Supplementary Material (ESI) for Chemical Communications

Supporting Information

Kagomé type extra-large microporous solid based on paddle-wheel Cu^{2+} dimer

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Experimental

Materials. Terephthalaldehydic acid, 4-(aminomethyl) benzoic acid, and sodium cyanoborohydride ($NaBH_3CN$) were obtained from TCI Co. MeOH and dehydrated MeOH were obtained from Wako without further purification. $Cu(NO_3)_2 \cdot 2.5H_2O$ was obtained from Aldrich Chemical Co.

Synthesis of bis(4-carboxy-benzyl)amine (4-bcba-H3). A suspension of 4-(aminomethyl) benzoic acid (3.25 g, 21.5 mmol) in MeOH (250 ml) was added to a solution of terephthalaldehydic acid (3.03 g, 20.2 mmol) in MeOH (100 ml). The mixture was stirred for 14 hours at room temperature. The white imine product was collected by filtration, washed with MeOH, and dried in air (4.89 g, 17.3 mmol, yield 85.4%) [^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.01 (bs, 2H), 8.61 (s, 1H), 8.01 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz), 7.92 (d, 2H, $J_{H\text{-}H}$ = 8.5 Hz), 7.90 (d, 2H, $J_{H\text{-}H}$ = 8.5 Hz), 7.46 (d, 2H, $J_{H\text{-}H}$ = 8.0 Hz), 4.88 (d, 2H). MS (*m/z*): calcd for $C_{16}H_{13}NO_4$: 283.08; found: 283]. $NaBH_3CN$ (1.812 g, 28.8 mmol) was added to a suspension of imine product (4.89 g, 17.3 mmol) in dehydrated MeOH (100 ml) at 273 K. Temperature was allowed to step up to room temperature. The reaction suspension was stirred subsequently for 20 hours. The white powder was collected by filtration, washed with MeOH, and dried in air (3.73 g, 13.1 mmol, 65%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.88 (d, 4H, $J_{H\text{-}H}$ = 8.0 Hz), 7.45 (d, 4H, $J_{H\text{-}H}$ = 8.0 Hz), 3.74 (s, 4H), 3.16 (s, 1H), the peak of carboxylic proton was not observed at this condition. FAB+-MS (*m/z*): calcd for $C_{16}H_{15}NO_4$: 285.10; found: 286. FAB-MS (*m/z*): calcd for $C_{16}H_{15}NO_4$: 285.10; found: 284.

Synthesis of $\{[Cu(4\text{-bcba-H})]\cdot H_2O\}_n$ (1⊃H_2O). A solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (1.39 g, 6.00 mmol) in DMF (100 ml) was added to a solution of 4-bcba-H3 (1.71 g, 6.00 mmol) and triethylamine (10.0 ml, 72.0 mmol) in DMF (100 ml). The reaction mixture was stirred for 3 hours and the precipitate was filtered and washed with MeCN. The crystalline sky-blue powder **1** (0.32 g,

0.89 mmol, yield 15%) was obtained by drying under vacuum for 6 hours at room temperature. Elemental analysis calcd (%) for desolvated $\{[Cu(4\text{-bcba-H})]\cdot H_2O\}_n$ (**1⊃H_2O**) $C_{16}H_{15}CuNO_5$ (364.84): C, 52.67; H, 4.14; N, 3.84. Found: C, 52.57; H, 3.59; N, 4.00. Single crystal **1⊃H_2O** was prepared by following procedure. A solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (0.06 mmol) in MeCN (1.5 ml) was carefully layered on to a solution of 4-bcba-H3 (0.09 mmol) and triethylamine (0.98 mmol) in DMF (1.5 ml), with MeCN/DMF (0.75 ml/0.75 ml) placed between the two layers. Blue-green crystals formed in a few weeks.

Preparation of the desolvated [Cu(4-bcba-H)]$_n$. The desolvated green powder **1** was obtained by drying of **1⊃H_2O** under vacuum for 6 hours at 140 ºC. The crystallinity of desovated **1** was checked by XRPD.

Single Crystal X-ray Diffraction. The single crystal of **1** was mounted on glass fibers with epoxy resin. X-ray data collection for the single crystal was carried out on a Rigaku Mercury diffractometer with graphite monochromated MoKα radiation (λ = 0.71070 Å) and a CCD two-dimensional detector at 223 K in a cold nitrogen stream. The condition of X-ray for **1** was 50 kV × 100 mA. The structure solution was solved by direct method (SIR-97) and refined (SHELXL-97) by full matrix least squares. All non-hydrogen atoms except guest water atom were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model.

Physical Measurements. Thermogravimetric analysis (TGA) were performed using a Rigaku Thermo plus TG 8120 apparatus with temperature range of 298 and 723 K in a N_2 atmosphere and at a heating rate of 5 $Kmin^{-1}$. XRD patterns were measured by the synchrotron radiation XRD experiment with the large Debye-Scherrer camera and imaging plate as detectors on the BL02B2 beam line at the Super Photon Ring (SPring-8, Hyogo, Japan). The sorption isotherms were measured with BELSORP-18 volumetric adsorption equipment from BEL Japan, Inc. Elemental analyses were carried out with a Thermo Finnigan EA1112. ^{1}H NMR spectra were measured with a 500 MHz JEOL JNM-A500 FT NMR system.