Supporting Information

Controlled Self-Assembly of a 2-D Sheet Coordination Polymer and Monomer Containing Eight-Membered Cu_4I_4 Ring Crown Motif

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Contents:

Materials and Methods. All reactions were carried out under an argon atmosphere or in a sealed tube. All reagents were purchased from Sigma-Aldrich Co. LLC. or Wako Pure Chemical Industries, Ltd. FT-infrared spectra were recorded on a Bruker Optics ALPHA FT-IR ATR spectrometer. The high precision isotope peak intensities ratios were determined by Fourier transformation-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) coupled with electron spray ionization (ESI) technique using a SolariX FT-ICR-MS spectrometer (Bruker Daltonics GmbH).

Preparation of $[Na(THF)_4][Na(THF)_3][Ni(mnt)_2Cu_4I_4](THF)$ (4). A suspension of $Na(mnt)_2$ (78.6 mg, 0.37 mmol), $NiCl_2•6H_2O$ (49.4 mg, 0.21 mmol) and CuI (158.5 mg, 0.83 mmol) in THF (20 ml) was stirred for 24 hours under Ar atmosphere at room temp. The resultant solution was filtered and the filtrate was poured into a glass tube. The same amount of ether was added slowly and the tube was sealed. After standing for one week at 10 °C, reddish black plate crystals of $[Na(THF)_4][Na(THF)_3][Ni(mnt)_2Cu_4I_4](THF)$ (**4**) were obtained (91.2 mg, 0.08 mmol, 38.1% based on Ni without solvent). FT-IR (cm^{-1}): 2204 ($\nu_{C\equiv N}$), 1601 ($\nu_{C=C}$); HRMS (ESI-FT-ICR) (*m*/*z*): $[M+H]^+$ calcd for $C_8N_4I_4Cu_4NiNaS_4$ ($Na[Ni(mnt)_2Cu_4I_4]^-$), 1122.160097; found, 1122.173162.

Preparation of $[Na(18\text{-crown-}6)(THF)_2]_2[Ni(mnt)_2Cu_4I_4]$ (5). A suspension of $Na(mnt)_2$ (79.9 mg, 0.43 mmol), $NiCl_2•6H_2O$ (52.1 mg, 0.22 mmol), CuI (159.5 mg, 0.84 mmol), and 18-crown-6 ether (113.7 mg, 0.43 mmol) in THF (20 ml) was stirred for 4 hours at room temp. The resultant solution was filtered and the filtrate was poured into a glass tube. The same amount of ether was added slowly and the tube was sealed. After standing for one week at 10 °C reddish black block crystals of $[Na(18\text{-crown-}6)(THF)_2]_2[Ni(mnt)_2Cu_4I_4]$ (**5**) were obtained (38.2 mg, 0.023 mmol, 10.5% based on Ni without solvent). FT-IR (cm^{-1}): 2209 ($\nu_{C\equiv N}$), 1605 ($\nu_{C=C}$). HRMS (ESI-FT-ICR) (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{24}N_4O_6I_4Cu_4NiNaS_4$ $[Na(18\text{-crown-}6)][Ni(mnt)_2Cu_4I_4]^-$, 1386.31641; found, 1386.31567.

Single crystal X-ray structure analysis. Single crystal x-ray diffraction data were collected at 100 K at the BL02B1 beamline at the SPring-8 synchrotron radiation facility (Hyogo, Japan) for tiny single crystals of complex **4** and **5**. The synchrotron radiation X-ray wavelength of 0.4592 Å for complex **4** and 0.6992 Å for complex **5** was selected with a double Si(311) crystal monochromator; X-ray wavelength calibration was performed with the standard reference material, CeO_2 (NIST 674b). The diffractometer was equipped with Rigaku Mercury2 CCD detector (Rigaku Co. Ltd., Tokyo, Japan). All structures were solved by direct method using SHELXS-2014 for **4** and SHELXT for **5** programs and refined by full-matrix least-squares on F^2 including all reflections by SHELXL-2016. All calculations were performed using the WINGX crystallographic software package. All hydrogen atoms were refined by using the AFIX command. In complex **4**, the disordered copper, iodide atoms, and tetrahydrofuran solvents were restrained to the same thermal displacement parameter and bond length by using the EADP and SADI commands. In complex **5**, the disordered 18-crown-6 molecules and tetrahydrofuran solvents were also restrained to the same thermal displacement parameter and bond length by using the EADP and SADI commands.

Thermogravimetric analysis (TG–DTA). Thermogravimetric analysis (TG–DTA) was carried out with a RIGAKU Thermo Plus 8120 under 20 ml/min flowing N_2 gas for complex **4** and **5** as

shown in Figure S3 and S4, respectively. The temperature was ramped at a rate of 2 °/min from room temperature to 650 K.

Table S1 Crystallographic information of **4** and **5**.

	[Na(THF)$_4$][Na(THF)$_3$] [Ni(mnt)$_2$Cu$_4$I$_4$](THF) (**4**)	[Na(18-crown-6)(THF)$_2$]$_2$ [Ni(mnt)$_2$Cu$_4$I$_4$] (**5**)
Formula	$C_{40}H_{64}N_4O_8I_4Cu_4NiNa_2S_4$	$C_{48}H_{80}N_4O_{16}I_4Cu_4Ni\ Na_2S_4$
Formula weight	1723.64	1963.85
Crystal system	monoclinic	orthorhombic
Space Group	$P2_1/c$ (#14)	$Fdd2$ (#43)
a /Å	13.3223(17)	62.019(8)
b /Å	22.440(3)	17.267(2)
c /Å	20.266(3)	25.293(3)
β/°	98.264(7)	90
V /Å^3	5995.6(13)	27086(6)
Z	4	16
D_{calc} /gcm^{-3}	1.910	1.926
F(000)	3352	15456
Wavelength /Å	0.4592	0.6992
μ /cm^{-1}	11.98	32.14
Temperature /K	100(1)	
Resolution max. / Å	0.77	0.77
Observed reflections	54129 (R_{int}=0.0572)	43875 (R_{int}=0.0595)
Refined reflections	13549	13722
Refined parameters	577	622
R (all data)	0.0867	0. 0687
R_1 (I>2σ(I))	0.0680	0. 0539
wR_2 (all data)	0.1472	0. 1326
GOF	1.218	1. 029
Frack parameter	-	0.068(10)

R=Σ||F_o|−|F_c||/Σ|F_o|. R_1=Σ||F_o|−|F_c||/Σ|F_o| (F_o>4σ(F_o)).
wR_2=[Σ(w(F_o^2–F_c^2)^2/Σw(F_o^2)^2]$^{1/2}$. GOF={Σ[w(F_o^2–F_c^2)^2]/(n–p)}$^{1/2}$.

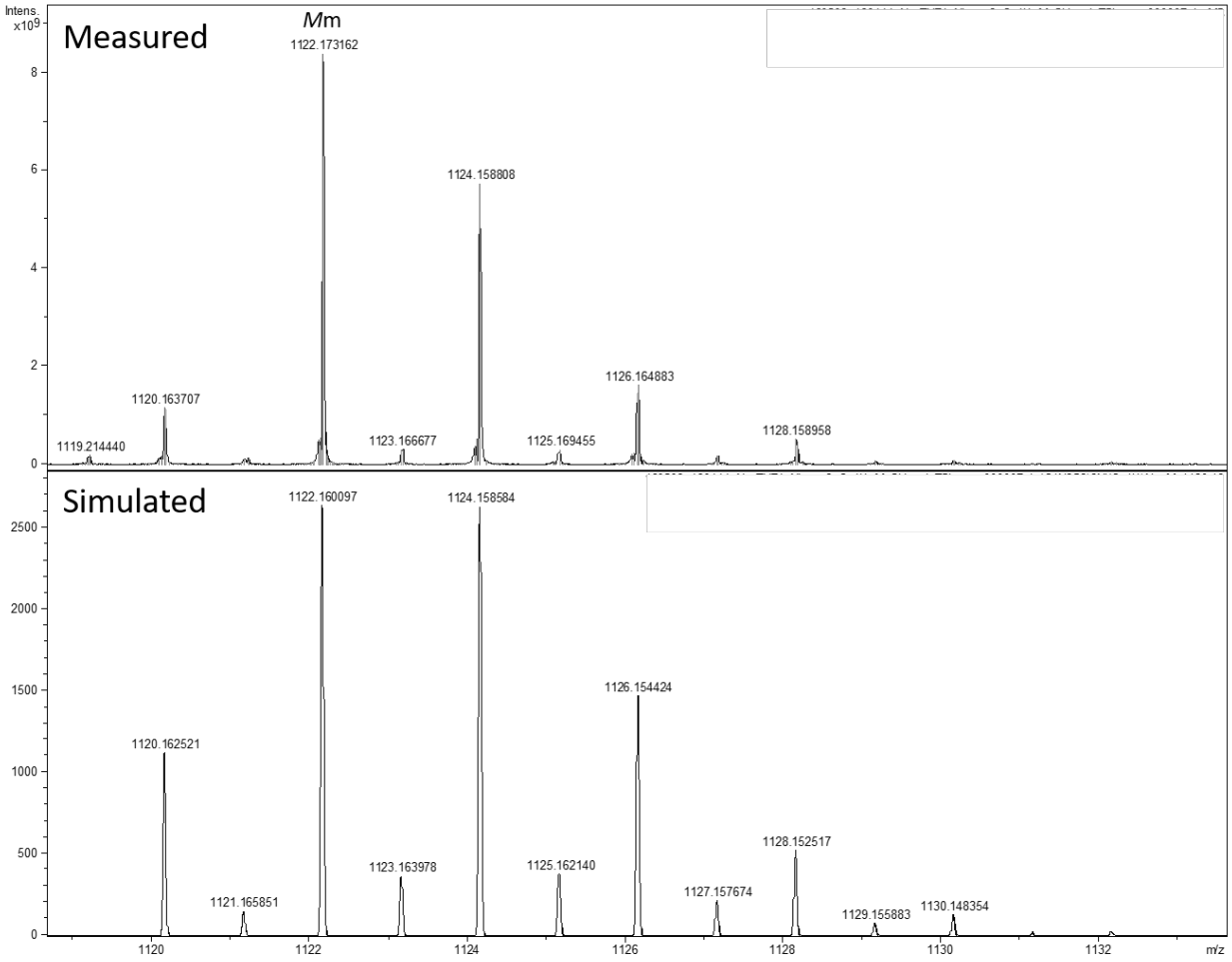

Figure S3. HRMS spectrum of **4**.

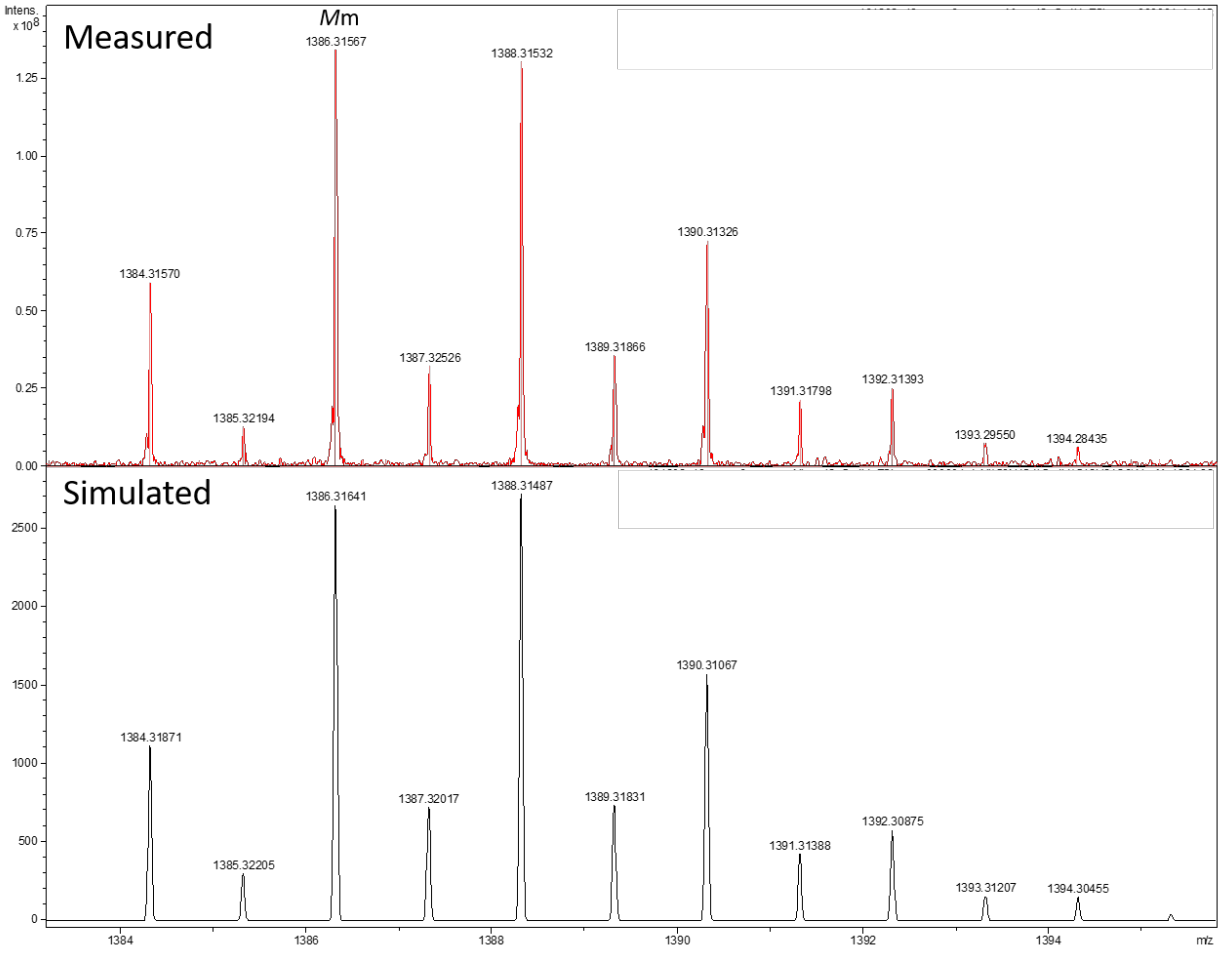

Figure S4. HRMS spectrum of **5**.

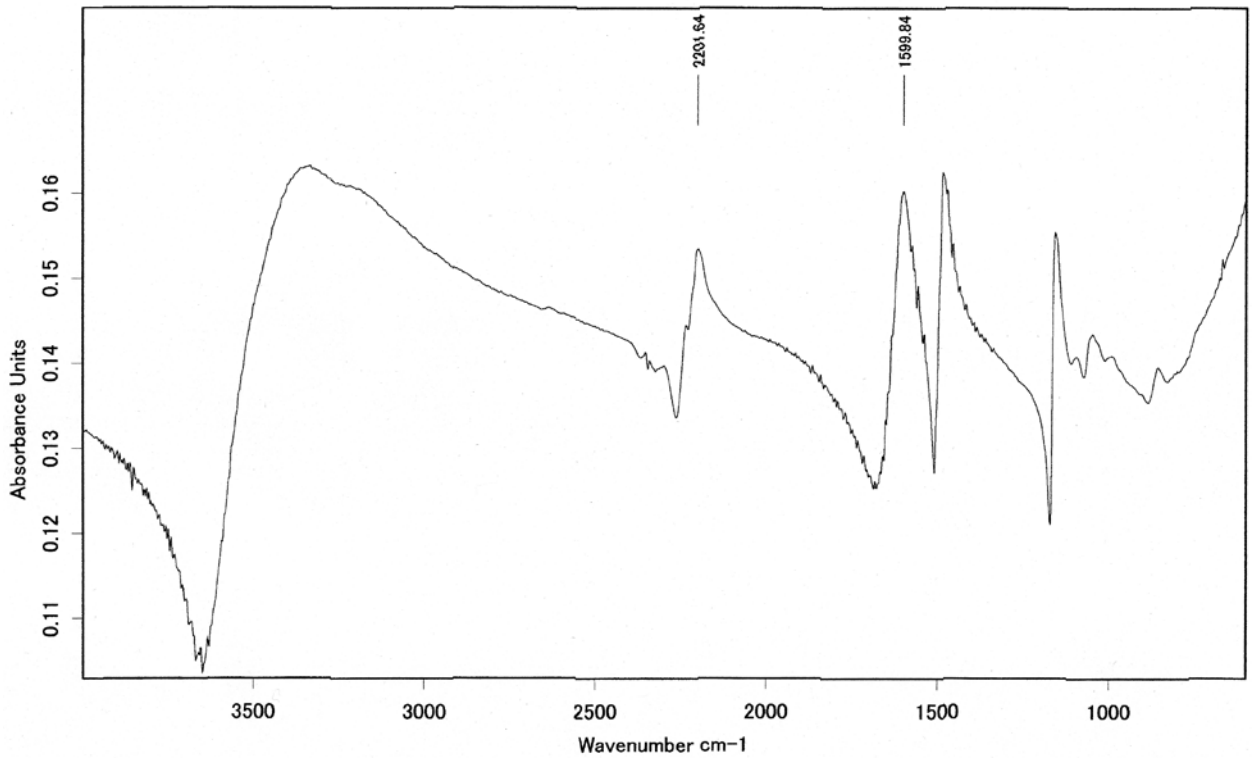

Figure S5. IR spectrum of **4**.

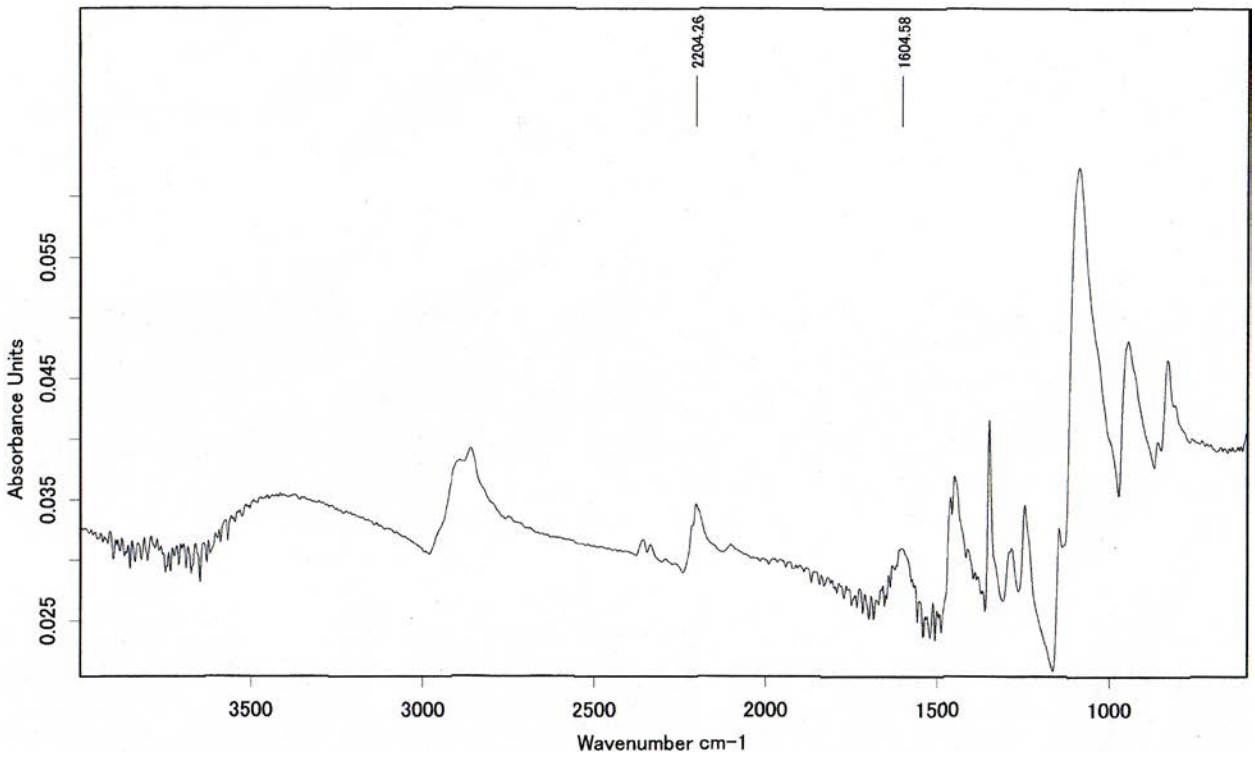

Figure S6. IR spectrum of **5**.

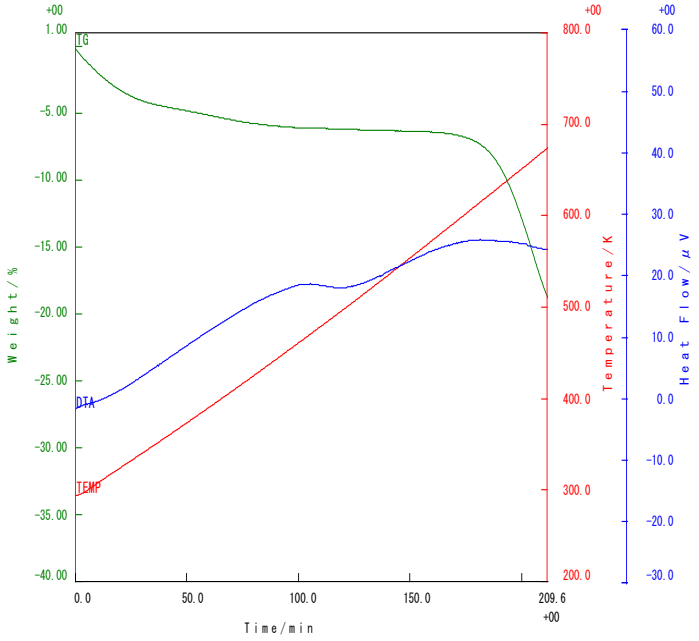

Figure S7. TG-DTA curve of complex **4** under flowing N_2 gas. Green line for TG (%), light blue line for DTA (μV), red line for temperature (K).

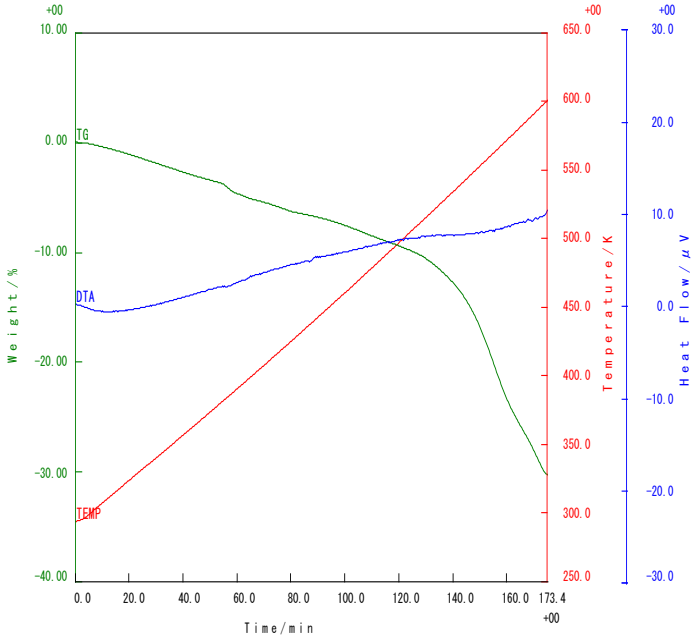

Figure S8. TG-DTA curve of complex **5** under flowing N_2 gas. Green line for TG (%), light blue line for DTA (μV), red line for temperature (K).