Supporting Information

Selective adsorption of water, methanol, ethanol by naphthalene diimide-based coordination polymers with constructed open Cu^{2+} metal sites and separation of ethanol/acetonitrile

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1. Physical Measurements

Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000-400 cm^{-1} on a VECTOR 22 spectrometer. The powder X-ray diffraction (PXRD) was recorded on a Bruker D8 ADVANCE diffractometer (Cu *Kα*, 1.5418 Å) at 40 kV and 40 mA. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in the air, and the data are consistent with the structures. The adsorption isotherms of CO_2 (at 195 K) and N_2 (at 77 K) were measured by using BELmax 00027 adsorption equipment (BEL Japan). An exactly measured amount of the sample was introduced into the gas sorption instrument after the sample was pre-desolvated in a Schlenk tube at 120 °C under vacuum for 24 h. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. The sorption properties were analyzed using

Autosorb 1 for Windows 1.24 software.

2. General Procedures. Chemicals were purchased from commercial sources and used without further purification.

Synthesis

{[Cu(4-pmntd)(CH_3OH)$_2$(opd)]·$CHCl_3$}$_n$(1·MeOH). A mixture of 4-pmntd (6 mg, 0.0125 mmol), $Cu(NO_3)_2·6H_2O$ (8 mg, 0.025 mmol), Na_2(opd) (21mg, 0.1 mmol) in $H_2O/CH_3OH/CHCl_3$ (1 mL / 3 mL / 10 mL) was stirred and then sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 70℃ and held at that temperature for 7 days, followed by further cooling to room temperature. Green crystals of **1** were collected in 32 % yield based on ligand. Anal. Calcd for $C_{37}H_{21}Cl_3CuN_4O_{10}$: C, 52.19; H, 2.49; N, 6.58%. Found: C, 51.85; H, 2.16; N, 6.69%. IR (KBr, cm^{-1}): 3428vs, 1709m, 1668vs, 1615m, 1580s, 1453w, 1429w, 1383s, 1336s, 1249m, 1179w, 754m, 565w.

3. X-ray crystallography

The diffraction data were collected on a Oxford Gemini S Ultra diffractometer equipped with Cu-Kα radiation (λ = 1.54178 Å) for complex **1·MeOH** and **1·EtOH**, or on the same diffractometer equipped with Mo-Kα radiation (λ = 0.71073 Å) for complexes **1·dry** and **1·H2O** by using φ and ω scans. Multiscan adsorption corrections were applied for all complexes. The structures were solved by the direct methods (SHELXS) and refined by the full matrix least-squares method against F_o^2 using the SHELXTL software.[1,2] The coordinates of the non-hydrogen atoms were refined anisotropically. Most of hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms, and the guest methanol hydrogen atoms have not been added. Details of the crystal parameters, data collections and refinement for all compoundsare summarized in Table S1. Further details are provided in Supporting Information. CCDC numbers 966848 (**1·MeOH**), 966849 (**1·dry**), 966850 (**1·H_2O**) and 1861423 (**1·EtOH**).

1. G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany 1997.

2. G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures From Diffraction Data, Univ. of Göttingen, Göttingen (Germany), 1997.

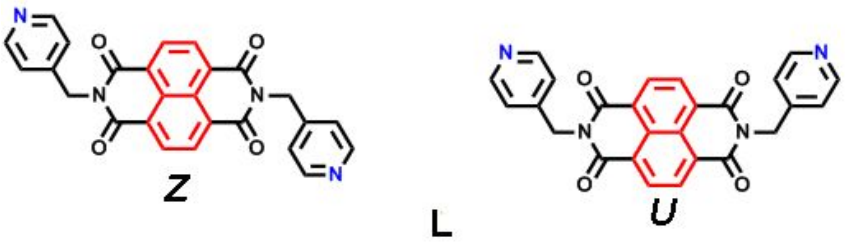

Figure S1. Two conformations of the ligand 4-pmntd *N*,*N*'-Bis(4-pyridymethy)naphthalene diimide.

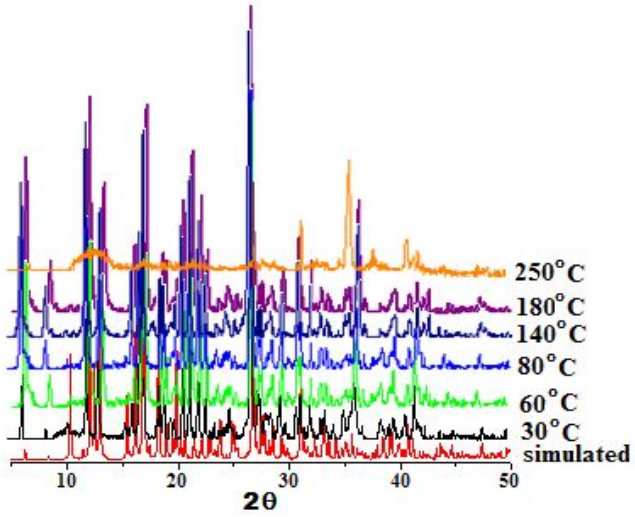

Figure S2. PXRD patterns of compound **1**.

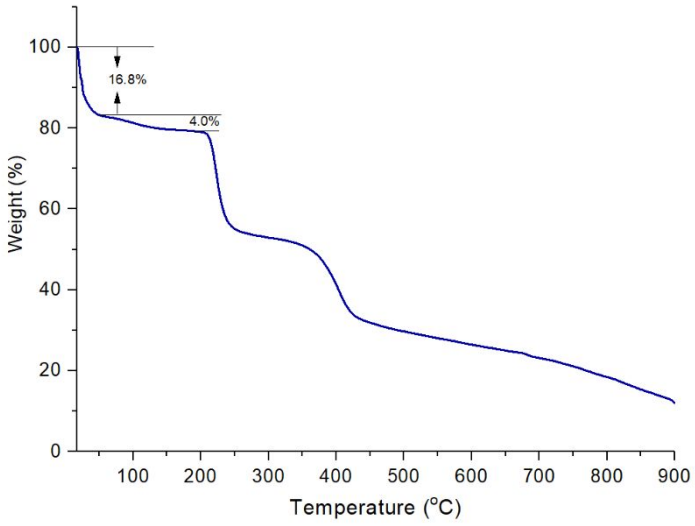

Figure S3. TG curve of **1·MeOH**.

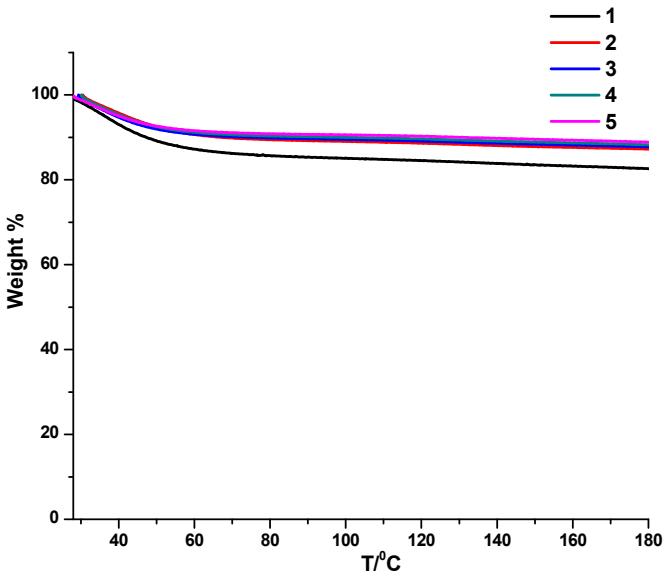

Figure S4. TGA measurements of cycling (5 runs) ethanol desorption/adsorption processes for **1**.

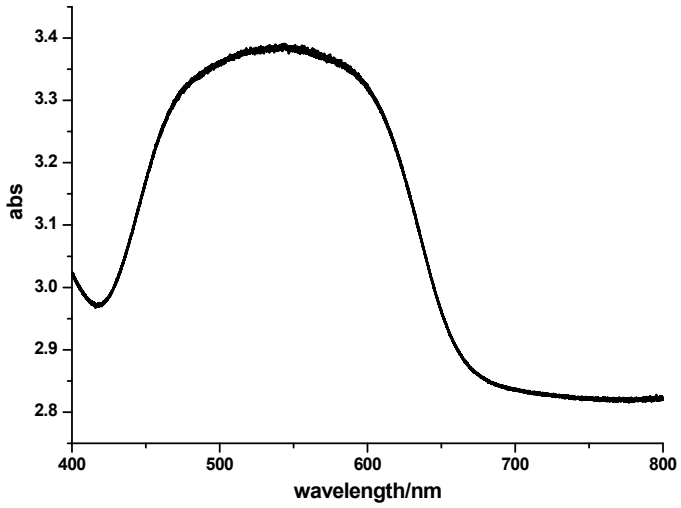

Figure S5. UV-Vis spectrum of **1·dry**