Electronic supplementary information

Zn(II) metal–organic framework with dinuclear [Zn_2(*N*-oxide)$_2$] secondary building units

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Experimental

Materials

Chemical reagents were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and were used without further purification.

Measurements

Elemental analyses (C, H and N) were performed on a Micro Corder JM10 (J-Science Lab Co., Ltd.) equipped with a thermal conductivity detector. Thermogravimetric (TG) analyses were performed using a Thermo Plus 2/TG-DTA8120 (Rigaku Corp.) over a 298–773 K temperature range under N_2 atmosphere with a heating rate of 10 K/min. Powder X-ray diffraction (XRD) data obtained from microcrystals were collected using a Rigaku RINT-Ultima III diffractometer (Rigaku Corp.) employing Cu Kα radiation. Fourier-transform IR (FT-IR) spectra were recorded with a FT/IR-4100 spectrometer (JASCO Corp.) having a resolution of 4 cm^{-1}. The adsorption and desorption isotherms were recorded on BELSORP-mini (N_2 at 77K), BELSORP-max (CO_2 at 195 K and H_2 at 77 K), and BELSORP-aqua (H_2O at 298 K) volumetric adsorption instruments (BEL Japan, Inc.).

Crystallographic data collection and structure refinement

Single-crystal XRD measurements were performed using a Rigaku RAXIS-RAPID imaging plate diffractometer (Rigaku Corp.) with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å). The structures were solved using a direct method (SHELXS-2014).[1] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms expected for H_2O molecules were refined using the riding model. All calculations were performed using the Yadokari-XG 2009 and Olex2 software packages.[2,3]

Synthesis of [Zn(pydcao)(DMF)] (1·DMF)

H_2-pydcao·H_2O was synthesized according to the previously reported method.[4] A DMF solution (5 mL) containing H_2-pydcao·H_2O (23 mg, 0.11 mmol) and $Zn(NO_3)_2$•$6H_2O$ (74 mg, 0.25 mmol) was heated at 373 K for 20 hours in a test

tube with a screw cap, and colourless crystals of [Zn(pydcao)(DMF)] (**1**·DMF) were obtained. The crystals were collected by decantation, washed with DMF using a centrifuge and finally dried under vacuum at 343 K for 3 hours. Yield: 33 mg (88%). One of these crystals was used for single-crystal X-ray structure analysis. Elemental analysis (%) calculated for $C_{10}H_{10}N_2O_6Zn$ ([Zn(pydcao)(DMF)] (**1**·DMF)): C 37.58; H 3.15; N 8.77. Found: C 37.40, H 2.99, N 8.70. FT-IR (KBr pellet): ν = 3422, 3118, 3100, 2360, 2342, 1645, 1590, 1386, 1374, 1252 (N^+–O^- stretching band), 1137, 1110, 1063, 1028, 990, 921, 793, 776, 734, 684, 669, 626, 586 and 500 cm^{-1}.

Preparation of the desolvated [Zn(pydcao)] (1)

The as-synthesized **1**·DMF was evacuated under vacuum at 478 K for 4 hours to afford the desolvated [Zn(pydcao)] (**1**). Elemental analysis (%) calculated for $C_7H_3NO_5Zn$: C 34.11; H 1.23; N 5.68. Found: C 34.30, H 1.59, N 5.50.

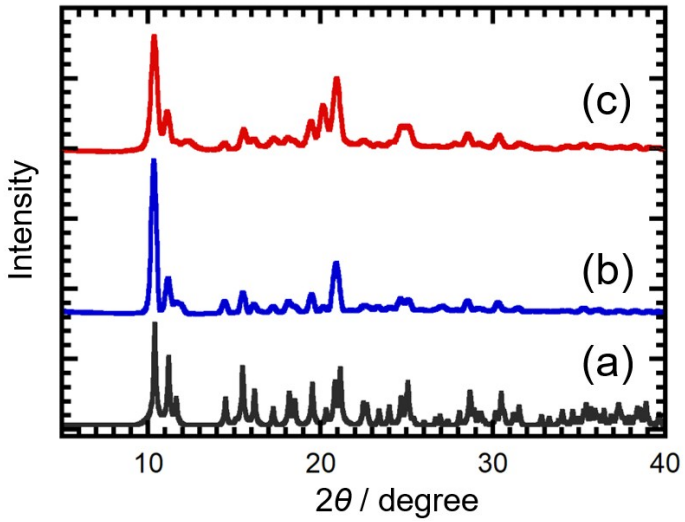

Fig. S1. Powder XRD patterns of (a) the simulated powder XRD pattern of **1**·DMF, (b) the as-synthesized **1**·DMF, (c) the desolvated **1** obtained by drying the as-synthesized **1**·DMF in a vacuum at 478 K for 4 hours.

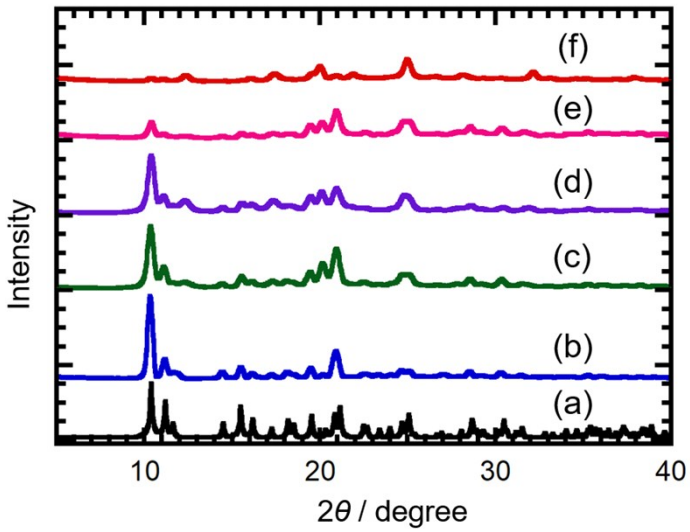

Fig. S2. Powder XRD patterns of (a) the simulated powder XRD pattern of **1**·DMF, (b) the as-synthesized **1**·DMF, and (c-f) the desolvated **1** obtained by drying the as-synthesized **1**·DMF under vacuum at (c) 478 K, (d) 493 K, (e) 533 K and (f) 548 K.

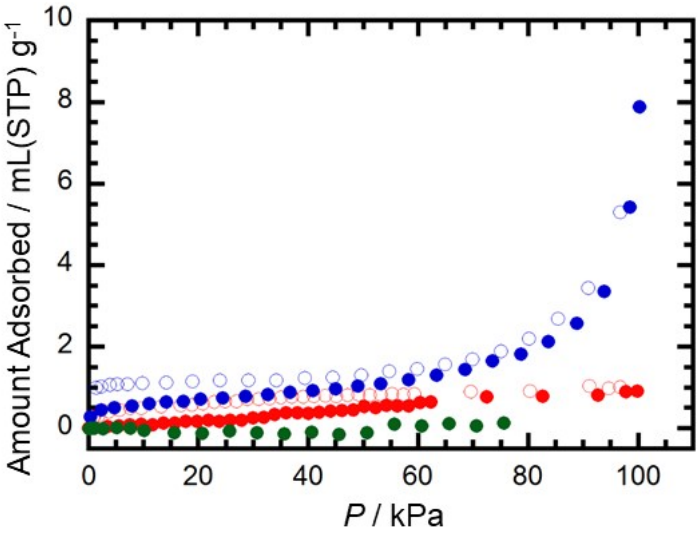

Fig. S3. Adsorption (closed circles) and desorption (open circles) isotherms of the desolvated **1** for N_2 (blue), CO_2 (red) and H_2 (green), at 77, 195 and 77 K, respectively.

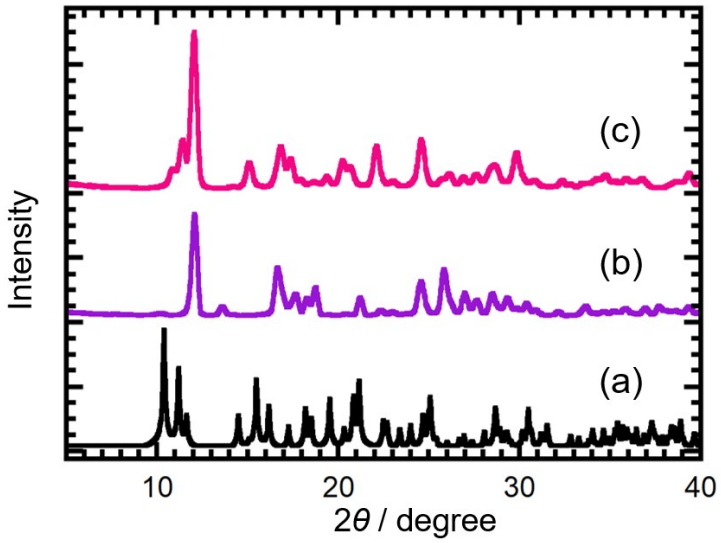

Fig. S4. Powder XRD patterns of (a) the simulated powder XRD pattern of **1**·DMF, (b) the hydrated sample after H_2O adsorption/desorption measurement, and (c) the re-dehydrated sample **1** obtained by drying the hydrated sample (b) at 393 K for 2.5 hours.

References

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