Supporting Information

One-pot gram-scale rapid synthesis of MN_4 complexes with 14-membered ring macrocyclic ligand as a precursor for carbon-based ORR and CO_2RR catalysts

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General procedure

Experiments were conducted under an Ar atmosphere using Schlenk techniques or in an Ar-filled glovebox. $Co(OTf)_2$ was purchased from STREM Chemicals, Inc. $Cu(OTf)_2$ and $Ni(OTf)_2$ were purchased from Tokyo Chemical Industry Co., Ltd. Ethylene glycol (EG) (dehydrated) and acetone were purchased from FUJIFILM Wako Pure Chemical Corporation. H_2HAM was prepared according to the literature methods.[1] Microwave irradiation was performed by Biotage Initiator. Powder X-ray diffraction (PXRD) was performed at ambient temperature on a Rigaku MiniFlex diffractometer using Cu-Kα radiation with a monochromator. TG-DTA analyses were performed with a Rigaku Thermo plus EVO_2 with a heating rate of 10 °C min^{-1} in air using Al_2O_3 as a reference. Infrared (IR) spectra were recorded on a Shimadzu IRSpirit spectrophotometer. Raman spectra were recorded on a JASCO NRS-5500 spectrophotometer using a 532- or 785-nm laser. Ultraviolet–visible light (UV–vis) absorption spectra were measured in the solid state using a JASCO V-750 spectrophotometer with an integrated sphere. Elemental analyses were performed on a J-Science JM10.

Synthesis of MN_4 complexes (M = Co, Ni, and Cu) 2-4 by microwave irradiation

CoN_4 Complex 2: The reaction vessel was charged with H_2HAM (0.6375 g, 1.65 mmol), $Co(OTf)_2$ (0.5918 g, 1.66 mmol), and ethylene glycol (EG) (15 mL). Subsequently, the reaction vessel was sealed tightly and placed into a microwave synthesis apparatus, Biotage initiator. The temperature was elevated to 200 °C by the irradiation of the microwave, followed by maintaining this temperature for 10 min. After the reaction flask was cooled to room temperature, the solvent was removed by filtration, and the residual solid was washed with acetone. The solid obtained as yellow single crystals was dried under reduced pressure to afford complex **2** (1.1624 g, 1.56 mmol, 95 % yield). Anal. Calcd for $C_{26}H_{14}CoF_6N_6O_6S_2$: C, 42.00; H, 1.90; N, 11.30. Found: C, 41.92; H, 2.22; N, 11.35.

CuN_4 Complex 3: The reaction vessel was charged with H_2HAM (0.6442 g, 1.66 mmol) and $Cu(OTf)_2$ (0.6049 g, 1.67 mmol), and ethylene glycol (EG) (15 mL). Subsequently, it was sealed tightly and placed into a microwave synthesis apparatus, Biotage initiator. The temperature was elevated to 200 °C by the irradiation of the microwave, followed by maintaining this temperature for 10 min. After the reaction flask was cooled to room temperature, the solvent was removed by filtration, and the residual solid was washed with acetone. The solid obtained as yellow single crystals was dried under reduced pressure to afford complex **3** (1.2078 g, 1.61 mmol, 97 % yield). Anal. Calcd for $C_{26}H_{14}CuF_6N_6O_6S_2$: C, 41.74; H, 1.89; N, 11.23. Found: C, 41.71; H, 2.16; N, 11.26.

NiN_4 Complex 4: The reaction vessel was charged with H_2HAM (0.6432 g, 1.66 mmol) and $Ni(OTf)_2$ (0.5968 g, 1.67 mmol), and ethylene glycol (EG) (15 mL). Subsequently, it was sealed tightly and placed into a microwave synthesis apparatus, Biotage initiator. The temperature was elevated to 200 °C by the irradiation of the microwave, followed by maintaining this temperature for 10 min. After the reaction flask was cooled to room temperature, the solvent was removed by filtration, and the residual solid was washed with acetone. The solid obtained as yellow single crystals was dried under reduced pressure to afford complex **4** (1.0561 g, 1.42 mmol, 86 % yield). Anal. Calcd for $C_{26}H_{14}NiF_6N_6O_6S_2$: C, 42.02; H, 1.90; N, 11.31. Found: C, 43.88; H, 2.34; N, 12.01.

Figure S1. Photographs of the MN_4 complexes **2**–**4** obtained by microwave irradiation.

Synthesis of CoN_4 complex 2 by heating using aluminium beads baths

The Schlenk tube was charged with H_2HAM (0.0955 g, 0.27 mmol), $Co(OTf)_2$ (0.1020 g, 0.26 mmol), and ethylene glycol (EG) (5 mL) under an Ar atmosphere. The reaction mixture was heated using an aluminium beads bath under Ar atmosphere. A small amount of the reaction mixture was taken out every few hours and powder X-ray diffraction measurements were performed. After 8 hours, it was observed that the diffraction peaks of H_2HAM disappeared and only the peaks attributable to 2 were observed (Figure S2).

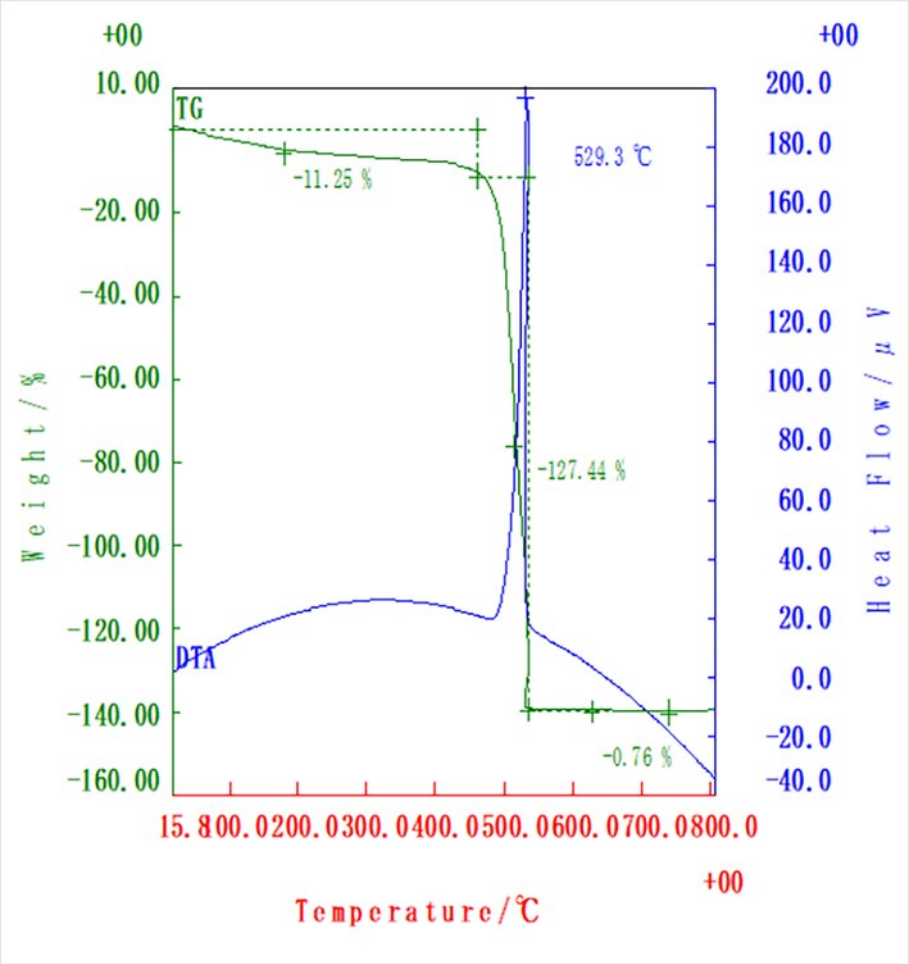

Figure S2. TG-DTA curves of **2**.

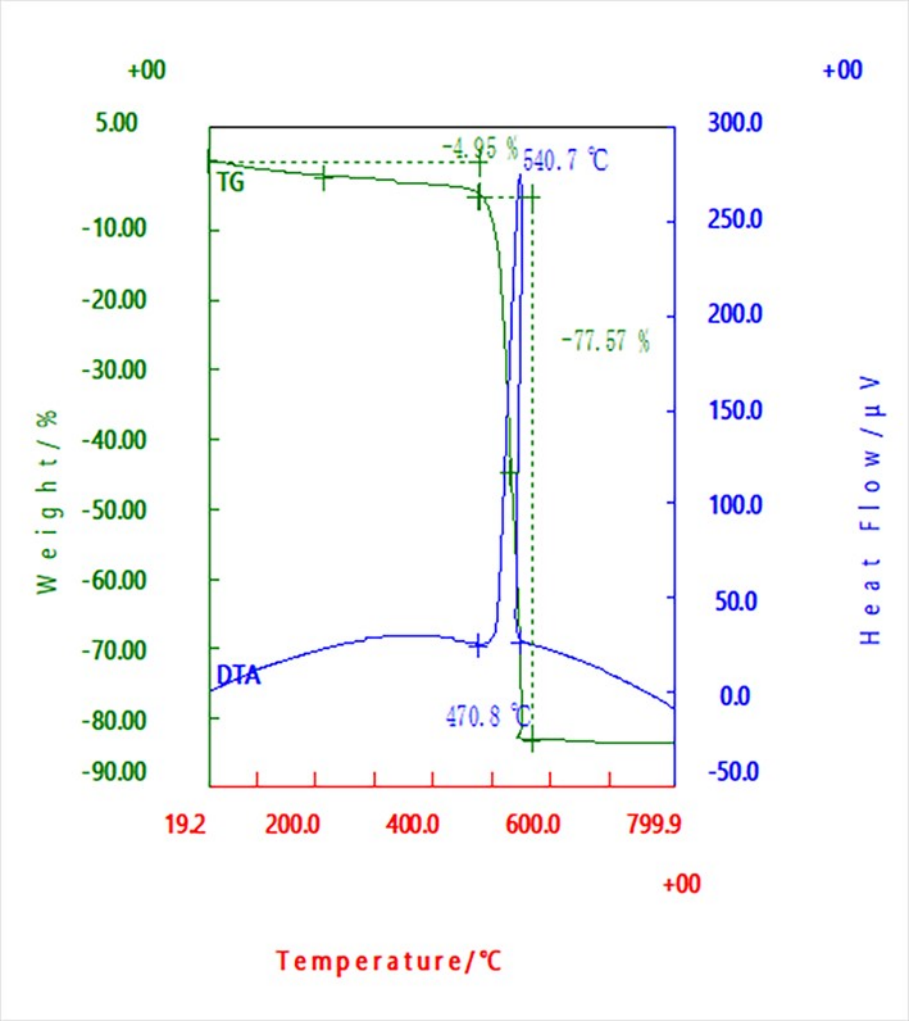

Figure S3. TG-DTA curves of **3**.

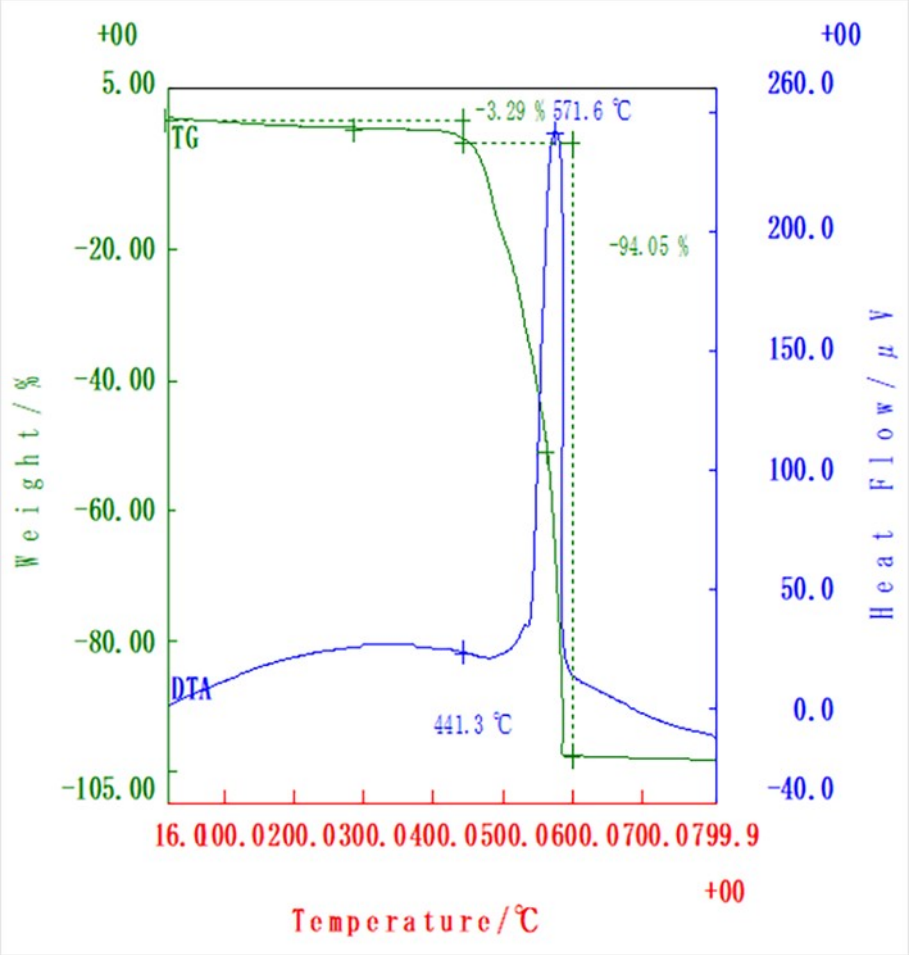

Figure S4. TG-DTA curves of **4**.

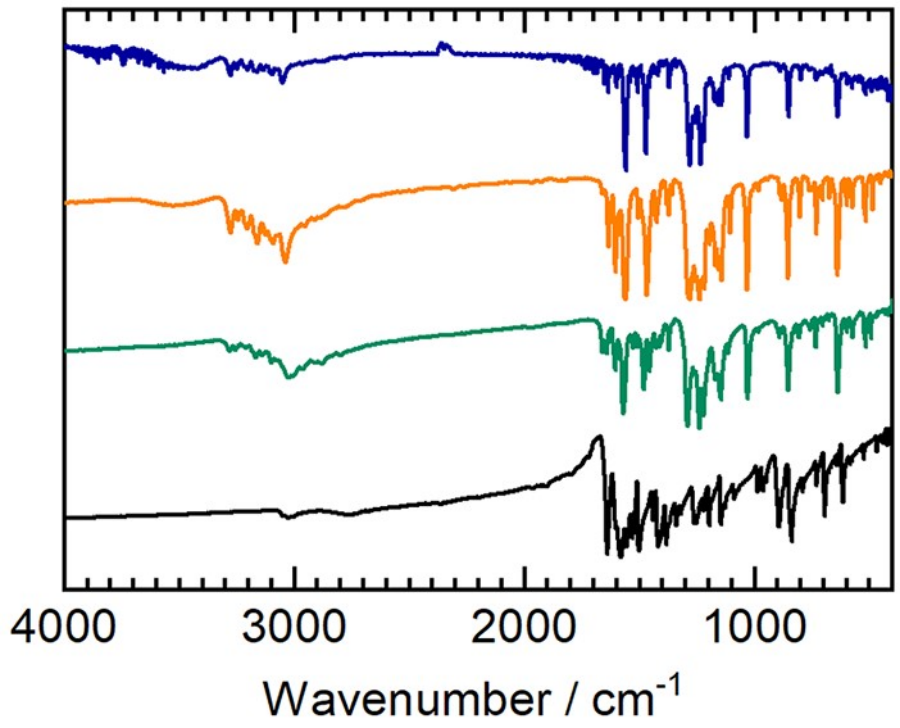

Figure S5. IR spectra of complexes **2**–**4** and H_2HAM. (**2**: navy, **3**: orange, **4**: green, H_2HAM: black).

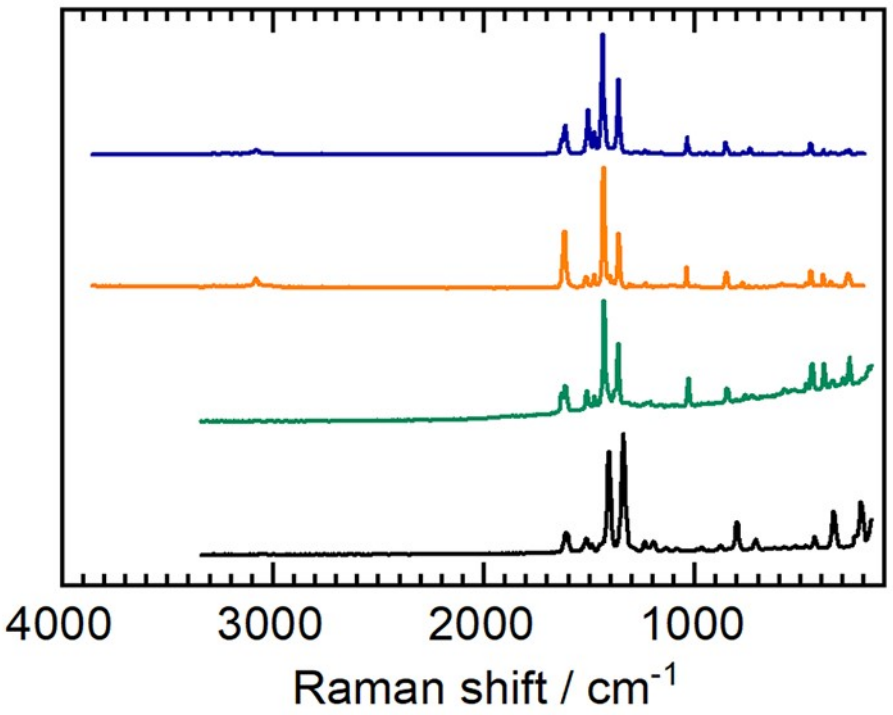

Figure S6. Raman spectra of complexes **2**–**4** and H_2HAM. (**2**: navy, **3**: orange, **4**: green, H_2HAM: black)

Single crystal X-ray diffraction study

Crystallographic structural determination: A Rigaku VariMax Saturn system was employed to collect the crystallographic data (Mo-Kα radiation, 1.2 kW rotating anode) for complexes **2**–**4**.

Crystal data for CoN_4 complex 2: Space group $P2_1/c$, a = 8.5555(3) Å, b = 18.4245(6) Å, c = 8.8580(3) Å, β = 106.596(4), V = 1338.13(8) Å^3, Z = 2, T = −120.0 °C, $\mu(MoK_\alpha)$ = 0.897 mm^{-1}, D_{calc} = 1.845 g/cm$_3$; reflections collected/unique reflections/parameters refined: 18782/3534/218, R_{int} = 0.0362, final R_1 = 0.0509 ($I > 2\sigma(I)$), wR_2 = 0.1269 (all data), and GOF = 1.156.

Crystal data for CuN_4 complex 3: Space group $P2_1/c$, a = 8.5956(2) Å, b = 18.2474(4) Å, c = 8.9518(2) Å, β = 106.020(2) °, V = 1349.54(5) Å^3, Z = 2, T = −120.0 °C, $\mu(MoK_\alpha)$ = 1.063 mm^{-1}, D_{calc} = 1.836 g/cm$_3$; reflections collected/unique reflections/parameters refined: 17249/3486/218, R_{int} = 0.0478, final R_1 = 0.0408 ($I > 2\sigma(I)$), wR_2 = 0.1102 (all data), and GOF = 1.063.

Crystal data for NiN_4 complex 4: Space group $P2_1/c$, a = 8.6317(5) Å, b = 18.0397(10) Å, c = 9.0167(5) Å, β = 105.391(6) °, V = 1353.67(14) Å^3, Z = 2, T = −120.0 °C, $\mu(MoK_\alpha)$ = 0.970 mm^{-1}, D_{calc} = 1.824 g/cm$_3$; reflections collected/unique reflections/parameters refined: 29658/3596/218, R_{int} = 0.0510, final R_1 = 0.0581 ($I > 2\sigma(I)$), wR_2 = 0.1819 (all data), and GOF = 1.064.

CCDC 2300847-2300849 contain the supplementary crystallographic data of 2-4 for this study, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

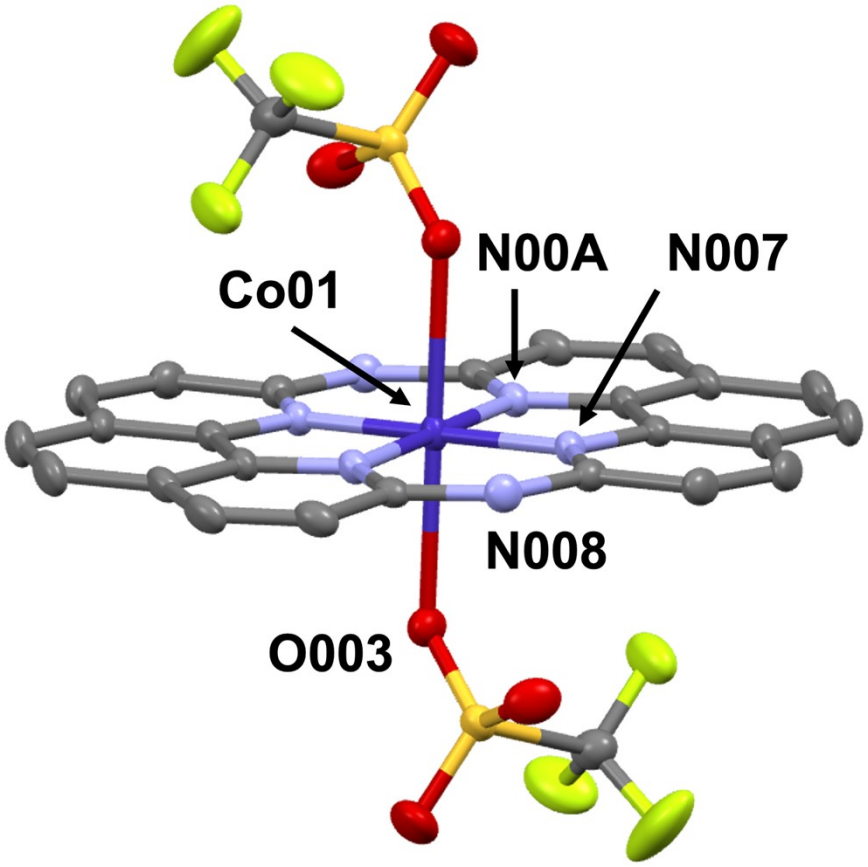

Figure S7. Molecular structure of CoN_4 complex **2** with ellipsoids set to a 50% probability level. Hydrogen atoms are omitted for clarity. Selected atom distances for **2**: Co01–N00A, 1.886(2) Å; Co01–N007, 1.871(2) Å; Co01–O003, 2.424 Å.

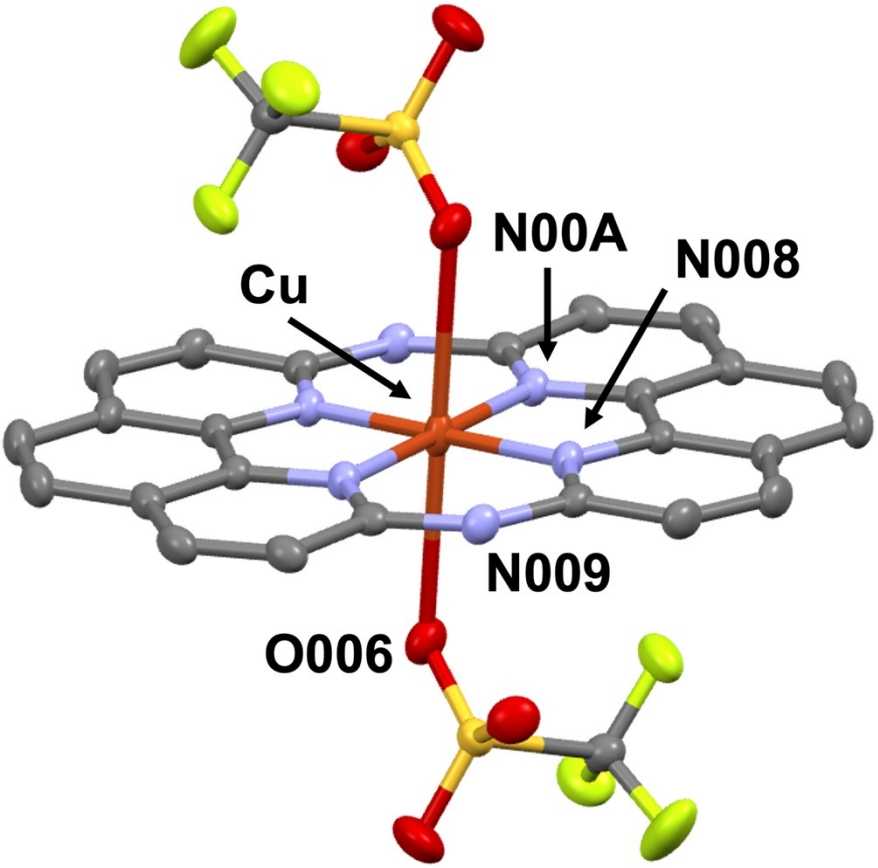

Figure S8. Molecular structure of CuN_4 complex **3** with ellipsoids set to a 50% probability level. Hydrogen atoms are omitted for clarity. Selected atom distances for **3**: Cu–N00A, 1.8992(15) Å; Cu–N008, 1.8984(14) Å, Cu–O006, 2.660 Å.

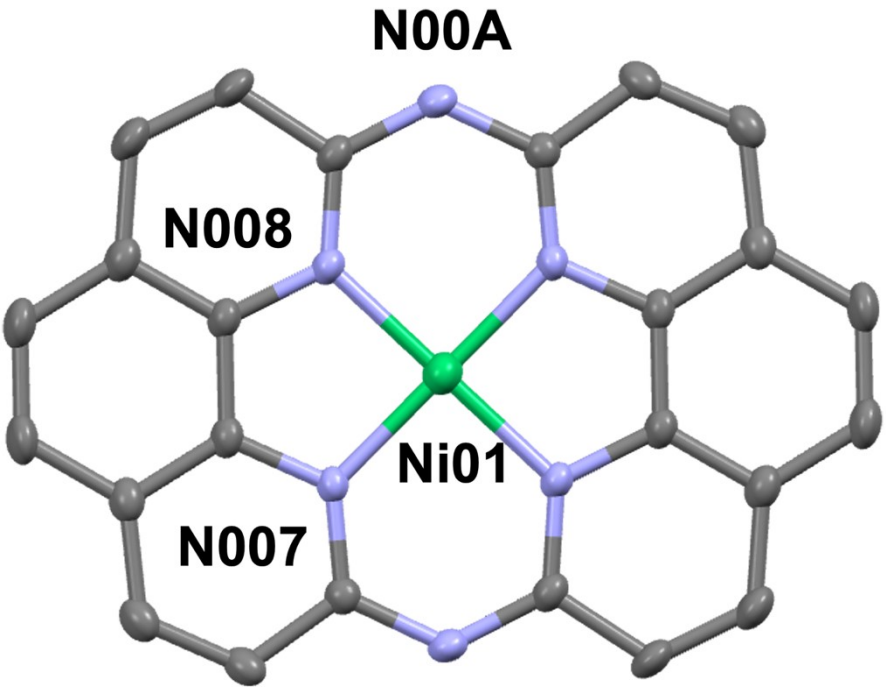

Figure S9. Molecular structure of NiN_4 complex **4** with ellipsoids set to a 50% probability level. Hydrogen atoms are omitted for clarity. Selected atom distances for **4**: Ni01–N007, 1.849(2) Å; Ni01–N008 1.853(2) Å.

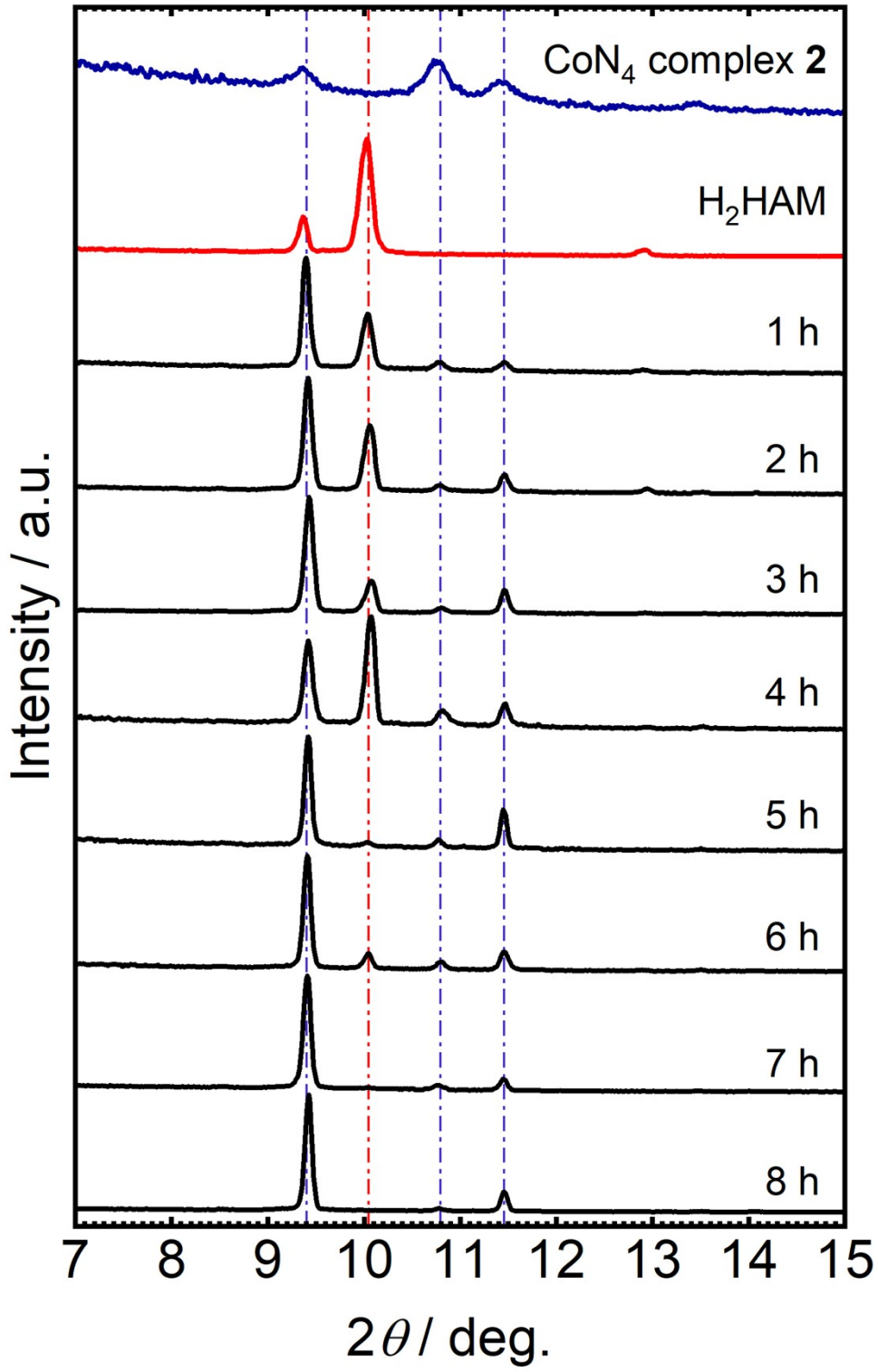

Figure S10. Time course changes of XRD patterns for reaction mixture of H_2HAM and $Co(OTf)_2$ at 120 °C.

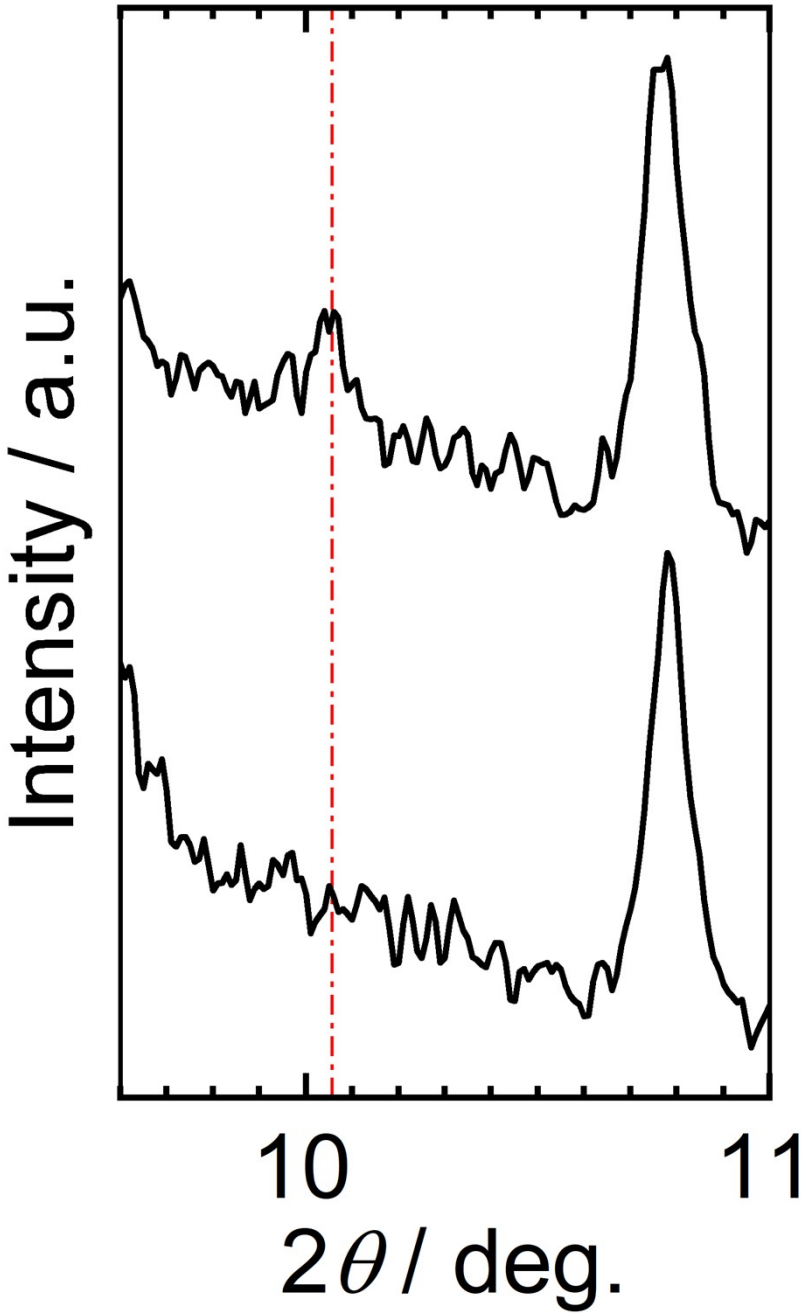

Figure S11. Magnified view of XRD patterns for reaction mixture of H2HAM and Co(OTf)2 at 120 °C for 7 h (top) and 8 h (bottom).

Reference

1. W.-J. Wang, K.-S. Chuang, C.-F. Luo and H.-Y. Liu, *Tetrahedron Lett.*, 2000, **41**, 8565–8568.