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Supporting Information

Electrical Bistability in a Metal-Organic Framework Modulated by Reversible

Crystalline-to-Amorphous Transformations

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Experimental Details

Synthesis of crystallite of 1.

Na[Cu(pdt)₂]·2H₂O was prepared by following a reported procedure.¹ Na[Cu(pdt)₂]·2H₂O (22 mg, 0.05 mmol) and CuI (9.8 mg, 0.05 mmol) were added into 20 mL of acetonitrile. The mixture was sonicated for 20 minutes at room temperature. Then the crystallite of Cu[Cu(pdt)₂] was obtained and washed with acetonitrile for six times and dried in vacuum for two hours at room temperature. The size of the obtained crystallite is around 1~2 μ m observed by SEM. The samples were activated in vacuum at 40°C for 24h before further tests.

Synthesis of large single-crystals of 1.

Single crystals **1** of Cu[Cu(pdt)₂] were prepared by slowly diffusing 2 mL of CuI acetonitrile solution (2.2 mg, 0.011 mmol) into 100 mL of Na[Cu(pdt)₂] (5 mg, 0.011 mmol) acetonitrile solution. Then the clearly yellow solution was ke pt at room temperature for a few days. Large scale of black single-crystals wit h size of 50 μ m can be found at the bottom of conical flask. The samples wer e activated in vacuum at 40°C for 24h before further tests.

Preparation of amorphous 2 from crystalline 1.

The transformation of crystalline 1 into amorphous 2 was conducted by heating 1 at 120 °C for 2 hours in the oven.

Measurement and characterization

The FT-IR spectra were recorded on a Bruker VERTEX70 FT-IR spectrometer in 4000-400 cm⁻¹ region using KBr pellets. The Raman spectra were collected using JY-Horiba Labram Raman Spectrometer with a laser of 638 nm wavelength. The powder X-ray pattern of the powdered samples were recorded on a Rigaku MiniFlex 600 diffractometer using Cu K_a radiation by keeping the powdered sample on a silicon substrate, from 5 to 45°. The CO₂ sorption isotherms of **1** were measured at 195 K with a Micromeritics Surface Area analyzer ASAP-2020. Before measurement, the samples were degassed in vacuum at 40 °C overnight. The CO2 sorption isotherms of **2** were measured by *in-situ* heating **1** in Micromeritics Surface Area analyzer at 120 °C for 2 hours for structure transformation and then performing the sorption measurements at 195 K. The surface chemical analyses were investigated by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific ESCALAB 250 Xi XPS system. Thermogravimetry analysis was made on a Netzsch STA449C simultaneous TG-DTA/DSC apparatus under air atmosphere with each sample heated in an Al₂O₃ crucible at a heating rate of 10 K·min⁻¹. The elemental analyses of C, H, and N were measured on an Elementar Vario EL III microanalyzer. The EXAFS measurements were carried out at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan.

The electrical measurements were performed using a Keithley 4200 semiconductor characterization system. The powder pellets were connected to the system by gold wires with both surfaces of the pellets covered by gold paste. The measurement of temperature-dependent conductivities was conducted by keeping the sample in an oven with the temperature rising from 30 to 110 °C. For the measurement of conductivity of single crystal, the opposite corners of the crystal were painted with gold paste and connected to Keithley 4200 by gold wires. The reversible switches between the electrically bistable states of Cu[Cu(pdt)₂] were conducted with the setup made by dipcoating the acetonitrile suspension of the crystallite of **1** on ITO interdigital electrodes. Then, the setup was heated from room temperature slowly to 120 °C and kept for 2 hours to remove acetonitrile and transfer **1** to **2**. Then the switching from **1** to **2** was conducted by immersing the setup into acetonitrile carefully and kept for 6 hours. After that, the setup was dried in vacuum for two hours at room temperature to remove the physically absorbed solvent for further tests.

Figures



Figure S1. PXRD patterns of pristine 1 and 2 treated in different solvents. The recovery from 2 to 1 was selectively triggered by acetonitrile while other solvents, such as ether, water, ethanol, methanol, acetone, ammonia water, benzonitrile, butyronitrile and valeronitrile failed.



Figure S2. Acetonitrile sorption isotherms of Cu[Cu(pdt)₂] for four circles.



Figure S3. Temperature-dependent I-V curves of amorphous 2.



Finger S4. Temperature-dependent conductivity of amorphous 2. The conductivity of amorphous 2 increased with the increasing of temperature, indicating 2 was a semiconductor.



Figure S5. Electrical response of crystalline 1 to MeCN and dry air.



Figure S6. TGA profile of Cu[Cu(pdt)₂] from 30 to 500 °C under air atmosphere.



Figure S7. Powder X-ray diffraction pattern of $Na[Cu(pdt)_2] \cdot 2H_2O$ heated at 180 °C for 2h.



Figure S8. Raman spectra of 1 and 2.



Figure S9. IR spectra of **1** and **2** from 4000 to 400 cm⁻¹. **2** displayed similar IR spectrum with 1, indicating the ligands were mainly preserved during the structure transformation.

Computational method

The bond energy of Cu-S is referred as the average energy of the complex $[Cu^{II}(L1)_2]^$ minus a metal ion and ligands L1 in vacuum respectively. For the bond Cu-N, the complexes $[Cu^{II} (L2)_4]^{2+}$ were calculated in the similar way but a different ligand L2 was adopted to void high charges accumulated on the complex. All calculations were using B3LYP²/def2-TZVP³ implemented in ORCA package.⁴ The stationary points were verified as minima by vibrational frequency analysis. All discussed energies are Gibbs free energies in gas phase (Δ G) at 298 K.



References

- X. Ribas, J. C. Dias, J. Morgado, K. Wurst, E. Molins, E. Ruiz, M. Almeida, J. Veciana and C. Rovira, *Chemistry*, 2004, 10, 1691-1704.
- 2. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
- 3. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297-3305.
- 4. F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci., 2012, 2, 73-78.