

## Electronic Supplementary Information (ESI)

Hydrogen-bonded metallocsupramolecular helices composed of a nona-protonated spherical  $\text{Rh}^{\text{III}}_4\text{Zn}^{\text{II}}_4$  cluster with twelve carboxylate arms

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## Experimental Section.

### Materials.

The cluster compounds,  $K_6[Rh_4Zn_4O(L-cys)_{12}] \cdot 47.5H_2O$  ( $K_6[1] \cdot 47.5H_2O$ ) and  $H_6[Rh_4Zn_4O(L-cys)_{12}] \cdot 15H_2O$  ( $H_6[1] \cdot 15H_2O$ ), were prepared according to the literature procedures.<sup>S1</sup> Other chemicals were of commercial grade and used without further purification.

### Preparation of compounds.

#### Preparation of $[H_9Rh_4Zn_4O(L-cys)_{12}]Br_3$ (**2**).

To a solution containing  $K_6[1] \cdot 47.5H_2O$  (100 mg, 31  $\mu$ mol) in water (20 mL) was added an aqueous HBr (1 M, 2.5 mL) solution slowly. The reaction mixture initially gave a suspension, which turned to a yellow solution (pH 1.5) at the end. The yellow solution was allowed to stand at room temperature for 2 days, which gave yellow needle crystals of **2**. The crystals were collected by filtration and washed with water. Yield: 29 mg (36%). Anal. Calcd for  $[H_91]Br_3 \cdot 13H_2O = C_{36}H_{95}N_{12}O_{38}S_{12}Rh_4Zn_4Br_3$ : C, 16.62; H, 3.68; N, 6.46 %. Found: C, 16.66; H, 3.68; N, 6.41%. IR (KBr disk,  $cm^{-1}$ ): 1724 (COOH), 1594 (COO<sup>-</sup>).

#### Preparation of $[H_9Rh_4Zn_4O(L-cys)_{12}](HSO_4)_3$ (**3**).

To a solution containing  $K_6[1] \cdot 47.5H_2O$  (100 mg, 31  $\mu$ mol) in water (20 mL) was added an aqueous  $H_2SO_4$  (1 M, 2.5 mL) solution slowly. The reaction mixture initially gave a suspension, which turned to a yellow solution (pH 1.3) at the end. The yellow solution was allowed to stand at room temperature for 2 days, which gave yellow block crystals of **3**. The crystals were collected by filtration and washed with water. Yield: 52 mg (63%). Anal. Calcd for  $[H_91](HSO_4)_3 \cdot 14H_2O = C_{36}H_{94}N_{12}O_{51}Rh_4S_{15}Zn_4$ : C, 16.22; H, 3.55; N, 6.31%. Found: C, 16.26; H, 3.68; N, 6.34%. IR (KBr disk,  $cm^{-1}$ ): 1718 (COOH), 1603 (COO<sup>-</sup>), 1110 (S–O).

### Physical measurements

Diffuse-reflectance spectra were recorded with a JASCO V-670 UV/VIS/NIR spectrometer at room temperature. The circular dichroism (CD) spectra in the solid state were performed on a JASCO J-820 spectropolarimeter at room temperature. The IR spectra were recorded with a JASCO FT/IR-4100 infrared spectrometer using KBr disks at room temperature. Elemental analyses (C, H, N) were performed at Osaka University using a Yanaco CHN Corder MT-5. The sorption isotherms for ammonia were obtained with a BELSORP-max volumetric adsorption instrument after the pretreatment under vacuum at room temperature for 6 hours. High-quality powder X-ray diffractions were recorded at room temperature, in transmission mode [synchrotron radiation  $\lambda = 0.999139(2)$  Å;  $0^\circ \leq 2\theta \leq 78^\circ$ ; step width = 0.005°; data collection time = 1 min] on a diffractometer equipped with a

MYTHEN microstrip X-ray detector (Dectris Ltd.) at the SPring-8 BL02B2 beamline.<sup>S2</sup> The crystals were loaded into glass capillary tubes (diameter = 0.3 mm), and the samples were rotated during the measurements. The diffraction data were collected with a large Debye-Scherrer camera. The powder simulation patterns were generated from the single-crystal X-ray structures using the Mercury 4.1.3 software.<sup>S3</sup> The thermogravimetry analyses were carried out by a SHIMADZU DTG-60. The data are shown in Figure S5.

#### **Proton conductivity measurements.**

The AC impedance measurements were carried out on a WR6430B LCR meter connected to a sample holder (Toyo Technica SH-Z type) with gold-coated electrodes (10.0 mm diameter) by a four-probe method. The samples for measurements were prepared by compressing 70 – 100 mg of compounds into the disks with steel cells (inner diameter 11 mm). The thickness of the disk-sample was measured with a micrometer equipped on the sample holder. The temperature and humidity were adjusted by ESPEC SH-242. The conductivity values were determined as follows. For the circle-shaped part of Nyquist plot (the real part of impedance vs. the imaginary one), the curve fitting of the equation  $(x-(R/2))^2 + ay^2 = (R/2)^2$ , where  $R$  corresponds to the resistance, was applied. The conductivity  $\sigma$  was gained from the relationship  $\sigma = l/SR$ , where  $l$  represents the thickness of samples and  $S$  represents the section area of electrodes.

#### **X-ray crystallography.**

The synchrotron X-ray diffraction study of **2** and **3** was carried out at the BL02B1 beamline in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) with a diffractometer equipped with a Rigaku Mercury 2 CCD detector or a PILATUS3 X CdTe 1M. The intensity data were collected in  $\omega$  scan mode, and empirical absorption corrections were applied. The structures of the complexes were solved by a direct method using SHELXS-2014.<sup>S4</sup> The structure refinements were carried out using full-matrix least-squares using SHELXL-2014.<sup>S4</sup> All calculations were performed using the Yadokari-XG software package.<sup>S5</sup>

For **2**, two carboxy groups (C15/O9/O10, C18/O11 O12), two Br<sup>-</sup> ions (Br1, Br2), and several water molecules were disordered. The disordered carboxy groups were modeled using DFIX, RIGU and ISOR instructions. All the non-hydrogen atoms except O atoms of disordered H<sub>2</sub>O molecules were refined anisotropically, while other atoms were refined isotropically. H atoms except those of water molecules were placed at the calculated positions and refined using riding models. The position of H atoms of COOH groups was decided based on the C–O bond distances and the neighboring hydrogen bond acceptors. The crystal structure possesses a large void space in a hydrogen-bonded porous supramolecular structure composed of [H<sub>3</sub>Rh<sub>4</sub>Zn<sub>4</sub>(L-cys)<sub>12</sub>O]<sup>3+</sup> clusters. The void space should be filled by the solvated water molecules based on the elemental analysis data. However, they are severely

disordered and only several solvated water molecules could be modeled in the void space. At this stage, the  $R1$  ( $I > 2\sigma(I)$ ) and  $wR2$  (all data) values were 0.0515 and 0.1429, respectively. The crystal data were treated by the SQUEEZE in the PLATON package.<sup>S6</sup> The SQUEEZE report indicated the void volume of 4498 Å<sup>3</sup> per cell, which is occupied by 1439 electrons. Their contribution was excluded for the final refinements, which provides  $R1$  ( $I > 2\sigma(I)$ ) and  $wR2$  (all data) values of 0.0428 and 0.1012, respectively. After the removal of water molecules from the crystal structure, the crystal data were treated by VOIDS program of Mercury 4.1.3.<sup>S3</sup> The VOIDS report indicates the solvent-accessible volume of 8791.61 Å<sup>3</sup> per cell, corresponding to the 45.5% of unit cell volume of **2**.

For **3**, one of the L-cys ligands and one of the HSO<sub>4</sub><sup>-</sup> ions, besides several water molecules, were disordered. The disordered L-cys ligand was modeled using FLAT, DFIX, and SIMU instructions. The disordered HSO<sub>4</sub><sup>-</sup> ions were modeled using DFIX, SADI, and SIMU instructions. All the non-hydrogen atoms except O atoms of disordered HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>O molecules were refined anisotropically, while other atoms were refined isotropically. H atoms except those of water molecules were placed at the calculated positions and refined using riding models. The position of H atoms of COOH and HSO<sub>4</sub><sup>-</sup> was decided based on the C–O bond distances and the neighboring hydrogen bond acceptors. After the removal of water molecules from the crystal structure, the crystal data were treated by VOIDS program of Mercury 4.1.3.<sup>S3</sup> The VOIDS report indicates the solvent-accessible volume of 3429.10 Å<sup>3</sup> per cell, corresponding to the 17.4% of unit cell volume of **2**.

S1 N. Yoshinari, S. Yamashita, Y. Fukuda, Y. Nakazawa, T. Konno, *Chem. Sci.* 2019, **10**, 587-593.

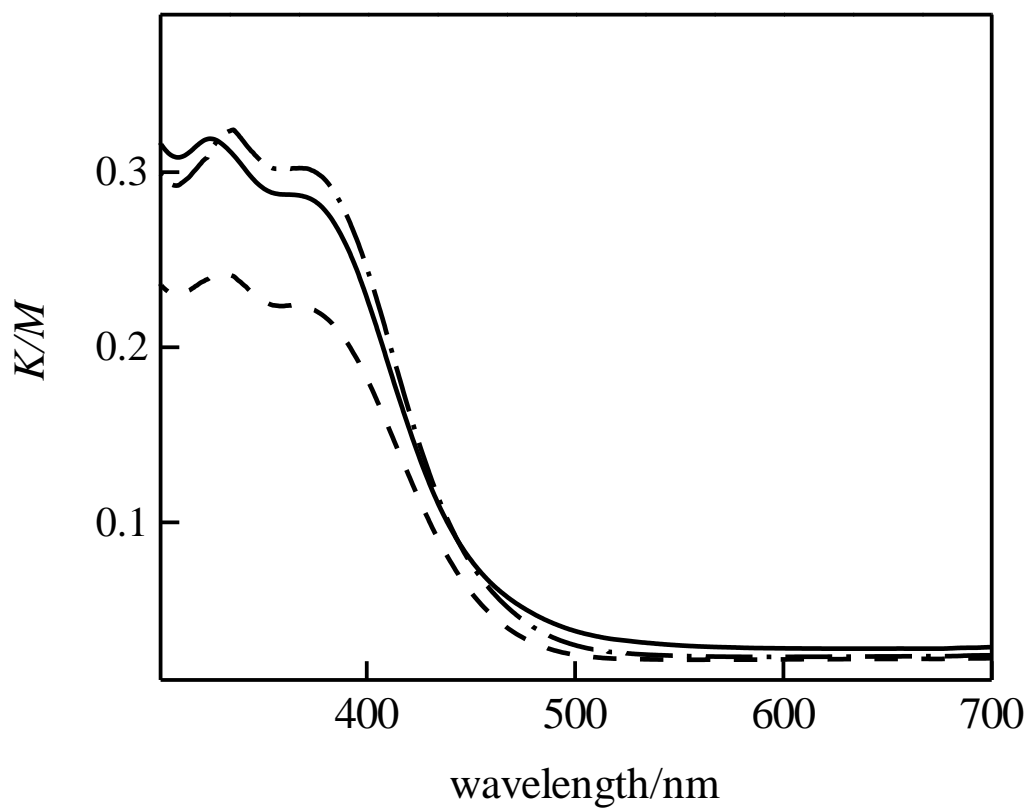
S2 S. Kawaguchi, M. Takemoto, K. Osaka, E. Nishibori, C. Moriyoshi, Y. Kubota, Y. Kuroiwa, K. Sugimoto, *Rev. Sci. Instrum.* 2017, **88**, 085111.

S3 C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst.* 2020, **53**. Doi: 10.1107/S1600576719014092.

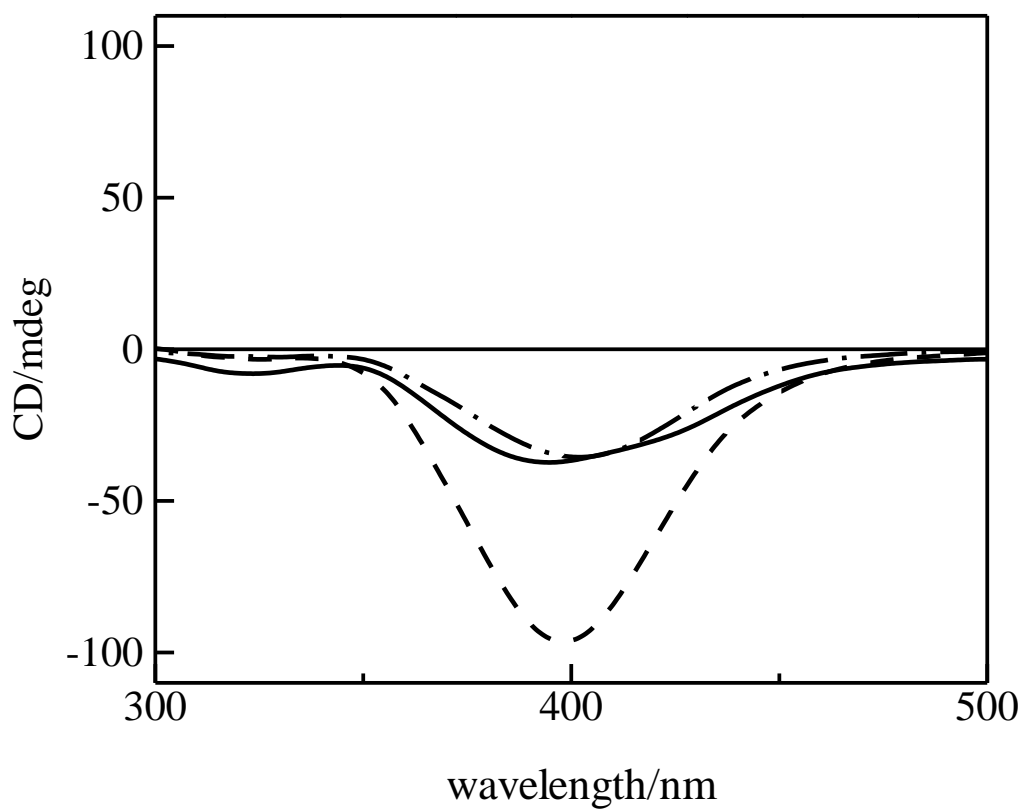
S4 G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8.

S5 C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Yadokari-XG 2009, Program for the Refinement of Crystal Structures, Nihon Kessho Gakkaishi*, 2009, **51**, 218.

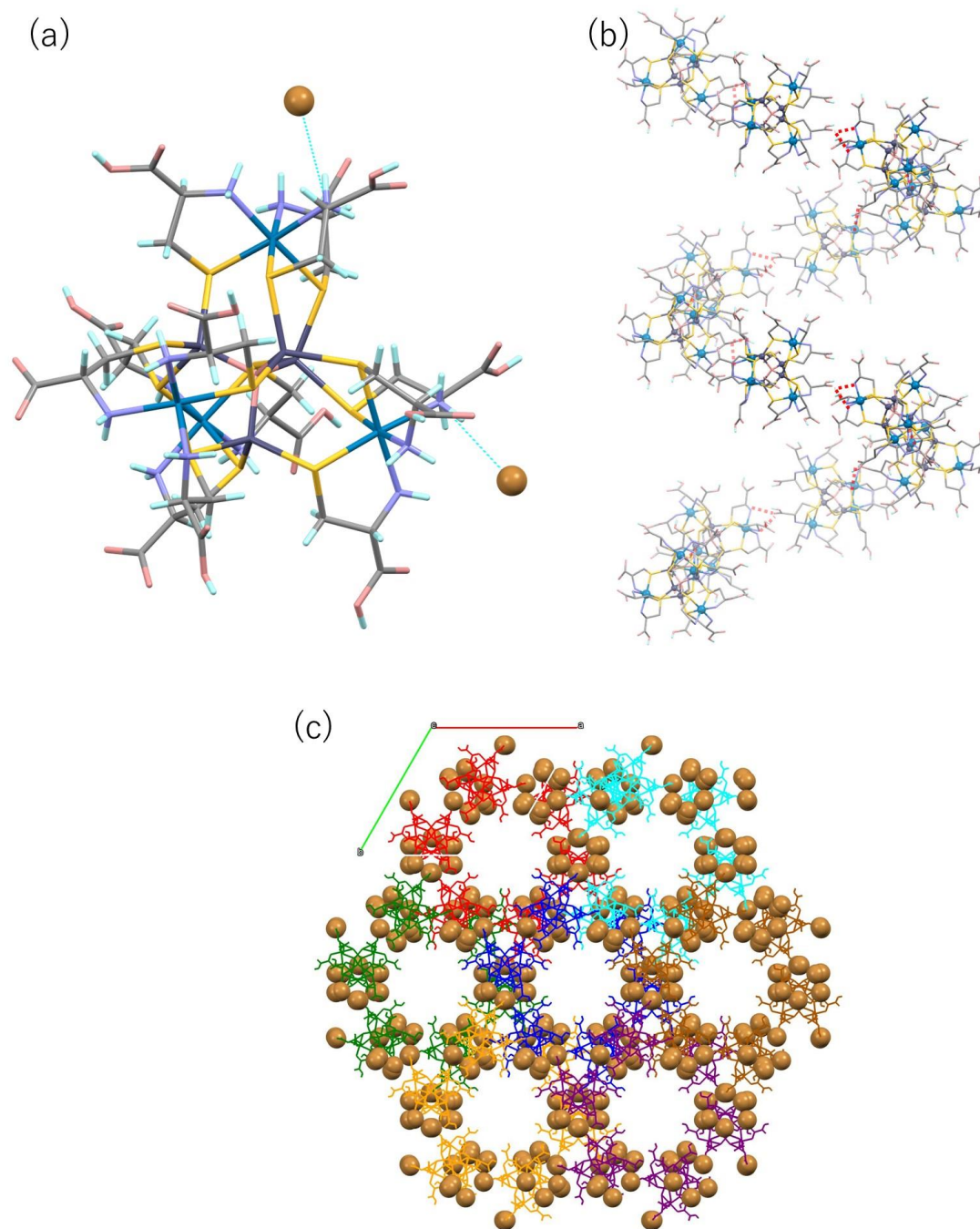
S6 A. L. Spek, *Acta Cryst.* 2015, **C71**, 9-18.



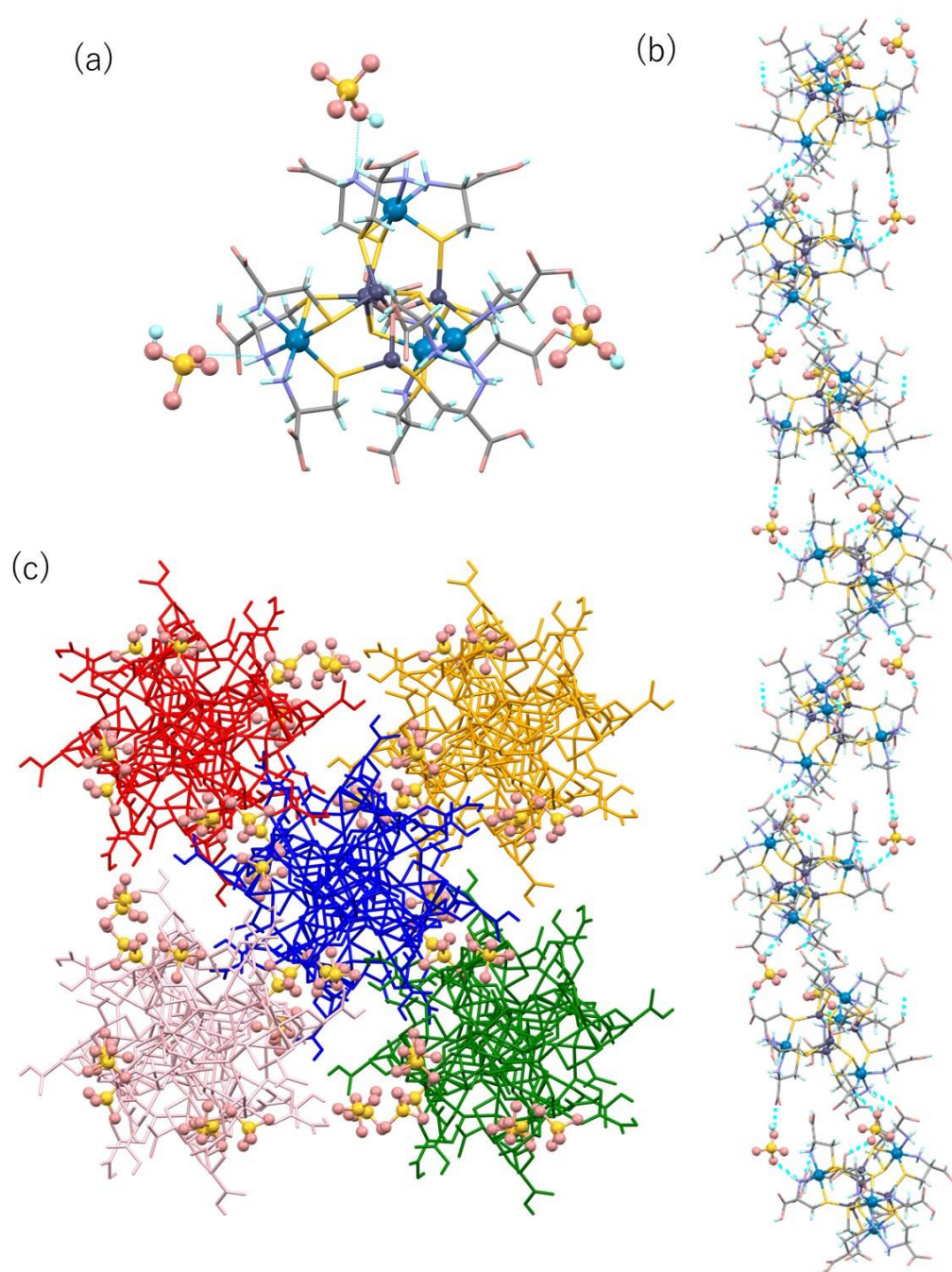
**Figure S1.** Diffuse reflection spectra of **2** (—), **3** (---), and K<sub>6</sub>[**1**] (- · - · -) in the solid state.



**Figure S2.** CD spectra of **2** (—), **3** (---), and K<sub>6</sub>[**1**] (- · - · -) in the solid state.

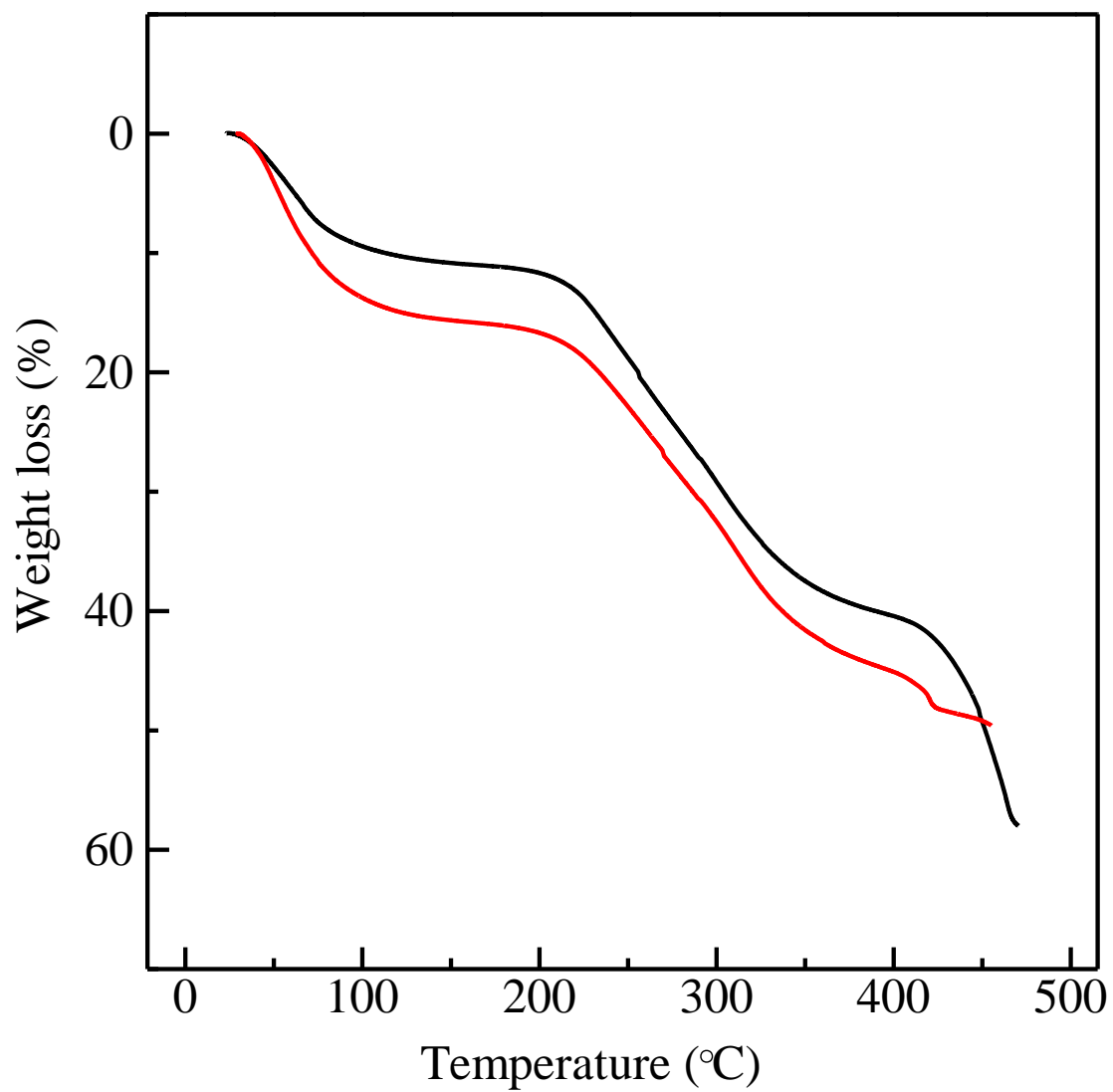


**Figure S3.** Crystal structure of **2**. (a) N–H···Br hydrogen bonds between [H<sub>91</sub>]<sup>3+</sup> and Br<sup>−</sup> ions. (b) The left-handed 6-hold helix showing intermolecular hydrogen bonds (red dashed lines). (c) Packing structure of **2** with bromide ions as the space-filling model. Colour code: Br, brown; Rh, blue-green; Zn, dark grey; S, yellow; O, pink; N, blue; C, grey; H, light blue. Each helix is illustrated using different colours in (c). Blue dotted lines indicates N–H···Br hydrogen bonds.



**Figure S4.** Crystal structure of **3**. (a) N–H···O and O–H···O hydrogen bonds between [H<sub>9</sub>1]<sup>3+</sup> and HSO<sub>4</sub><sup>-</sup> ions. (b) the left-handed 4-fold helix supported by the hydrogen bonds with HSO<sub>4</sub><sup>-</sup> ions. (c) Packing structure of **3** with HSO<sub>4</sub><sup>-</sup> ions as the ball and stick model. Colour code: Rh, blue-green; Zn, dark grey; S, yellow; O, pink; N, blue; C, grey; H, light blue. Each helix is illustrated using different colours in (c). Dotted lines indicates hydrogen bonds.





**Figure S5.** Thermogravimetric curves for **2** (red) and **3** (black).