O9–Ni2–O11	77.09(15)	O3W–Ce1–O5W	66.40(12)
N5–Ni2–O11	168.11(18)	O21–Ni4–N11	91.68(16)
O7–Ni2–O11	97.85(15)	O21–Ni4–O19	86.35(16)
O13–Ni3–O17	86.92(15)	N11–Ni4–O19	94.39(17)
O13–Ni3–N7	91.67(18)	O21–Ni4–N10	176.87(19)
O17–Ni3–N7	96.59(18)	N11–Ni4–N10	85.76(19)
O13–Ni3–N9	176.63(18)	O19–Ni4–N10	92.05(17)
O17–Ni3–N9	91.21(17)	O21–Ni4–N12	96.45(19)
N7–Ni3–N9	85.76(19)	N11–Ni4–N12	84.86(19)
O13–Ni3–O15	82.39(16)	O19–Ni4–N12	177.12(18)
O17–Ni3–O15	86.44(15)	N10–Ni4–N12	85.12(19)
N7–Ni3–O15	173.20(18)	O21–Ni4–O23	98.49(16)
N9–Ni3–O15	100.29(17)	N11–Ni4–O23	169.14(17)
O13–Ni3–N8	96.71(17)	O19–Ni4–O23	90.07(16)
O17–Ni3–N8	175.81(17)	N10–Ni4–O23	84.19(19)
N7–Ni3–N8	85.45(19)	O15–Ni3–N8	91.94(17)
N9–Ni3–N8	85.27(19)		

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**Compound 2-Co**

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Co1-O1	1.9258(17)	Co1-N1	1.949 (2)
O1-Co1-N1	93.83(8)	O1-Co1-O1#1	87.05(7)
O1-Co1-N1#1	91.04(7)	N1-Co1-O1#1	177.85(8)
N1-Co1-N1#1	88.11(8)		

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Symmetry code: #1  $-x + y, -x + 1, z$ .

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**Compound 3-NiLa**

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Ni1-O1	2.056(3)	N1-Ni1	2.056(4)
Ni2-O2	2.100(3)	Ni2-O3	2.112(5)
Ni2-O4	2.010(5)	Ni2-O5	2.075(4)
La1-O6	2.643(4)	La1-O7	2.637(3)
O7#2-La1-O7	112.89(7)	O7-La1-O6#2	70.07(11)
O7#3-La1-O7	67.11(7)	O7-La1-O6#4	131.58(10)
O7#4-La1-O7	180.00(19)	O6-La1-O6#3	112.79(13)
O6-La1-O6#4	180.00(16)	O7#3-La1-O6	67.86(11)
O7-La1-O6	48.42(10)	O7-La1-O6#3	109.93(11)
O6-La1-O6#2	67.21(13)	O7#5-La1-O6#3	112.14(11)
O2-Ni2-O3	92.95(14)	N1#1-Ni1-N1	85.47(16)
O4-Ni2-O5	91.45(16)	N1-Ni1-O1#1	96.93(13)
O5#6-Ni2-O5	99.3(2)	N1#1-Ni1-O1	176.07(13)
O4-Ni2-O2	89.40(15)	N1-Ni1-O1	91.60(14)
O5-Ni2-O2	86.01(15)	O1-Ni1-O1#1	86.14(13)
O5-Ni2-O2#6	174.62(15)	O5-Ni2-O3	86.43(15)
O2-Ni2-O2#6	88.7(2)	O4-Ni2-O3	176.7(2)

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Symmetry codes: #1  $-x + y, -x + 1, z$ ; #2  $-x + y + 2, -x + 1, z$ ; #3  $x - y, x - 1, -z$ ; #4  $-x + 2, -y, -z$ ; #5  $y + 1, -x + y + 1, -z$ ; #6  $x, y, -z + 1/2$ .

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**Compound 4-Ni**

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Ni1–Ni1	2.070(3)	Ni3–O4	2.064(3)
Ni1–Ni2	2.075(3)	Ni3–O8	2.077(4)
Ni1–Ni3	2.070(3)	Ni3–O10	2.078(3)
Ni1–O3	2.050(3)	Ni4–O12	2.043(3)
Ni1–O5	2.067(3)	Ni4–O6	2.064(3)
Ni1–O1	2.072(3)	Ni4–O11	2.074(4)
Ni2–O2	2.050(3)	Ni4–O13	2.103(4)
Ni2–O7	2.096(4)	Ni3–O9	2.051(5)
O3–Ni1–O5	85.82(11)	O2–Ni2–O2#1	89.98(18)
O3–Ni1–N3	176.24(13)	O2–Ni2–O2#2	180.00(12)
O5–Ni1–N3	91.37(13)	O2–Ni2–O2#3	90.02(18)
O3–Ni1–O1	87.19(11)	O2–Ni2–O7#2	93.26(11)
O5–Ni1–O1	88.03(11)	O2–Ni2–O7	86.74(11)
N3–Ni1–O1	95.23(13)	O7–Ni2–O7#2	180.000(1)
O3–Ni1–N1	97.18(13)	O9–Ni3–O4	87.11(12)
O5–Ni1–N1	176.48(13)	O4–Ni3–O4#3	92.99(19)
N3–Ni1–N1	85.70(14)	O9–Ni3–O8	177.91(17)
O1–Ni1–N1	90.28(12)	O6–Ni4–O12	91.14(13)
O3–Ni1–N2	91.94(12)	O6–Ni4–O12#3	176.44(13)
O5–Ni1–N2	96.03(12)	O6–Ni4–O6#3	87.56(18)
N3–Ni1–N2	85.85(13)	O12–Ni4–O11	88.45(13)
O1–Ni1–N2	175.77(12)	O6–Ni4–O11	94.96(11)
N1–Ni1–N2	85.73(13)	O12–Ni4–O13	88.30(13)
O4–Ni3–O8	94.32(11)	O6–Ni4–O13	88.35(12)
O9–Ni3–O10	91.83(14)	O11–Ni4–O13	175.41(16)
O4–Ni3–O10#3	89.48(13)	O4–Ni3–O10	177.27(14)
O4–Ni3–O10	177.27(14)	O4–Ni3–O10#3	89.48(13)
O8–Ni3–O10	86.67(13)	O8–Ni3–O10	86.67(13)
O12–Ni4–O12#3	89.97(19)	O10–Ni3–O10#3	88.04(19)

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Symmetry codes: #1 2 – x, y, 2 – z; #2 2 – x, –y, 2 – z; #3 x, –y, z;



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**Compound 5-NiYb**

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Yb1-O2	2.160(6)	Ni1-N1	2.065(6)
Ni1-O1	2.035(5)		
O2-Yb1-O2#2	180.0(3)	O1-Ni1-O1#1	86.9(2)
O2-Yb1-O2#3	90.8(3)	O1-Ni1-N1#1	94.06(18)
O2-Yb1-O2#4	89.2(3)	N1-Ni1-N1#1	85.0(3)
O1-Ni1-N1	178.7(2)		

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Symmetry codes: #1  $-x + y, -x + 1, z$ ; #2  $-x, -y + 2, -z$ ; #3  $x - y + 1, x + 1, -z$ ; #4  $-x + y - 1, -x + 1, z$ .

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**Compound 6-CoTb**

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Co1-O1	1.892(9)	Tb1-O2	2.317(9)
Co1-N1	1.944(10)	Tb1-O3	2.52(2)
O1-Co1-N1	178.5(4)	O1-Co1-N1#1	93.2(3)
N1-Co1-N1#1	87.9(4)	O1-Co1-O1#1	85.7(4)
O2-Tb1-O3	138.8(2)	O2-Tb1-O2#2	135.81(17)
O3-Tb1-O3#2	120.000(3)	O2-Tb1-O3#2	67.91(8)
O2#2-Tb1-O2#4	81.3(4)	O2#3-Tb1-O2#4	82.4(5)

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Symmetry codes: #1  $-x + y, -x + 1, z$ ; #2  $-x + y + 1, -x + 1, -z + 1/2$ ; #3  $-y + 1, x - y, z$ ; #4  $-y + 1, x - y, -z + 1/2$ .

**Table S3** Hydrogen bonding for compounds **2-Co**, **3-NiLa** and **4-Ni**.**Compound 2-Co**

Hydrogen bond	D–H	H...A	D...A	D–H...A
O3–H3C...O2#1	0.85	2.040	2.782(3)	145
O3–H3D...O3#2	0.85	2.370	2.790(5)	111

Symmetry codes: #1  $y, x, 1/2 - z$ ; #2  $x - y, x, -z$ .**Compound 3-NiLa**

Hydrogen bond	D–H	H...A	D...A	D–H...A
O3–H3C...O1	0.85	1.950	2.666(10)	141
O5–H5D...C11#1	0.85	2.250	3.025(12)	151
O10–H10C...O3	0.85	2.060	2.88(3)	159

Symmetry codes: #1  $1 + x, y, z$ ; #2  $1 - y, x - y, z$ .**Compound 4-Ni**

Hydrogen bond	D–H	H...A	D...A	D–H...A
O7–H7D...O1#1	0.85	2.100	2.683(3)	126
O8–H8C...O3	0.85	1.910	2.661(4)	146
O8–H8D...O3#2	0.85	1.910	2.661(4)	147
O9–H9D...O23	0.85	2.080	2.694(10)	129
O10–H10C...O19#3	0.85	2.430	3.083(7)	134
O10–H10D...O22#4	0.85	2.160	2.779(5)	129
O11–H11C...O5	0.85	1.910	2.684(4)	150
O11–H11D...O5#1	0.85	2.000	2.684(4)	137
O12–H12D...O20	0.85	2.260	2.673(7)	110
O13–H13C...O9#4	0.85	2.470	3.067(6)	128
O13–H13D...O13#5	0.85	2.330	3.012(6)	138
O13–H13D...O6#1	0.85	2.200	2.878(4)	137
O20–H20D...O16	0.85	2.2900	3.107(8)	162
O23–H23C...O22#4	0.85	2.530	3.149(10)	132

Symmetry codes: #1  $2 - x, -y, 2 - z$ ; #2  $x, -y, z$ ; #3  $1 - x, -y, 1 - z$ ; #4  $1 - x, y, 1 - z$ ; #5  $2 - x, y, 1 - z$ .

**Table S4** Major species assigned in positive ion mode ESI-MS spectrum of compound **4-Ni**.

Peaks	Observed $m/z$	Calculated $m/z$
$[\text{Ni}^{\text{II}}_2(\text{tacntp})]^+$	458.03	458.04
$[\text{Ni}^{\text{II}}_2(\text{tacntp})(\text{H}_2\text{O})]^+$	476.04	476.05
$[\text{Ni}^{\text{II}}_2(\text{tacntp})(\text{CH}_3\text{OH})]^+$	490.06	490.06
$[\text{Ni}^{\text{II}}_2(\text{tacntp})(\text{CH}_3\text{OH})(\text{CH}_3\text{CH}_2\text{OH})]^+$	536.11	536.11

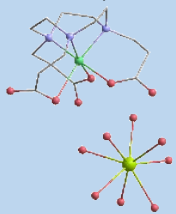
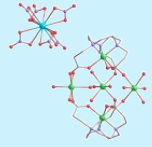
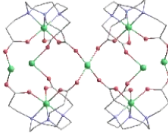
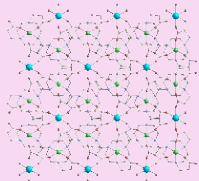
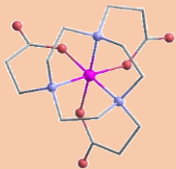
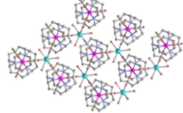
**Table S5** The major intermediates observed in the time-dependent ESI-MS spectra of the reaction solution during the assembly of compound **4-Ni** from **1-NiCe**.

Peaks	Observed $m/z$	Calculated $m/z$
$[\text{Ni}^{\text{II}}(\text{tacntpH}_2)]^+$	402.11	402.12
$[\text{Ni}^{\text{II}}_2(\text{tacntpH})(\text{NO}_3)(\text{H}_2\text{O})_3(\text{CH}_3\text{OH})_2]^+$	639.13	639.12
$[\text{Ni}^{\text{II}}_4(\text{tacntp})(\text{CN})(\text{NO}_3)(\text{OH})_2(\text{H}_2\text{O})]^+$	715.90	715.91
$[\text{Ni}^{\text{II}}_4(\text{tacntp})(\text{OH})_2(\text{OCH}_3)_2(\text{H}_2\text{O})_5(\text{CH}_3\text{OH})]^+$	794.02	794.02
$[\text{Ni}^{\text{II}}_4(\text{tacntp})_2(\text{ClO}_4)]^+$	1017.02	1017.02
$[\text{Ni}^{\text{II}}_5(\text{tacntp})_2(\text{OH})_3(\text{H}_2\text{O})]^+$	1045.02	1045.02
$[\text{Ni}^{\text{II}}_5(\text{tacntp})_2(\text{CO}_3)(\text{HCO}_3)(\text{NO}_3)_2(\text{CH}_3\text{OH})]^+$	1193.00	1193.00
$[\text{Ni}^{\text{II}}_4(\text{tacntpH})_2(\text{CO}_3)(\text{NO}_3)(\text{H}_2\text{O})_5(\text{CH}_3\text{OH})_3]^+$	1228.19	1228.19

**Table S6** The major species observed in the time-dependent ESI-MS spectra of the hydrothermal reaction mixture of **2-Co** and excess Co(II) salt.

Peaks	Observed <i>m/z</i>	Calculated <i>m/z</i>
$[\text{Co}^{\text{III}}(\text{tacntpH})]^+$	402.11	402.11
$[\text{KCo}^{\text{III}}(\text{tacntp})]^+$	440.06	440.06
$[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tacntp})(\text{ClO}_4)]^+$	558.98	558.98
$[\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tacntpH})(\text{OCH}_3)(\text{ClO}_4)(\text{CH}_3\text{CH}_2\text{OH})]^+$	637.04	637.05
$[\text{Co}^{\text{III}}_2(\text{tacntpH}_2)(\text{ClO}_4)_4(\text{H}_2\text{O})_2]^+$	895.86	895.86
$[\text{NaKCo}^{\text{III}}_2(\text{tacntp})(\text{ClO}_4)_4(\text{H}_2\text{O})_3]^+$	973.82	973.81
$[\text{K}_3\text{Co}^{\text{II}}\text{Co}^{\text{III}}(\text{tacntp})(\text{ClO}_4)_4(\text{H}_2\text{O})(\text{CH}_3\text{OH})(\text{CH}_3\text{CH}_2\text{OH})]^+$	1070.79	1070.79

**Table S7** The reaction parameters for the modular assembly of polynuclear metallocages and heterometallic coordination networks from two mononuclear metalloligands.

Metalloligand precursor	Type of added metal salt	Temperature	pH	Assembled architecture
<b>1-NiLn</b> (Ln = La, Ce, Yb) 	Ln(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (Ln = La, Ce)	160 °C	2 (aq HCl)	Crystalline <b>3-NiLn</b> 
	Ni(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	160 °C	3	Crystalline <b>4-Ni</b> 
	Yb(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	160 °C	5–6 (aq NaOH)	Crystalline <b>5-NiYb</b> 
	Yb(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	160 °C	5–6 (aq NaOH)	Microcrystalline <b>5-NiYb-NO<sub>3</sub></b>
<b>2-Co</b> 	Ln(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (Ln = La, Ce, Yb)	160 °C	2 (aq HCl)	Unidentified solid products
	Co(ClO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	160 °C	3	Unidentified solid products
	Ln(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O (Ln = La, Eu, Tb, Dy)	160 °C	4 (aq HCl)	Crystalline <b>6-CoLn</b> 
	Tb(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	160 °C	4 (aq HCl)	Microcrystalline <b>6-CoTb-NO<sub>3</sub></b>

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