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Electronic Supplementary Information

Transformations of empty Cu^{I}_{4} core to $Cu^{I}_{2}Cu^{II}_{2}O$ and $Cu^{I}_{6}S$ cores via oxide and sulfide insertions

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Author Contributions

Y.F. and N.Y. performed the syntheses and the spectroscopic characterization of the compounds; N.Y. performed the single X-ray diffraction analyses and powder X-ray diffraction measurements; K.Y. conducted the X-ray absorption spectral measurements; Y.F., N.Y. and T.K. wrote the manuscript; T.K. conceived and designed the project. All authors discussed the results and commented on the manuscript.

Experimental Procedures

Preparation of $Na_8[Cu_4\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot nH_2O$ ($Na_8[\mathbf{1}]$)

A 0.5 M aqueous NaOH solution was added to a yellow suspension containing Δ-$H_3[Rh(\textsc{l}\text{-cys})_3]$ [S1] (200 mg, 394 μmol) in degassed water (20 mL) until the suspension became a clear yellow solution (pH 5). A solid sample of CuCl (39 mg, 394 μmol) was added. The mixture was stirred at room temperature for 3 h under a N_2 atmosphere, which gave a dark brown solution. After filtration, 40 mL of EtOH was added to the filtrate to afford a brown powder, which was collected by centrifugation and washed with EtOH. Yield 242 mg (87%). Anal. calcd for $Na_8[Cu_4\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot 30H_2O = C_{36}H_{120}Cu_4N_{12}Na_8O_{54}Rh_4S_{12}$: C, 15.33; H, 4.29; N, 5.96%. Found: C, 15.34; H, 4.28; N, 5.86%. ^{1}H NMR in D_2O: δ 2.54 (dd, J_{HH} = 12.2, 2.9 Hz, 12H), 2.88 (t, J_{HH} = 12.7 Hz, 12H) 3.29 (m, 12H). IR, cm^{-1}: 1595(s).

Single crystals of $Na_8[\mathbf{1}]$ suitable for X-ray diffraction analysis were obtained by adding EtOH to the reaction solution.

Preparation of $Na_8[Cu_4O\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot nH_2O$ ($Na_8[\mathbf{2}]$)

A 0.5 M aqueous NaOH solution (6 mL) was added to a yellow suspension containing Δ-$H_3[Rh(\textsc{l}\text{-cys})_3]$ (200 mg, 0.39 mmol) in degassed water (20 mL), which gave a clear yellow solution (pH 12). A solid sample of $CuCl_2$ (53 mg, 0.39 mmol) was added. The mixture was stirred at room temperature for 30 min under a N_2 atmosphere, which gave a dark green solution. After filtration, 25 mL of EtOH was added to the filtrate to afford a dark green powder, which was collected by centrifugation and washed with EtOH and acetone. Yield 35 mg (46%). Anal. calcd for $Na_8[Cu_4O\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot 42H_2O = C_{36}H_{144}Cu_4N_{12}Na_8O_{67}Rh_4S_{12}$: C, 14.17; H, 4.76; N, 5.51%. Found: C, 14.23; H, 4.67; N, 5.46%. ^{1}H NMR ($NaOD/D_2O$): δ 3.02 (d, J_{HH} = 9.3 Hz, 12H), 3.67 (dd, J_{HH} = 12.7, 2.8 Hz, 12H), 23.75 (t, J_{HH} = 12.1 Hz 12H). IR, cm^{-1}: 1589(s).

Single crystals of $Na_8[\mathbf{2}]$ suitable for X-ray diffraction analysis were obtained by diffusing EtOH into a 0.1 M aqueous NaOH solution of the dark green powder.

The exposure of $Na_8[\mathbf{1}]$ dissolved in aqueous NaOH to air gave a dark green solution containing $[\mathbf{2}]^{8-}$, which was confirmed by absorption and ^{1}H NMR spectra (Figure S11).

Preparation of $Na_8[Cu_6S\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot nH_2O$ ($Na_8[\mathbf{3}]$)

An aqueous NaHS solution (0.1 M, 710 μL, 71 μmol) was added to a dark brown solution containing $Na_8[\mathbf{1}]$ (100 mg, 35 μmol) in a degassed aqueous CF_3COONa solution (0.1 M, 20 mL). Stirring the mixture at room temperature for 30 min under N_2 gas gave an orange solution. After filtration, 15 mL of EtOH was added to the filtrate to afford a yellow powder, which was collected by centrifugation and washed with EtOH. Yield: 55 mg (79%). Anal. calcd for $Na_8[Cu_6S\{Rh(\textsc{l}\text{-cys})_3\}_4]\cdot 29H_2O = C_{36}H_{118}Cu_6N_{12}Na_8O_{53}Rh_4S_{12}$: C, 14.60; H, 4.02; N, 5.68%. Found: C, 14.56; H, 3.88; N, 5.61%. ^{1}H NMR ($NaOD/D_2O$): δ 2.69 (t, J_{HH} = 12.4 Hz, 12H), 2.75 (dd, J_{HH} = 12.1, 3.9 Hz, 12H), 3.26 (dd, J_{HH} = 12.6, 4.2 Hz, 12H). IR, cm^{-1}: 1595(s).

Single crystals of $Na_8[\mathbf{3}]$ suitable for X-ray diffraction analysis were obtained by diffusing EtOH vapour into the reaction solution.

Physical Measurements

Absorption spectra were recorded with a JASCO V-660 spectrophotometer at room temperature. IR spectra were measured with a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks. ^{1}H NMR spectra were recorded with a JEOL ECAMX-500SP spectrometer. Sodium 4,4-dimethyl-4-silaphentane-1-sulfonate (DSS) was used as an internal reference. All measurements were carried out at the probe temperature. Elemental analysis (C, H, N) was performed on a YANACO CHN Corder MT-5, and X-ray fluorescence analyses were conducted using a Shimadzu EDX-7000 spectrometer. X-ray absorption spectroscopy (XAS) measurements were carried out at BL-11 of the Synchrotron Radiation Center at Ritsumeikan University, Japan. XAS spectra at 300 K were obtained in partial fluorescence yield (PFY) mode by using a large-area silicon drift detector capturing photon-energy-dependent luminescence. We confirmed the data reproducibility with neither serious radiation damage nor sample-position dependence of XAS spectra from the repeated measurements on the same and different sample positions. The measurement was supported by the Project for Creation of Research Platforms and Sharing of Advanced Research Infrastructure, Japan (Proposal No. S18004).

Quantitative ^{23}Na NMR analysis

The numbers of Na^+ ions in Na_8[**1**] and Na_8[**2**] were determined by the ^{23}Na NMR measurements. The ^{23}Na NMR spectra were recorded with a JEOL ECAMX-400SP spectrometer in D_2O. A 100 mM NaCl/D_2O solution was used as an external reference of the chemical shift. For the quantitative elemental analysis of Na^+, a series of NaCl solutions in D_2O with different concentrations (0 mM, 20.06 mM, 40.12 mM, 80.24 mM) were prepared and measured as the standard samples. The peak height at δ 4.0 ppm and the Na^+ concentration showed an excellent linear regression coefficient ($R = 0.9997$). Based on the regression coefficient, the concentrations of Na^+ ions (C_{Na}) in unknown sample solutions were determined. The C_{Na} value was divided by the concentration of sample solution to give the number of Na^+ ions per formula.

Finally, the evaluated Na^+ numbers were 8.3±0.3 for Na_8[**1**] and 7.7±0.2 for Na_8[**2**], which matched well with the proposed formula.

Magnetic Measurements

Magnetic measurements for Na_8[**1**], Na_8[**2**] and Na_8[**3**] were carried out using a Quantum-Design MPMS XL7AC SQUID magnetometer. Crystalline samples were packed in a hand-made aluminium sample holder and fixed in a plastic straw. Magnetic moment data were corrected for the contribution of the sample holder and the straw. The molar susceptibility data were corrected for the diamagnetic contribution (χ_{dia}) by the equation $\chi_{\mathrm{dia}} = -1/2 \times \mathrm{M} \times 10^{-6}$ emu/mol.

For Na_8[**1**] and Na_8[**3**], the samples were loaded into the magnetometer, which was set at 300 K, and then the temperature-dependent magnetic susceptibility measurement progressed from 5 K to 300 K at a magnetic field of 5000 Oe. The $\chi_{\mathrm{M}}T$ versus T plots are shown in Figure S2.

For Na_8[**2**], the sample was loaded into the magnetometer at 150 K to prevent sample decomposition, and then sequential temperature-dependent magnetic susceptibility measurements (i) progressed from 5 K to 300 K, (ii) from 300 K to 350 K and (iii) from 350 K to 5 K at a magnetic field of 5000 Oe. The data for process (i) were analysed using the PHI program. [S2] The data were fitted to a theoretical curve based on the Hamiltonian $\widehat{H} = -2J\mathbf{S_1}\cdot\mathbf{S_2} + g\beta\mathrm{H}(\mathbf{S_1}+\mathbf{S_2})$, where J is the isotropic exchange constant between two $\mathrm{Cu^{II}}$ centres in the ^2E_g ground state ($S = 1/2$, $L = 0$) and g is Landé's factor. The fraction of monomeric magnetic impurities (ρ) was also considered. The best-fit parameters were $J = -260.7(11)$ cm^{-1}, g = 2.240(12) and $\rho = 0.0423(5)$ with a coefficient of determination (R^2) of 0.9981. The experimental and simulated $\chi_{\mathrm{M}}T$ versus T plots are illustrated in the same chart in Figure 2.

Single-crystal X-ray Analysis

Single-crystal X-ray analysis for Na_8[**1**] was performed using a RIGAKU XtaLAB Synergy Custom X-ray diffractometer equipped with a Hypix-6000HE hybrid photon counting detector and a Rigaku VariMax rotating-anode X-ray source with a Mo-target ($\lambda = 0.71075$ Å). Single-crystal X-ray analyses for Na_8[**2**] and Na_8[**3**] were carried out using a PILATUS3 X CdTe 1M detector with a synchrotron X-ray source ($\lambda = 0.4126$ Å) at the

BL02B1 beamline in SPring-8. The synchrotron radiation experiments were performed at the BL02B1 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2020A0603 and 2020A1213).

For all the crystals, the intensity data were collected in ω scan mode, and empirical absorption corrections were applied. The structures of the complexes were solved by a direct method using SHELXS-2018.[S3] The structure refinements were carried out using full-matrix least-squares in SHELXL-2018/1.[S3] All calculations were performed using the Yadokari-XG software package.[S4] All the nonhydrogen atoms were refined anisotropically. The crystallographic data are summarised in Table S1.

For Na_8[**1**], there is one-third of the complex anion and eight-thirds sodium cations in the asymmetric unit. All the H atoms were placed at the calculated positions using a riding model. RIGU restraints were applied to model parts of L-cys ligands. ISOR restraints were applied for Na atoms. Four kinds of revel B alerts are found in the CheckCIF report. The alerts relating to the U_{eq} are caused by the disordered Na^+ cations, and the alert of the Flack parameter is due to the limited crystal quality.

For Na_8[**2**], there is one-third of the complex anion and eight-thirds sodium cations in the asymmetric unit. All the H atoms were placed at the calculated positions using a riding model. FLAT and RIGU restraints were applied to model parts of carboxylate groups. ISOR restraints were applied for Na atoms. Two kinds of revel B alerts are found in the CheckCIF report. The alert relating to the U_{eq} are caused by the disordered Na^+ cations, and the alert of the low precision of C-C bonds is caused by the vibration of carboxylate of C atoms.

For Na_8[**3**], the asymmetric unit contains one complex anion. The contributions of Na^+ cations and solvated H_2O molecules were excluded using the SQUEEZE program in the PLATON software package.[S5] All the H atoms were placed at the calculated positions using a riding model. Two L-cys ligands and one Rh atom (Rh3) were disordered over two positions with site occupancies of 0.5. The disordered part was modelled using FLAT and DFIX restraints. A global RIGU and two ISOR restraints were applied. Three kinds of revel B alerts are found in the CheckCIF report. The alert relating to the Hirshfeld test is due to the low standard deviation of the heavy atom position, and the alert of the low U_{eq} for C30 is caused by the vibration of neighbouring carboxy O atoms (O19, O20). In addition, the beam-stop hid several low angle reflections, leading to the revel B alert because the unit cell is relatively large.

The X-ray crystallographic coordinates of the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2064378-2064380. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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S1. T. Konno, K. Okamoto, J. Hidaka, *Inorg. Chem.* 1994, **33**, 538-544.

S2: N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*, 2013, **34**, 1164.

S3. G. M. Sheldrick, *Acta Cryst*. 2015, **A71**, 3-8.

S4. C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *Nihon Kessho Gakkaishi* 2009, **51**, 218-224.

S5. A. L. Spek, *Acta Crystallogra.* 2015, **C71**, 9-18.

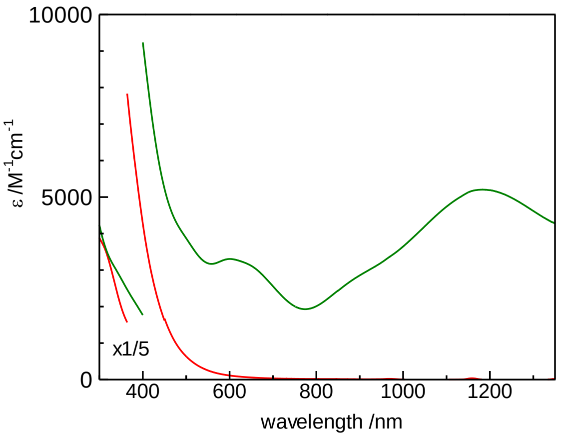

Figure S1. Absorption spectra of Na_8[**1**] in water (red) and Na_8[**2**] (green) in 0.1 M aqueous NaOH. Absorption maxima for Na_8[**2**]: 600 nm ($\varepsilon = 3300\ M^{-1}cm^{-1}$), 1183 nm ($\varepsilon = 5170\ M^{-1}cm^{-1}$).

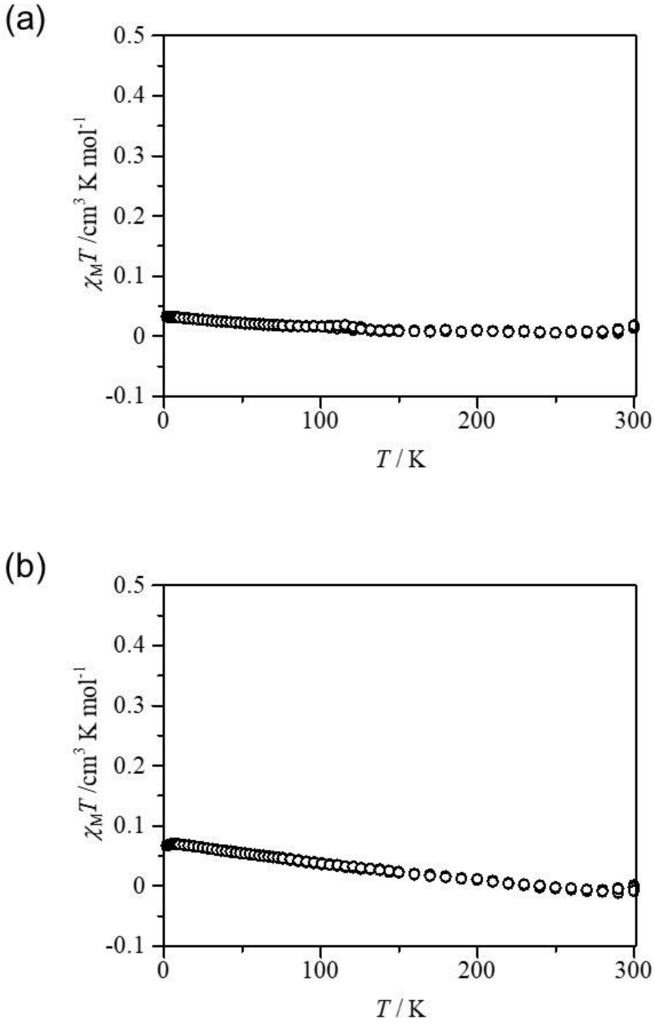

Figure S2. $\chi_M T$ versus *T* plots for (a) Na_8[**1**] and (b) Na_8[**3**].

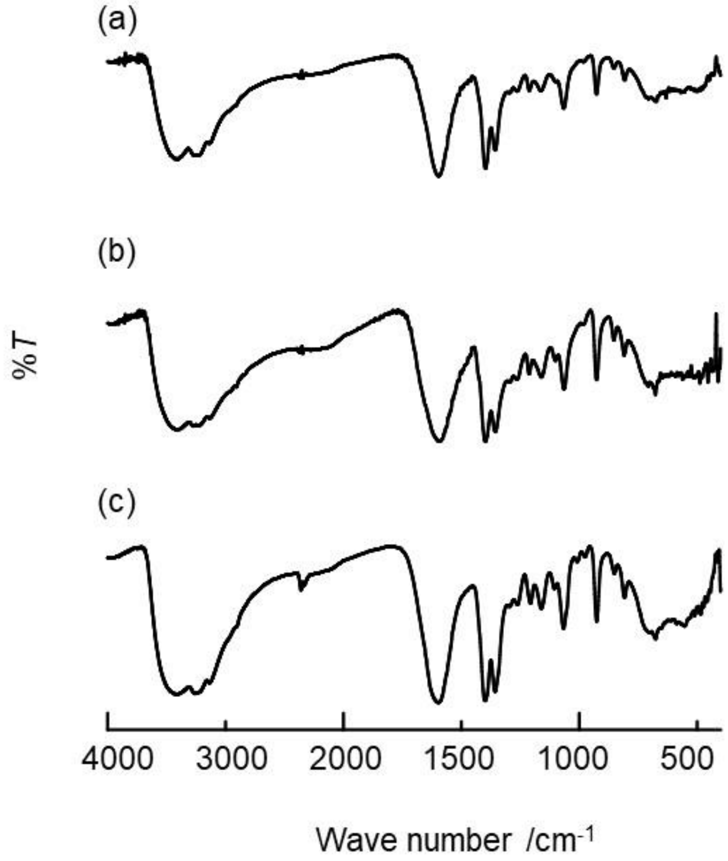

Figure S3. IR spectra of (a) Na_8[**1**], (b) Na_8[**2**] and (c) Na_8[**3**].

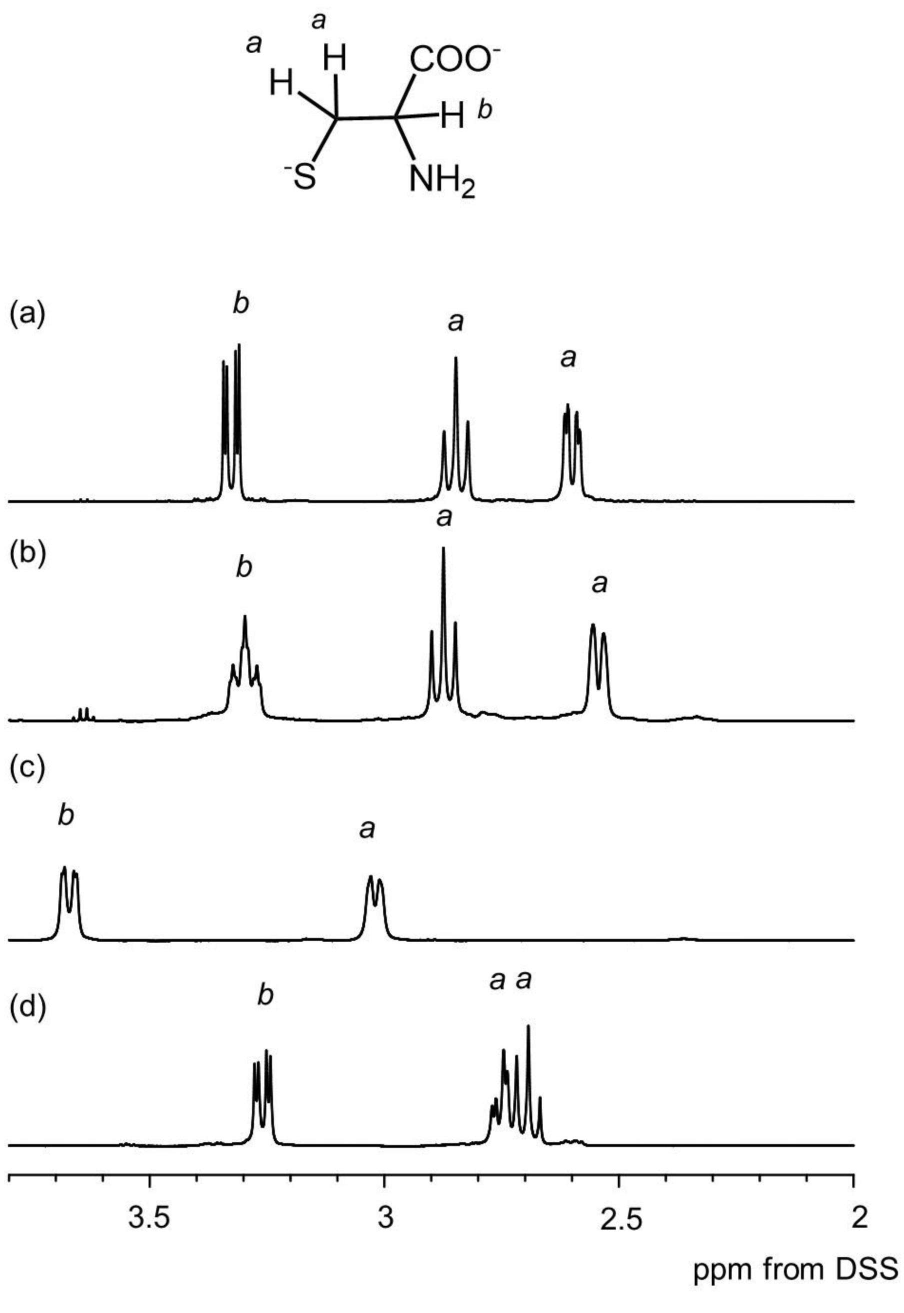

Figure S4. ^{1}H NMR spectra of (a) $Na_8[Ag_4\{Rh(\text{L-cys})_3\}_4]$ in NaOD/D_2O,[17] (b) $Na_8[\mathbf{1}]$ in D_2O, (c) $Na_8[\mathbf{2}]$ in NaOD/D_2O and (d) $Na_8[\mathbf{3}]$ in D_2O.

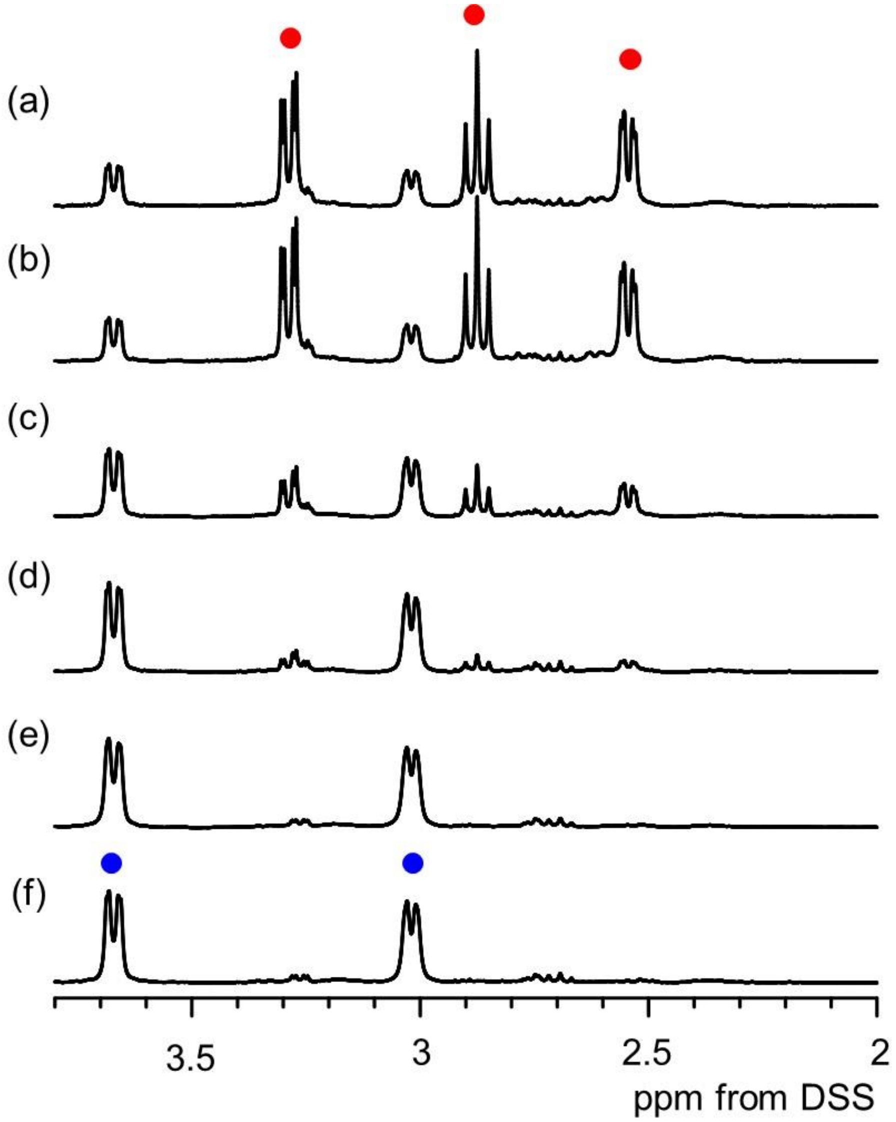

Figure S5. Time-dependent ^{1}H NMR spectra of Na_8[**1**] in NaOD/D_2O. The spectra were recorded after (a) 1 min, (b) 20 min, (c) 1 h, (d) 3 h, (e) 6 h, (f) and 12 h.

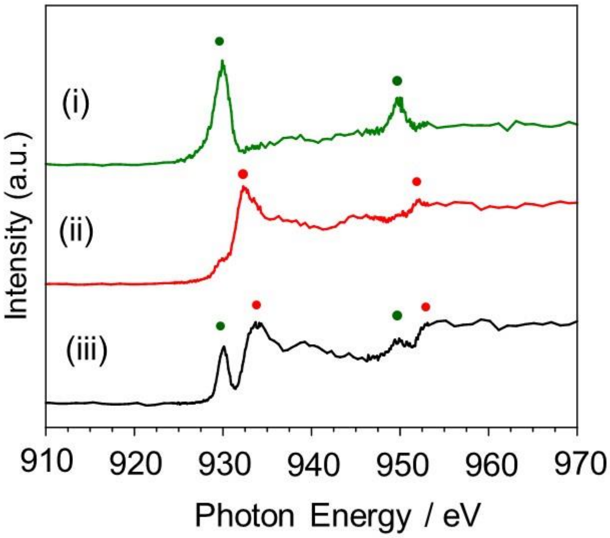

Figure S6. Cu L-edge X-ray absorption spectra of (i) CuO, (ii) Cu_2O and (iii) Na_8[**2**].

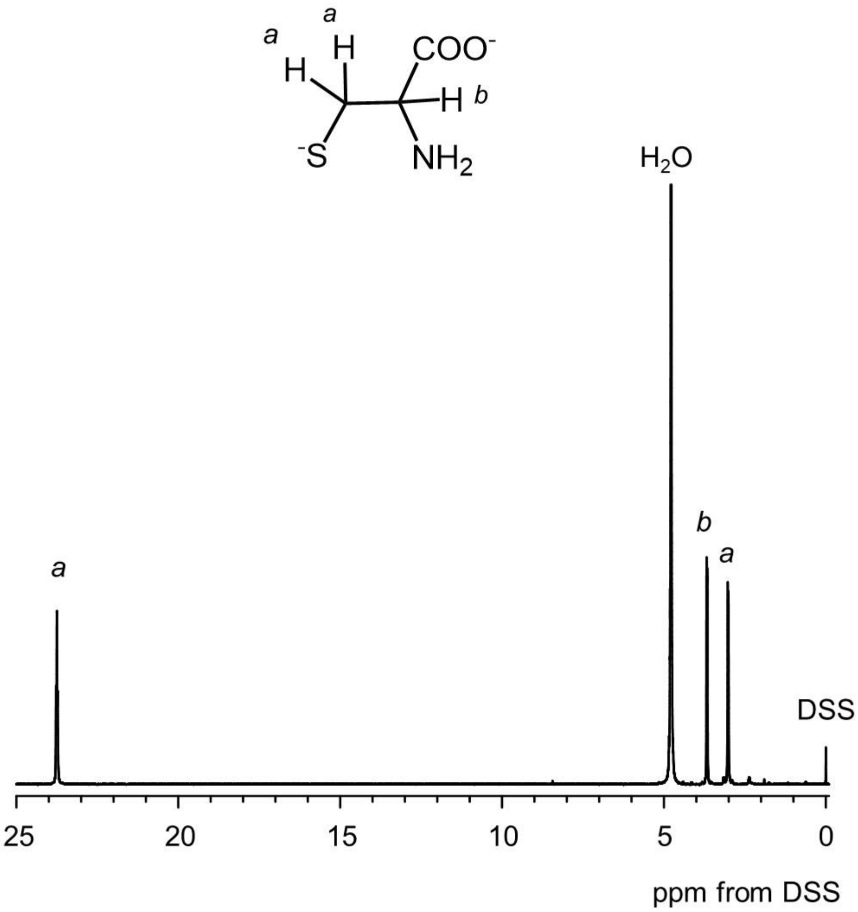

Figure S7. ^{1}H NMR spectrum of Na_8[**2**] in NaOD/D_2O in an expanded chemical shift range.

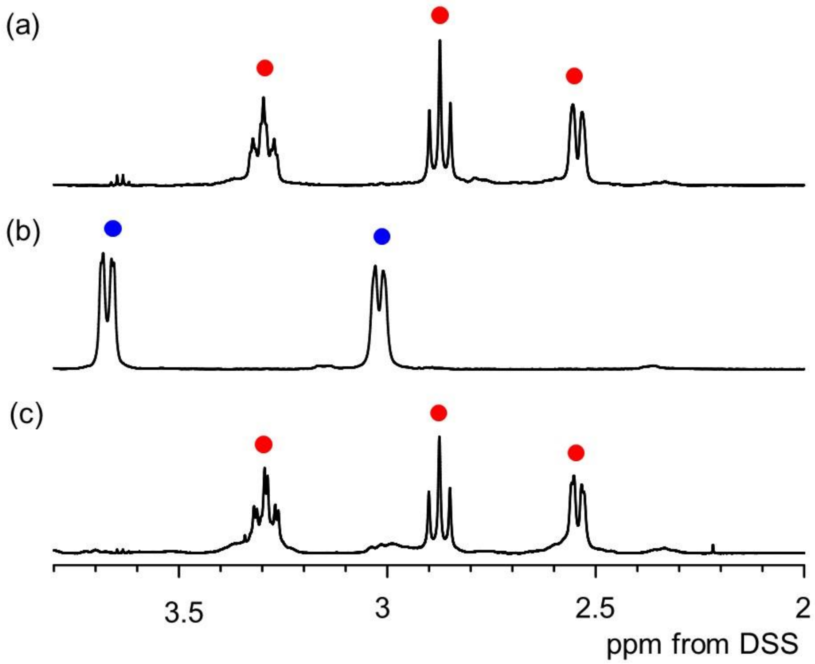

Figure S8. ^{1}H NMR spectra of (a) Na_8[**1**] in D_2O, (b) Na_8[**2**] in NaOD/D_2O and (c) Na_8[**2**] sample after magnetic measurement in D_2O.

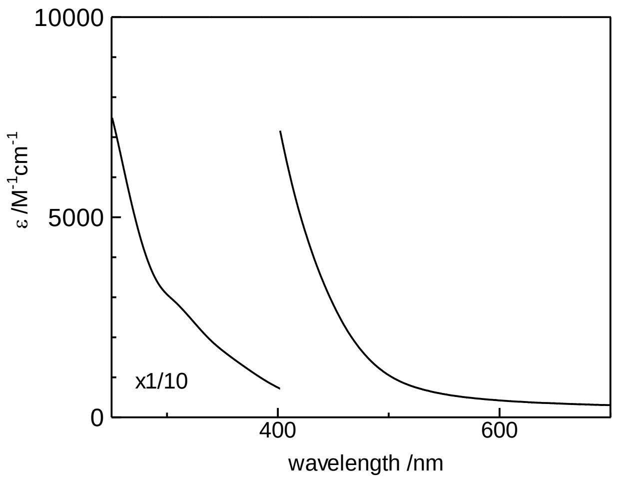

Figure S9. Absorption spectrum of Na_8[**3**] in water.

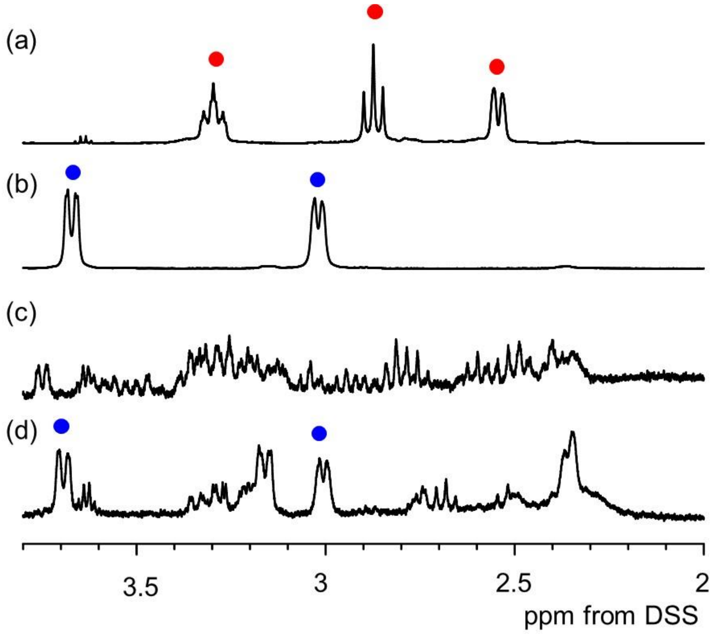

Figure S10. ^{1}H NMR spectra of (a) Na_8[**1**] in D_2O, (b) Na_8[**2**] in NaOD/D_2O, (c) the reaction solution of Na_8[**1**] with H_2O_2 in NaOD/D_2O for 1 h, and (d) the solution of Na_8[**1**] in NaOD/D_2O stood in an N_2O atmosphere for 1 h.

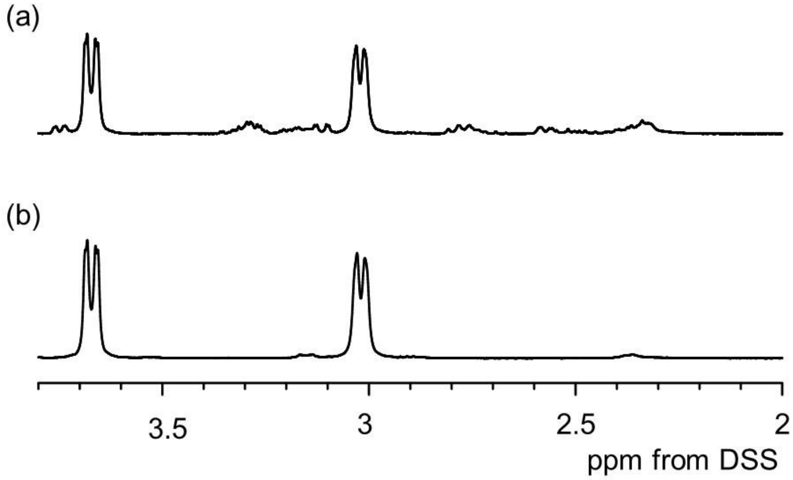

Figure S11. ^{1}H NMR spectra of $Na_8[\mathbf{2}]$ in NaOD/D_2O. (a) The sample prepared by the air-oxidation of $Na_8[\mathbf{1}]$ and (b) the sample prepared from the 1:1 reaction of $Cu^{II}Cl_2$ and H_3L^{Rh}.

Table S1. Crystallographic data for Na$_8$[**1**], Na$_8$[**2**] and Na$_8$[**3**].

	Na$_8$[**1**]	Na$_8$[**2**]	Na$_8$[**3**]
wavelength, λ/Å	0.71073	0.4126	0.4126
empirical formula	$C_{36}H_{60}Cu_4N_{12}$ $Na_8O_{24}Rh_4S_{12}$	$C_{36}H_{60}Cu_4N_{12}$ $Na_8O_{25}Rh_4S_{12}$	$C_{36}H_{60}Cu_6N_{12}Na_3$ $O_{36}Rh_4S_{13}$
Fw	2279.40	2295.40	2515.59
size/mm^3	0.20×0.20×0.12	0.15×0.13×0.08	0.10×0.10×0.05
colour	dark-red	dark-green	yellow
shape	block	block	plate
crystal system	cubic	cubic	monoclinic
space group	$P2_13$	$P2_13$	$P2_1$
a/Å	23.5649(2)	23.6536(15)	15.6933(3)
b/Å			29.5973(4)
c/Å			15.8253(3)
β/°			119.634(2)
V/Å^3	13085.7(2)	13234(3)	6389.1(2)
Z	4	4	2
T/K	123(2)	100(2)	100(2)
R(int)	0.0253	0.0834	0.0795
ρ_{calcd}/g cm^{-3}	1.064	1.060	1.308
μ (Mo Kα), mm^{-1}	1.361	0.878	0.946
θ_{Max}/°	30.712	14.391	23.569
no. of total reflections	24032	83360	261534
no. of unique reflections	10371	8124	77119
no. of parameters	304	316	1117
no. of restraints	78	80	1198
Flack parameter	0.023(6)	0.046(7)	0.023(4)
R_1 (I>2σ(I)) [a]	0.0384	0.0592	0.0651
Rw [b]	0.1151	0.1792	0.1583
Goodness of fit	0.996	0.980	0.983
CCDC No.	2064378	2064379	2064380

[a] $R = \Sigma|(|F_o|–|F_c|)|/\Sigma(|F_o|)$. [b] $Rw = [\Sigma w(Fo_2–Fc_2)^2/\Sigma w(Fo_2)^2]^{1/2}$.