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# Self-assembled metal-organic framework composed of one-dimensional Rh(II/III) chains with an octahedral [RhN<sub>6</sub>] coordination

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## Materials

H<sub>2</sub>bdtz·2H<sub>2</sub>O was synthesized via Pinner reaction of 1,4-dicyanobenzene according to the literature<sup>1</sup> and was characterized by elemental analysis, FT-IR, and <sup>1</sup>H NMR. RhCl<sub>3</sub>·3H<sub>2</sub>O (99.5%), K<sub>2</sub>CO<sub>3</sub> (99.5%), ethanol (99.5%) were purchased from FUJIFILM Wako Pure Chemical Corporation and used without any further purification. Water was deionized prior to use.

#### Synthesis of Rh<sub>2</sub>(H<sub>x</sub>bdtz)<sub>3</sub>·19H<sub>2</sub>O (1)

Compound 1 was synthesized by the conventional solvothermal method. Typically, 79 mg (0.30 mmol) of RhCl<sub>3</sub>·3H<sub>2</sub>O, 100 mg (0.40 mmol) of H<sub>2</sub>bdtz, and 39 mg (0.28 mmol) of K<sub>2</sub>CO<sub>3</sub> were dissolved in 40 mL of water/ethanol (3:7) mixed solvent in 100 mL screw-capped glass vial. The vial was then sealed, placed in an oven, and heated at 80 °C for 5 h with a heating rate of ca. 1 °C h<sup>-1</sup>, and cooled to room temperature with a cooling rate of ca. -5 °C h<sup>-1</sup>. The brown precipitate was recovered by centrifugation, repeatedly washed with water, and dried in vacuo. Yield: 127 mg (0.11 mmol, 80.3%). Elemental analysis calcd (%) for Rh<sub>2</sub>(bdtz)<sub>3</sub>·19H<sub>2</sub>O): C, 24.33; H, 4.25; N, 28.38. Found (%): C, 24.24; H, 4.00; N, 28.24.

## Characterizations

<sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub> with a JEOL JNM-ECA 600 spectrometer operating at 600 MHz. Powder X-ray diffraction (PXRD) measurements were performed with a Rigaku MiniFlex600 with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) in the 2 $\theta$  ranging from 5–50° with a 0.01° step. Scanning electron microscopy (SEM) images were taken with a HITACHI SU1510 scanning electron microscope at 15 kV. Sample was mounted on adhesive carbon tape. Fourier transform infrared (FT-IR) spectra were measured using a PerkinElmer Spectrum 100 spectrometer in attenuated total reflection (ATR) mode. The X-ray absorption fine structure (XAFS) measurements of the Rh K-edge (23.22 keV) were performed using a Si(311) doublecrystal monochromator at the beamline BL01B1 at SPring-8, Japan. Sample was diluted with boron nitride powder to be pressed into the pellet (7.0 mm in diameter). The  $k^2$ -weighted EXAFS oscillation was Fourier transformed in the range of 2–17 Å<sup>-1</sup> with a Hanning window function, whereas the range of inverse Fourier transformation was 0.8-2.0 Å. The overall amplitude factor  $(S_0)$  was obtained from the spectrum of the Rh foil as a reference. The N<sub>2</sub> (77 K), H<sub>2</sub> (77 K), CO<sub>2</sub> (195 K), and water vapor (298 K) sorption measurements were performed using a BELSORP-max volumetric adsorption system (Microtrac BEL Corp.). Before each measurement, the activated sample was activated at 70 °C for 14-20 h. Thermal stability was characterized by thermogravimetric and differential thermal analysis on a Bruker TG-DTA2000SA at a heating rate of 2 K min<sup>-1</sup> under N<sub>2</sub> atmosphere. X-ray photoelectron spectra (XPS) spectra were collected on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using Mg K $\alpha$  anode. The binding energies of the photoelectron peaks were corrected with carbon as a reference at 284.6 eV. DC magnetic measurements were conducted in the temperature range of 2–300 K using a quantum design MPMS-XL superconducting quantum interference device (SQUID) magnetometer under 10 kOe magnetic field. Sample was wrapped in plastic wrap and placed in a plastic straw for the measurement. Core diamagnetism values were estimated on the basis of the sum of Pascal's constants ( $-4.82 \times 10^{-4}$  emu mol<sup>-1</sup>).<sup>2</sup> Proton conductivities of the compressed pellet (2.5 mm in diameter, 1.24 mm in thickness) were measured by the AC impedance technique with an applied voltage of 100 mV in the frequency range from 0.1 Hz to 1 MHz. The pellet was sandwiched between two SUS430 stainless electrodes connected with a Solartron SI 1260 Impedance/Gain-Phase Analyzer and 1296 Dielectric Interface. Measurements were performed in the humidity- and temperature-controlled chamber. Lattice modeling and Pawley refinement were conducted with Materials Studio software (Accelrys Inc.). H<sub>2</sub>O-adsorbed structure was geometrically optimized with a molar ratio of Rh/H<sub>2</sub>O = 1:3 based on the grand canonical Monte Carlo simulation using Materials Studio software (Accelrys) based on the universal force field (UFF).<sup>3</sup>



Fig. S1 Photograph of polycrystalline 1.



**Fig. S2** PXRD pattern of **1** with simulated patterns of  $Fe_2(H_xbdtz)_3 \cdot 13H_2O$  at 293 K (brown),<sup>4</sup>  $Co_2(H_xbdtz)_3 \cdot 20H_2O$  at 90 K (blue),<sup>5</sup> and  $Ni_2(H_xbdtz)_3 \cdot 10.5H_2O$  at 98 K (green).<sup>6</sup>



**Fig. S3** FT-IR spectra of **1** (blue) and  $H_2bdtz \cdot 2H_2O$  (black). An orange area shows the N–H stretching mode region. A broad band with a peak at ca. 3000 cm<sup>-1</sup> observed for **1** is attributed to the O–H stretching mode of water molecules in the pores.



Fig. S4 Normalized XAFS spectrum at the Rh K-edge of 1.



**Fig. S5** Simulated structure of **1** viewed along the *c* axis. Colour code: C: grey; H: hydrogen; N: blue; Rh: green.



**Fig. S6** Simulated interactions between the ligands and adsorbed H<sub>2</sub>O molecules in **1** with a molar ratio of Rh/H<sub>2</sub>O = 1:3. The C–H···O and  $\pi$ ···O interactions are shown in pale blue and pink dotted lines, respectively.



Fig. S7 TGA (red) and DTA (blue) profiles of 1 under  $N_2$  atmosphere.



**Fig. S8** PXRD patterns of **1** after being heated at 250 °C (pink), 300 °C (green), and 350 °C (blue) under N<sub>2</sub> atmosphere. The red line is the pattern of pristine sample, whereas the black line is the simulated pattern of rhodium (space group:  $Fm\overline{3}m$ ).



**Fig. S9** PXRD patterns of **1** after being immersed in water (pink), ethanol (green), acetone (blue), and diethyl ether (red) at room temperature for 24 h. The black line is the pattern of pristine sample.



**Fig. S10** Schematic representation of the proposed spin arrangement in the 1D chain of **1**, where the green and orange spheres represent the Rh(II) and Rh(III) ions, respectively.



Fig. S11  $H_2$  gas adsorption (closed circles) and desorption (open circles) isotherms of 1 at 77 K.



**Fig. S12** CO<sub>2</sub> gas adsorption (closed circles) and desorption (open circles) isotherms of **1** at 195 K.



**Fig. S13** Nyquist plot of 1 (blue open circles) at 298 K under 98% RH. A red line shows the fitting curve, where the equivalent circuit used for the simulation is shown in the inset.



**Fig. S14** PXRD patterns of **1** before (red) and after (blue) the electrochemical impedance measurement at 50 °C under 98% RH.

## References

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