Supplementary Material (ESI) for Chemical Communications

Supporting Information

Coordination pillared layer-type compounds having pore surface functionalization by anionic sulfonate groups

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All the reagents and solvents employed were commercially available and used as supplied without further purification.

X-ray Crystal Analysis. Single crystal X-ray diffraction data collection was carried out on a Rigaku mercury diffractometer with a graphite monochromated MoKα radiation (γ = 0.71069 Å) and a CCD detector. The crystal structure was solved by a direct method (SIR97) and refined by full-matrix least-squares refinement using the SHELXL-97 computer program. The positions of non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined using a riding model.

Physical Measurements. The elemental analysis was carried out on a Flash EA 1112 series, Thermo Finnigan instrument. Thermogravimetric analyses (TGA) were carried out with a Rigaku Instrument Thermo plus TG 8120 in a nitrogen atmosphere. X-ray powder diffraction (XPD) data were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with CuKα radiation. The adsorption isotherms of CO_2 (195 K), methanol and acetonitrile (298K) were measured in the gaseous state by using BELSORP18-Plus volumetric adsorption equipment from BEL Japan, Inc. NMR experiment was carried out on a JEOL JNM-LA300WB spectrometer operating at a resonance frequency of 75.45 MHz for ^{13}C at room temperature. A 7 mm double-resonance magic-angle spinning (MAS) probe was used at a spinning speed ranging 4.5 kHz.

Synthesis of $\{[Zn_3(\mu_3\text{-}OH)_3(2\text{-stp})(bpy)_{1.5}(H_2O)](EtOH)(2H_2O)\}_n$ (2-stp = 2-sulfonyl terephthalate, bpy = 4,4'-bipyridine) (1⊃G).

The ethanol solution (100 mL) containing $Zn(NO_3)_2{\cdot}4H_2O$ (1.16 g, 3.9 mmol) was added to H_2O/ethanol (1:2) solution (150 mL) dissolved 2-stp monosodium salt (0.35 g, 1.3 mmol) and bpy (0.30 g, 1.95 mmol) and NaOH (0.26 g, 6.5 mmol) to give white

powder precipitates. After stirring for one day, the resultant precipitate was filtered, washed with ethanol and dried at RT under reduced pressure. Elemental analysis of crystal **1⊃G** (**G** = $2H_2O$ and EtOH), found C, 36.01%, H, 3.00%, N, 5.09%; calculated 36.41%, H, 3.67%, N, 5.09%.

Synthesis of $\{[Zn_3(\mu_3\text{-}OH)_3(2\text{-stp})(dpe)_{1.5}(H_2O)](EtOH)(4H_2O)\}_n$ (2-stp = 2-sulfonyl terephthalate, dpe = 1,2-di(4-pyridyl)ethylene) (2⊃G).

The ethanol solution (100 mL) containing $Zn(NO_3)_2{\cdot}4H_2O$ (1.16 g, 3.9 mmol) was added to H_2O/ethanol (1:2) solution (150 mL) dissolved 2-stp monosodium salt (0.35 g, 1.3 mmol) and dpe (0.36 g, 1.95 mmol) and NaOH (0.26 g, 6.5 mmol) to give white powder precipitates. After stirring for one day, the resultant precipitate was filtered, washed with ethanol and dried under reduced pressure. Elemental analysis of crystal **2⊃G** (**G** = $4H_2O$ and EtOH, which was also confirmed by TGA; calcd 15.1%, found 15.4%), found C, 37.07%, H, 3.69%, N, 5.38%; calculated 37.34%, H, 4.14%, N, 4.67%.

Fig. S1 TGA curves on (a) **1⊃G** and (b) **2⊃G**. Each scan rate is 5 $Kmin^{-1}$.

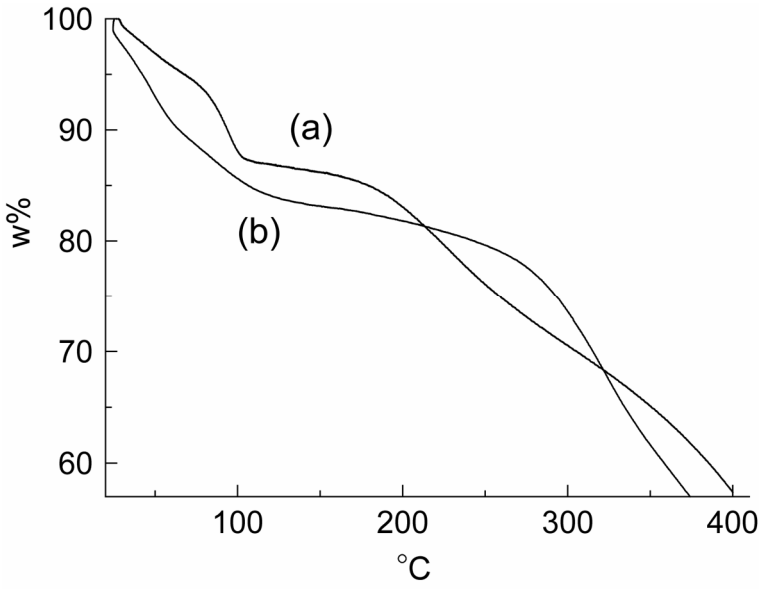

Fig. S2 Solid-state ^{13}C CPMAS NMR spectra of **2⊃G**. Peaks at 18.1 and 57.8 ppm is EtOH, 43.2 is ethylene group of dpe, and peaks between 120 to 155 ppm are aromatic carbons of dpe and stp, and 171.3 and 176.7 ppm are carbonyl carbon of stp, respectively. Asterisks are spinning side band.

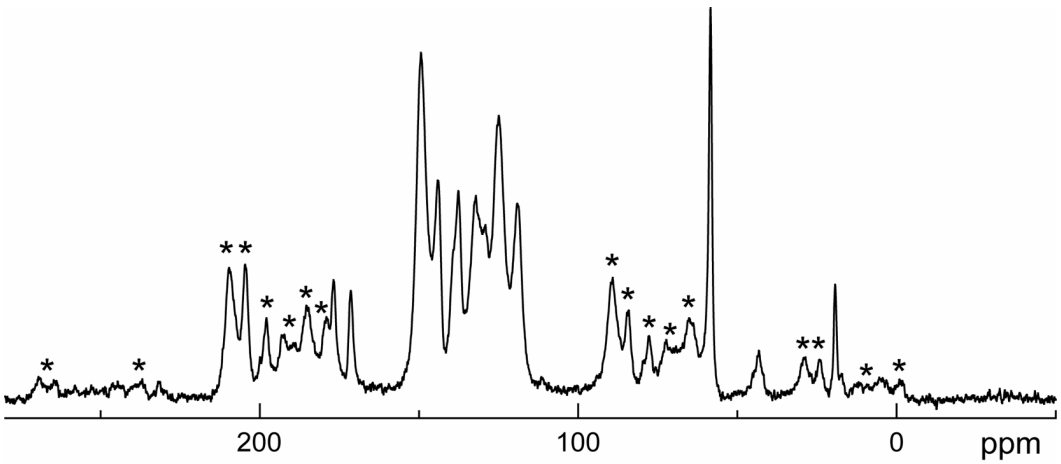

Fig. S3 Adsorption/desorption isotherms of MeOH at 298 K for (a) **1** and (b) **2**.

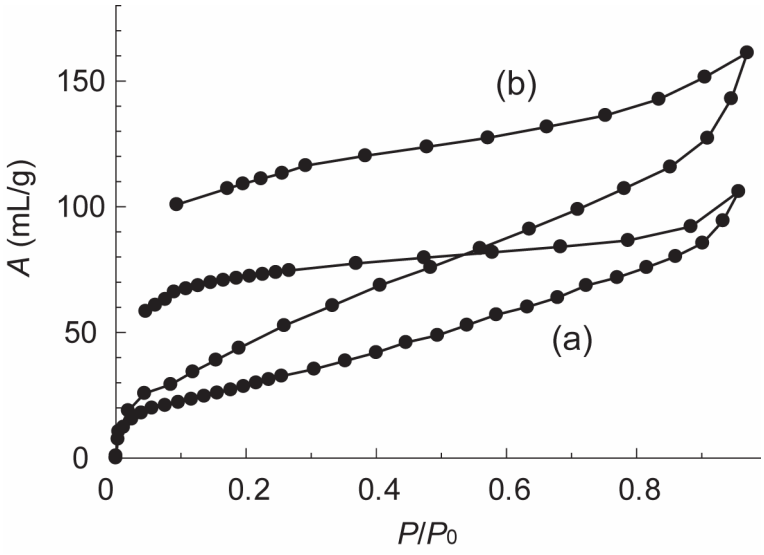

Fig. S4 Adsorption and desorption isotherms of (a) MeOH and (b) MeCN at 298 K for **1**.