

# Metal-Mediated One-Step In Situ Oxidation of 2,9-Dimethyl-1,10-phenanthroline and Formation of Transition-Metal and Lanthanoid Complexes

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**Keywords:** Copper / Nickel / Lanthanides / Oxidation / Ligand design

One-step in situ oxidations of 2,9-dimethyl-1,10-phenanthroline to 9-methyl-1,10-phenanthroline-2-carboxylic acid and 1,10-phenanthroline-2,9-dicarboxylic acid were carried out by utilizing  $\text{HNO}_3$  as the oxidant in the presence of  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}\text{--Ln}^{\text{III}}$  salts under hydrothermal conditions,

showing that different transition-metal ions can tune the oxidation products through different coordination modes in metal complexes of the in situ formed ligands.

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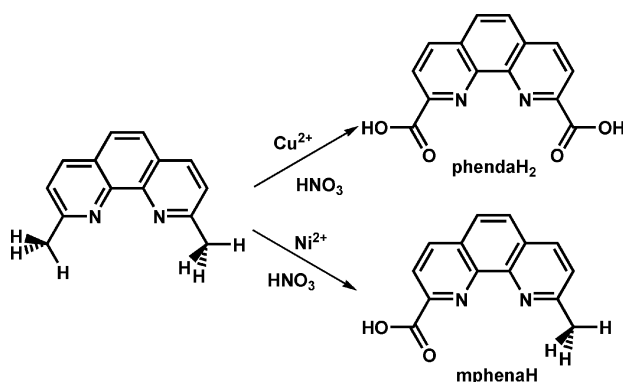
## Introduction

As a very important research field in both coordination chemistry and organic chemistry, in situ metal/ligand reactions have been extensively investigated for many decades for the discovery of new organic reactions and the elucidation of reaction mechanisms, as well as the generation of novel coordination compounds, especially those that are inaccessible by direct preparation from the ligands.<sup>[1–3]</sup> These reactions can be conducted under mild conditions or in a sealed tube at elevated temperatures and pressures, that is, by conventional methods or by hydrothermal (solvothermal) methods. Owing to the special reaction conditions, hydrothermal in situ metal/ligand reactions<sup>[2–4]</sup> may provide not only very stable functional coordination polymer materials, but also products that are inaccessible or not easily obtainable by conventional methods. We focused our interest on hydrothermal metal/ligand reactions towards the discovery of new ligand reactions and their application in the crystal engineering of functional coordination polymers; we also explored many interesting phenomena such as the redox process of copper, ligand oxidative coupling, hydrolysis, and substitution.<sup>[5]</sup>

Chelating 1,10-phenanthroline ligands and its substituted derivatives play an important role in the development of coordination chemistry.<sup>[6]</sup> However, 1,10-phenanthroline-2,9-dicarboxylic acid (phendaH<sub>2</sub>) and 9-methyl-1,10-phenanthroline-2-carboxylic acid (mphenaH) are not well exploited as ligands in coordination chemistry.<sup>[7]</sup> The phen-

daH<sub>2</sub> ligand was previously prepared from 2,9-dimethyl-1,10-phenanthroline (dmphen) by a two-step oxidation reaction by using deadly poisonous  $\text{SeO}_2$  and  $\text{HNO}_3$  as the oxidants for each step, respectively.<sup>[8]</sup> However, the one-step synthesis of phendaH<sub>2</sub>, to the best of our knowledge, has not been developed to date. Moreover, selective oxidation of only one methyl group of dmphen remains a challenge, as both methyl groups are in the same environment.

Herein we report four complexes with phenda<sup>2–</sup> and mphena<sup>–</sup> ligands,  $[\text{Cu}_2(\text{phenda})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$  (**1**),  $[\text{Ni}(\text{mphena})_2] \cdot \text{H}_2\text{O}$  (**2**),  $[\text{Ln}_2(\text{phenda})_3(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Eu}$  **3** and  $\text{Tb}$  **4**), which were formed by a one-step in situ oxidation (Scheme 1) of dmphen to mphenaH and phendaH<sub>2</sub> by utilizing  $\text{HNO}_3$  as the oxidant in the presence of  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Cu}^{\text{II}}\text{--Ln}^{\text{III}}$  salts under hydrothermal conditions.



Scheme 1. Metal-mediated one-step in situ oxidation of 2,9-dimethyl-1,10-phenanthroline.

## Results and Discussion

In the hydrothermal reaction system of **1**, there are three potential oxidants,  $\text{Cu}^{2+}$  ion,  $\text{O}_2$ , and  $\text{NO}_3^-$ , which may ox-

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idize the methyl group to a carboxyl group under hydrothermal conditions. In order to identify which is the true oxidant, a series of parallel experiments were therefore carried out to test the following combinations of potential oxidants for oxidation of dmphen:  $\text{Cu}(\text{NO}_3)_2/\text{Ar}$ ,  $\text{Cu}(\text{NO}_3)_2/\text{HNO}_3/\text{Ar}$ , and  $\text{Cu}(\text{NO}_3)_2/\text{O}_2$ . As a result, the IR spectra of the resultant product from the  $\text{Cu}(\text{NO}_3)_2/\text{HNO}_3/\text{Ar}$  system exhibits strong peaks for the carboxyl group, showing that dmphen was oxidized to phenda $\text{H}_2$ . When the reaction was carried out in the presence or absence of air by using  $\text{CuSO}_4$  or  $\text{CuCl}_2$  instead of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{HNO}_3$ , only other products were obtained, as confirmed by IR spectroscopy. Thus, the  $\text{Cu}^{2+}$  ion and  $\text{O}_2$  can be excluded as oxidants, and the remaining  $\text{HNO}_3$  should be the oxidant, which was further testified by the reaction of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{HNO}_3$  with dmphen in the presence or absence of air, which led to the formation of **2** in high yield. More interestingly, the oxidation of dmphen into phenda $\text{H}_2$  in **1** and into mphenah in **2**, suggests that transition-metal ions with different coordination habits may mediate the oxidation and stabilize the related oxidized species.<sup>[2]</sup> Moreover,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Ni}(\text{NO}_3)_2$  are necessary in the synthesis of **3** and **4**.

X-ray crystal structure analysis reveals that **1** is a dinuclear copper(II) complex (Figure 1). The asymmetric unit of **1** contains one crystallographically unique  $\text{Cu}^{\text{II}}$  center, one phenda $^{2-}$  ligand, one aqua ligand, and one lattice water molecule. The Cu1 shows a slightly distorted square pyramidal geometry completed by two nitrogen atoms [Cu1–N 1.926(2) and 2.152(2) Å], two oxygen atoms from two phenda $^{2-}$  ligands [Cu1–O 1.9041(18)–2.0734(19) Å], and one aqua ligand [Cu1–O1w 2.171(2) Å]. Interestingly, one carboxyl group is coplanar with the phen plane, whereas another one is almost perpendicular to the phen plane with dihedral angles of 4.1 and 99.8° between the phen group and the two carboxyl groups of phenda $^{2-}$ , respectively.

Along the direction of the *c* axis, each  $\text{Cu}_2(\text{phenda})_2(\text{H}_2\text{O})_2$  molecule forms two donor hydrogen bonds and two acceptor hydrogen bonds with two neighboring molecules [O1w...O4<sup>i</sup> 2.764(3) Å, O1w–H1wb...O4<sup>i</sup> 148.5(4)°; symmetry code: *i* =  $-x + 2, -y, -z$ ], leading to 1D hydrogen-bonded chains. Adjacent 1D chains are stacked into a 2D layer structure (Figure S1, Supporting Information) through interchain offset  $\pi$ – $\pi$  interactions with distances of 3.274–3.373 Å. The 3D supramolecular architecture with 1D channels was further formed by the interlayer hydrogen-bonded interactions [O1w...O2<sup>j</sup> 2.718(3) Å, O1w–H1wa...O2<sup>j</sup> 167.3(5)°; symmetry code: *j* =  $x, -y + 1/2, z - 1/2$ ]. The lattice water molecules are located at these channels and contact the inner walls through rich classical O–H...O and nonclassical C–H...O hydrogen bonds [O2w...O1<sup>k</sup> 3.018(4) and 3.137(3) Å, O2w–H2wa/H2wb...O1<sup>k</sup> 152.2 and 170.4°; C9–H9...O2w<sup>l</sup> 3.278(4) Å, C9–H9...O2w<sup>l</sup> 159.7°; C12–H12...O1w<sup>m</sup> 3.576(3) Å, C12–H12...O1w<sup>m</sup> 154.8°; symmetry codes: *k* =  $x, -y + 1/2, z + 1/2$ ; *l* =  $-x + 2, -y, -z + 1$ ; *m* =  $-x + 1, -y, -z$ ].

Compound **2** is a mononuclear complex and the asymmetric unit contains one  $\text{Ni}^{\text{II}}$  atom, two mphenah $^-$  ligands,

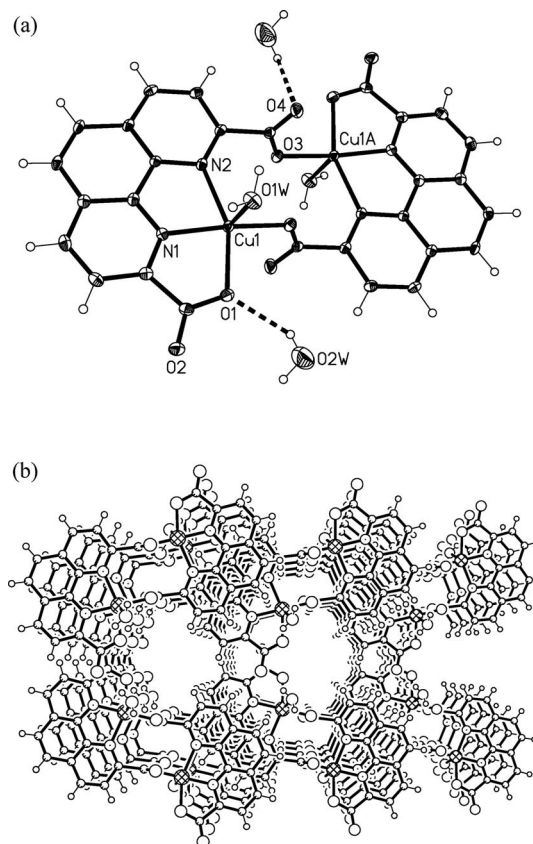


Figure 1. Perspective views of the molecular structure (a) and 3D supramolecular architecture along the *c* axis (b) in **1**; symmetry code: *a* =  $-x + 2, -y, -z + 1$ .

and one lattice water molecule (Figure 2). The Ni1 atom is coordinated in a rare tetragonally compressed geometry with the Ni1–N1 and Ni1–N3 bonds forming the compressed axes with bond lengths of 1.966(2) and 1.964(2) Å, respectively, which are significantly shorter than those of the bond lengths [2.1019(19)–2.233(2) Å] of the Ni1–O/N bonds at the basal positions, mainly owing to the steric hindrance of the neighboring methyl groups.

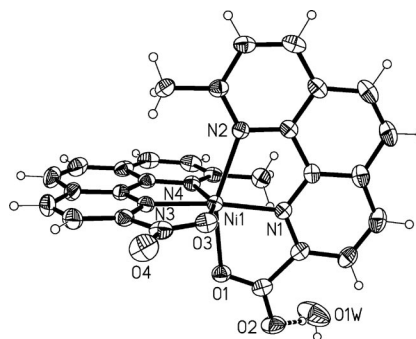


Figure 2. Drawing of the asymmetric unit of compound **2**. The Ni1–N1 and Ni1–N3 bonds are shorter than the others owing to steric hindrance.

By comparison of the coordination fashions and the bond lengths of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  in **1** and **2**, we could see that compound **1** is more slack than compound **2**. When the

first methyl group is oxidized to a carboxyl group, the tight coordination of  $\text{Ni}^{\text{II}}$  with the preformed  $\text{mphen}^-$  ligand leads to steric hindrance and prevents further oxidation of another methyl group.

Complexes **3** and **4** are isomorphic. Both **3** and **4** have a 1D coordination polymer structure with left-handed and right-handed helices. The asymmetric unit of **3** contains two crystallographically unique  $\text{Eu}^{\text{III}}$  atoms, three  $\text{phenda}^{2-}$  ligands, two coordinated water molecules, and three uncoordinated water molecules (Figure 3). Four O atoms and four N atoms from two  $\text{phenda}^{2-}$  ligands complete the coordination sphere of the Eu1 center, which conforms most closely to a dodecahedron [Eu1–O 2.345(3)–2.419(3); Eu1–N 2.530(4)–2.546(3) Å]. The Eu2 center is coordinated to two coordinated water molecules, two N atoms, and four O atoms from three  $\text{phenda}^{2-}$  ligands [Eu2–O 2.344(3)–2.442(3), Eu2–N 2.554(3)–2.565(3) Å]. The Eu atoms and  $\text{phenda}^{2-}$  ligands construct helix chains with  $2_1$  helical axes, which are parallel to the *b* axis (Figure 4a). The whole structure of **3** is racemic due to the packing of different

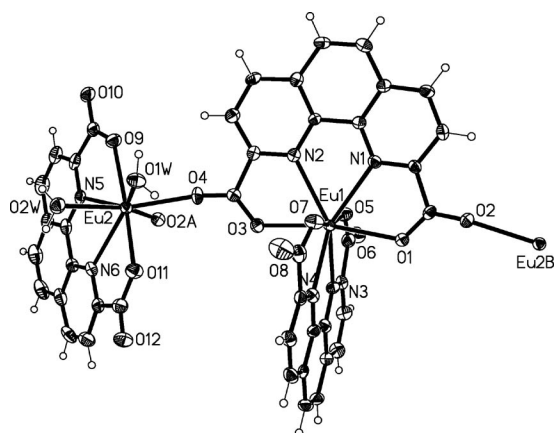


Figure 3. Perspective views of coordination environments of the Eu ions and the coordination modes of the  $[\text{phenda}]^{2-}$  ligands in **3**.

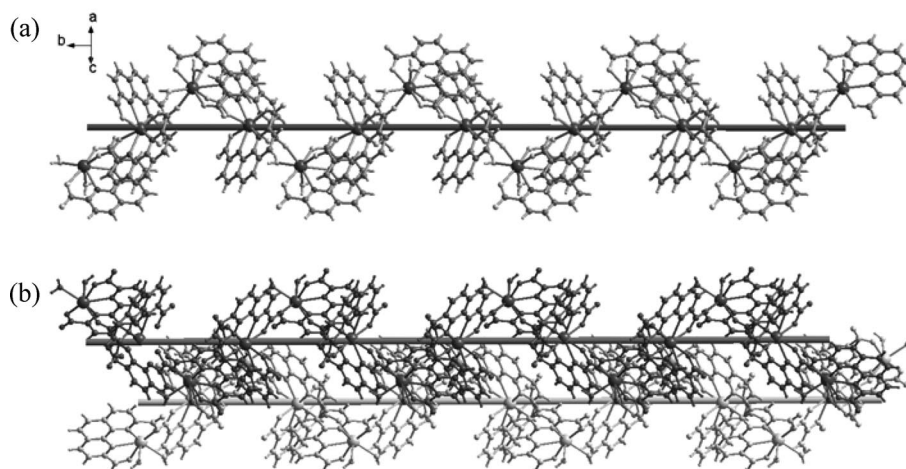


Figure 4. The single  $2_1$  helix chain (a) and the alternate packed right-handed and left-handed helices (b) in **3**. The helical axis is parallel to the *b* axis.

helices, right-handed and left-handed, with an ABAB fashion (Figure 4b).

The solid-state fluorescent properties of as-synthesized **3** and **4** were studied at room temperature, and the XPRD patterns were measured to confirm the purity of the two complexes (Figures S2 and S3, Supporting Information). At room temperature, **3** exhibits strong red fluorescence with an emission maximum at 612 nm upon excitation at 363 nm (Figure 5a). The spectrum of **3** presents three characteristic

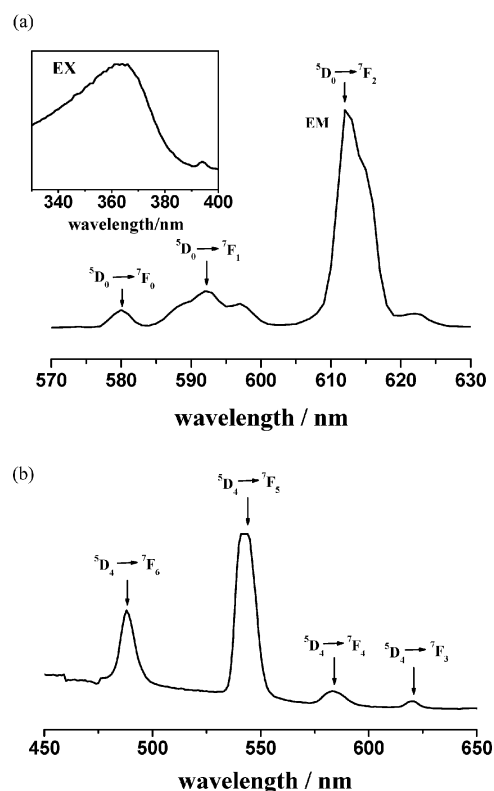


Figure 5. The emission spectra and excitation spectra (inset) of **3** (a) and **4** (b) in the solid state at room temperature.



bands centered at 580, 592, and 612 nm corresponding to radiative transitions from the  $^5D_0$  excited state to the  $^7F_0$ ,  $^7F_1$ , and  $^7F_2$  ground-state manifold, respectively.<sup>[9]</sup> The strongest transition is  $^5D_0 \rightarrow ^7F_2$ , whereas  $^5D_0 \rightarrow ^7F_3$  and  $^5D_0 \rightarrow ^7F_4$  are too weak to show in the picture. The fluorescent spectrum of **4** was not carried out owing to the low yield. At room temperature, **4** emits strong green fluorescence upon excitation at 334 nm (Figure 5b). Two intense emission bands at 488 and 541 nm correspond to  $^5D_4 \rightarrow ^7F_6$  and  $^5D_4 \rightarrow ^7F_5$ , whereas the weaker emission bands at 583 and 620 nm originate from  $^5D_4 \rightarrow ^7F_4$  and  $^5D_4 \rightarrow ^7F_3$ .<sup>[10,11]</sup>

## Conclusions

In this work, we prepared and characterized four complexes with phenda<sup>2-</sup> and mphen<sup>-</sup> ligands generated from the in situ one-step oxidation of 2,9-dimethyl-1,10-phenanthroline. Our results suggest a potential strategy to tune the oxidation products of other organic species by metal coordination under hydrothermal conditions. We are expanding this reactivity to other transition-metal systems and trying to prepare the functional materials with new generated ligands.

## Experimental Section

**1:** A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.8 mmol), 2,9-dimethyl-1,10-phenanthroline (0.2 mmol),  $\text{HNO}_3$  (0.2 mmol), and  $\text{H}_2\text{O}$  (10 mL) was stirred. The mixture was then transferred to a 20-mL Teflon reactor and kept at 180 °C for 3 d under autogenous pressure and then cooled to room temperature. Blue crystals of **1** were obtained. Yield: 0.071 g (97% based on 2,9-dimethyl-1,10-phenanthroline). Compound **1** could also be synthesized from the  $\text{Cu}(\text{NO}_3)_2/\text{HNO}_3/\text{Ar}$  system, which was treated by blowing Ar gas to remove  $\text{O}_2$  from the reaction system.  $\text{C}_{28}\text{H}_{20}\text{Cu}_2\text{N}_4\text{O}_{12}$  (731.58): calcd. C 45.97, H 2.76, N 7.66; found C 45.63, H 2.61, N 7.35. IR (KBr):  $\tilde{\nu}$  = 3458 (s), 3205 (m), 3047 (m), 2356 (w), 1645 (s), 1396 (s), 1174 (s), 821 (m), 626 (w), 597 (m), 501 (m)  $\text{cm}^{-1}$ .

**2:** Synthesized by following a procedure similar to that of compound **1**, except that  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ . Brown crystals of **2** were obtained. Yield: 0.049 g (89% based on 2,9-dimethyl-1,10-phenanthroline). Compound **2** could be also synthesized from the  $\text{Ni}(\text{NO}_3)_2/\text{HNO}_3/\text{Ar}$  system, which was treated by blowing Ar gas to remove  $\text{O}_2$  from the reaction system.  $\text{C}_{28}\text{H}_{20}\text{Ni}_2\text{N}_6\text{O}_{17}$  (551.20): calcd. C 61.01, H 3.66, N 10.16; found C 59.08, H 3.66, N 9.97. IR (KBr):  $\tilde{\nu}$  = 3500 (s), 3421 (m), 3051 (w), 2362 (m), 1623 (s), 1357 (s), 1035 (w), 831 (m), 721 (m), 655 (m), 522 (w)  $\text{cm}^{-1}$ .

**3:** A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.4 mmol), 2,9-dimethyl-1,10-phenanthroline (0.2 mmol),  $\text{Eu}_2\text{O}_3$  (0.1 mmol),  $\text{HNO}_3$  (0.2 mmol), and  $\text{H}_2\text{O}$  (10 mL) was stirred. The mixture was then transferred to a 20-mL Teflon reactor and kept at 180 °C for 3 d under autogenous pressure and then cooled to room temperature. Yellow crystals of **3** were obtained. Yield: 0.093 g (78% based on Eu).  $\text{C}_{42}\text{H}_{28}\text{Eu}_2\text{N}_6\text{O}_{17}$  (1192.63): calcd. C 42.30, H 2.37, N 7.05; found C 41.81, H 2.44, N 6.94. IR (KBr):  $\tilde{\nu}$  = 3454 (s), 3240 (m), 1986 (w), 1598 (s), 1458 (s), 1380 (s), 1269 (s), 1176 (m), 812 (m), 713 (m), 651 (m), 590 (m)  $\text{cm}^{-1}$ .

**4:** Synthesized by following a procedure similar to that of compound **3**, except that  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{Eu}_2\text{O}_3$  and  $\text{HNO}_3$ . Yellow crystals of **4** were obtained. Yield: 0.013 g (23% based on Tb). Compound **4** could not be synthesized from the reaction of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , dmphen,  $\text{Tb}_4\text{O}_7$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{O}$  carried out under the same hydrothermal conditions as that of **3**.

**X-ray Crystallographic Study:** Data were collected with a Bruker SMART Apex CCD diffractometer with graphite-monochromated Mo- $K_\alpha$  radiation (Mo- $K_\alpha$ ,  $\lambda$  = 0.71073 Å). The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  by using SHELXTL.<sup>[12]</sup>

**Crystal and Structure Refinement Parameters:** Compound **1** (123 K):  $\text{C}_{28}\text{H}_{20}\text{Cu}_2\text{N}_4\text{O}_{12}$ ,  $M$  = 731.56, monoclinic, space group  $P2_1/c$  (no. 14),  $a$  = 9.3267(10) Å,  $b$  = 20.2793(19) Å,  $c$  = 6.9133(7) Å,  $\beta$  = 93.725(2)°,  $U$  = 1304.8(2) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{\text{calcd.}}$  = 1.862  $\text{g cm}^{-3}$ ,  $\mu(\text{Mo}-K_\alpha)$  = 1.711  $\text{mm}^{-1}$ . A total of 7686 reflections collected, 2816 independent reflections ( $R_{\text{int}}$  = 0.0339) with 2564 [ $I > 2\sigma(I)$ ] observed data.  $R_1$  = 0.0377 [ $I > 2\sigma(I)$ ],  $wR_2$  = 0.1047 (for all data). Compound **2** (293 K):  $\text{C}_{28}\text{H}_{20}\text{Ni}_2\text{N}_6\text{O}_{17}$ ,  $M$  = 551.19, triclinic, space group  $P\bar{1}$  (no. 2),  $a$  = 7.5752(7) Å,  $b$  = 11.1892(10) Å,  $c$  = 14.9943(14) Å,  $\alpha$  = 75.664(2)°,  $\beta$  = 88.699(2)°,  $\gamma$  = 70.404(2)°,  $U$  = 1157.49(18) Å<sup>3</sup>,  $Z$  = 2,  $\rho_{\text{calcd.}}$  = 1.581  $\text{g cm}^{-3}$ ,  $\mu(\text{Mo}-K_\alpha)$  = 0.889  $\text{mm}^{-1}$ . A total of 7811 reflections collected, 4743 independent reflections ( $R_{\text{int}}$  = 0.0195) with 4141 [ $I > 2\sigma(I)$ ] observed data.  $R_1$  = 0.0496 [ $I > 2\sigma(I)$ ],  $wR_2$  = 0.1287 (for all data). Compound **3** (123 K):  $\text{C}_{42}\text{H}_{28}\text{Eu}_2\text{N}_6\text{O}_{17}$ ,  $M$  = 1192.62, monoclinic, space group  $P2_1/c$  (no. 14),  $a$  = 14.0489(3) Å,  $b$  = 18.5549(5) Å,  $c$  = 15.6531(4) Å,  $\beta$  = 104.023(3)°,  $U$  = 3958.78(17) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd.}}$  = 2.001  $\text{g cm}^{-3}$ ,  $\mu(\text{Mo}-K_\alpha)$  = 3.230  $\text{mm}^{-1}$ . A total of 27491 reflections collected, 8923 independent reflections ( $R_{\text{int}}$  = 0.0426) with 6172 [ $I > 2\sigma(I)$ ] observed data.  $R_1$  = 0.0336 [ $I > 2\sigma(I)$ ],  $wR_2$  = 0.0872 (for all data). Compound **4** (123 K):  $\text{C}_{42}\text{H}_{28}\text{Tb}_2\text{N}_6\text{O}_{17}$ ,  $M$  = 1206.54, monoclinic, space group  $P2_1/c$  (no. 14),  $a$  = 14.0443(4) Å,  $b$  = 18.4893(5) Å,  $c$  = 15.6278(6) Å,  $\beta$  = 104.025(3)°,  $U$  = 3937.1(2) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd.}}$  = 2.036  $\text{g cm}^{-3}$ ,  $\mu(\text{Mo}-K_\alpha)$  = 3.655  $\text{mm}^{-1}$ . A total of 17898 reflections collected, 8724 independent reflections ( $R_{\text{int}}$  = 0.0313) with 5641 [ $I > 2\sigma(I)$ ] observed data.  $R_1$  = 0.0292 [ $I > 2\sigma(I)$ ],  $wR_2$  = 0.0639 (for all data).

CCDC-674097 (for **1**), -674098 (for **2**), -674099 (for **3**), and -674100 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): XPRD patterns of **3** and **4**; 2D stacked layer constructed from **1**; crystal data and structure refinements for **1–4**; selected bond lengths and angles for **1–4**.

## Acknowledgments

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