

## Supporting Information

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### A Unique 3D Metal-organic Framework Based on 12-connected Pentanuclear Cd(II) Cluster Exhibiting Proton Conduction

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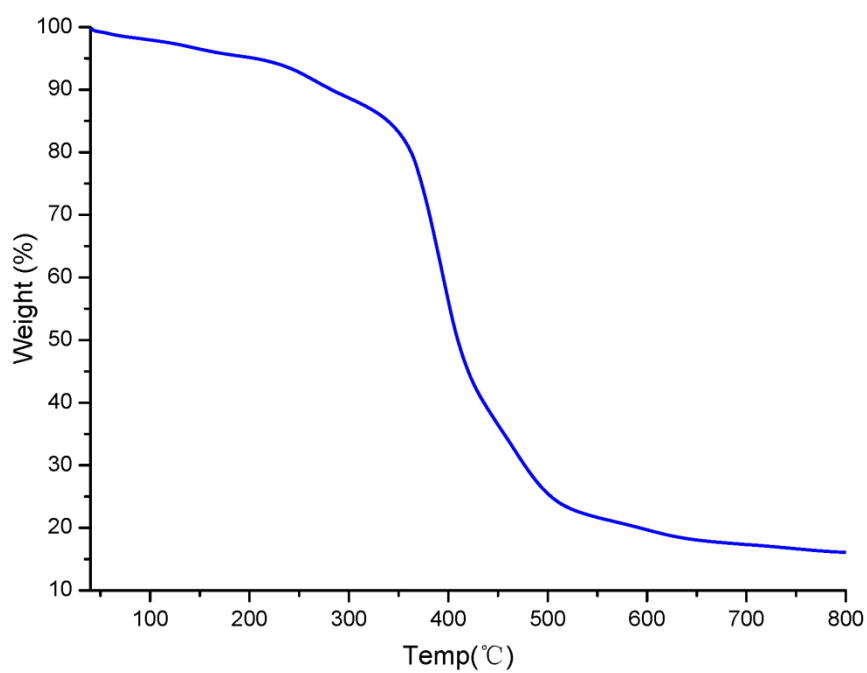
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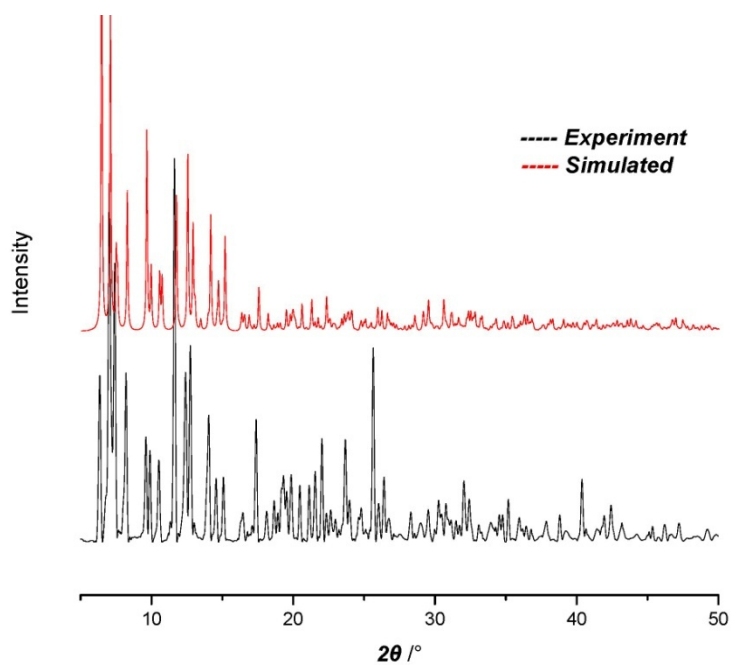
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#### Measurements and characterization

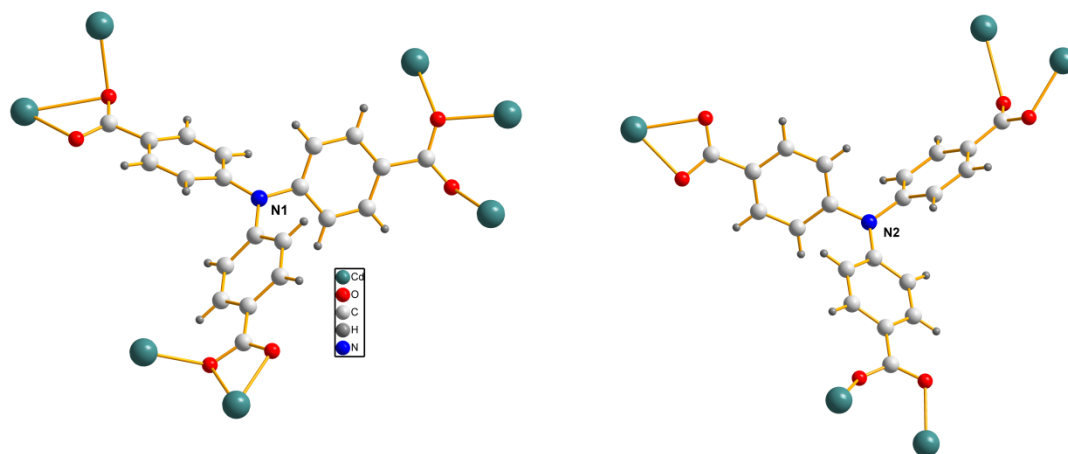
The UV-Vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer and fluorescence emission spectra collected on a Horiba FluoroMax 4 spectrometer. Thermogravimetric analyses were carried out on a TA Instruments SDT-Q600 simultaneous DTA-TGA under N<sub>2</sub> with a heating rate of 5°C/min. Powder X-ray diffraction (PXRD) data were recorded on Siemens Bruker D5000 X-ray Powder Diffractometer. N<sub>2</sub> adsorption-desorption isotherms were measured on a Quantachrome NOVA 2000e sorption analyzer at liquid nitrogen temperature (77 K). For AC conductivity measurements, the powdered crystalline samples were compressed to 5mm in thickness and 13 mm in diameter under a pressure of 12-14MPa. The two flat surfaces of the pellet were coated with a thin layer of silver paste then sandwiched by a circle brass electrode (9 mm in diameter). AC impedance spectroscopy measurement was conducted on a CHI604E (Chenghua, Shanghai) electrochemical impedance analyzer over a frequency range from 1Hz to 0.1MHz with an input voltage amplitude of 200 mV. Samples were placed in a temperature-humidity controlled chamber (GDS-50A, Hasuc, Shanghai). The bulk conductivity ( $\sigma$ ) of the pellet was estimated from the Nyquist plot by arc extrapolation to the Z' axis on the low frequency side.



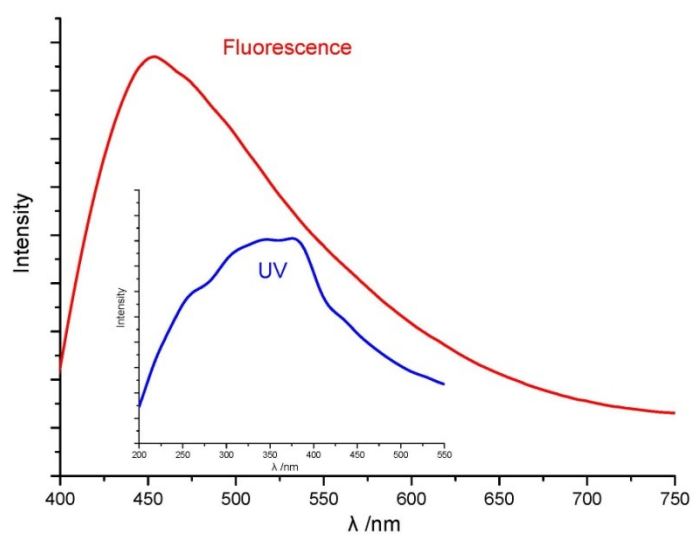
**Fig. S1:** TGA curve of **1**.



**Fig. S2:** Comparison between the experimental and simulated PXRD patterns of **1**.



**Fig. S3:** Two coordination modes of TCA ligands.



**Fig. S4:** The photoluminescence spectra of **1** ( $\lambda_{\text{ex}} = 350$  nm) (Inset: UV-Vis absorption spectra of **1**).

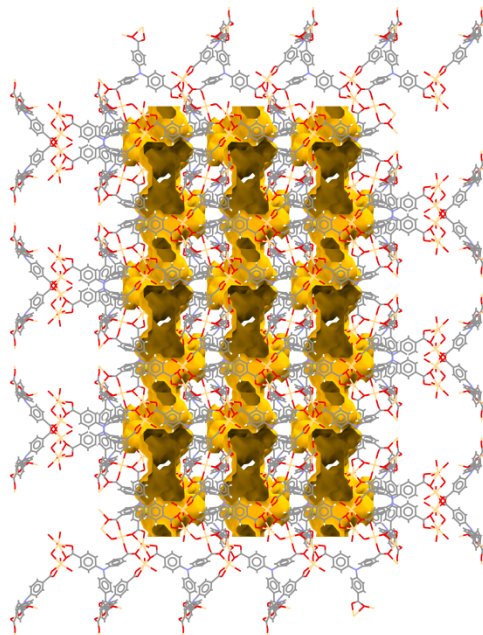


Fig. S5: Schematic showing of the curved narrow channels of **1** (highlighted in yellow color).

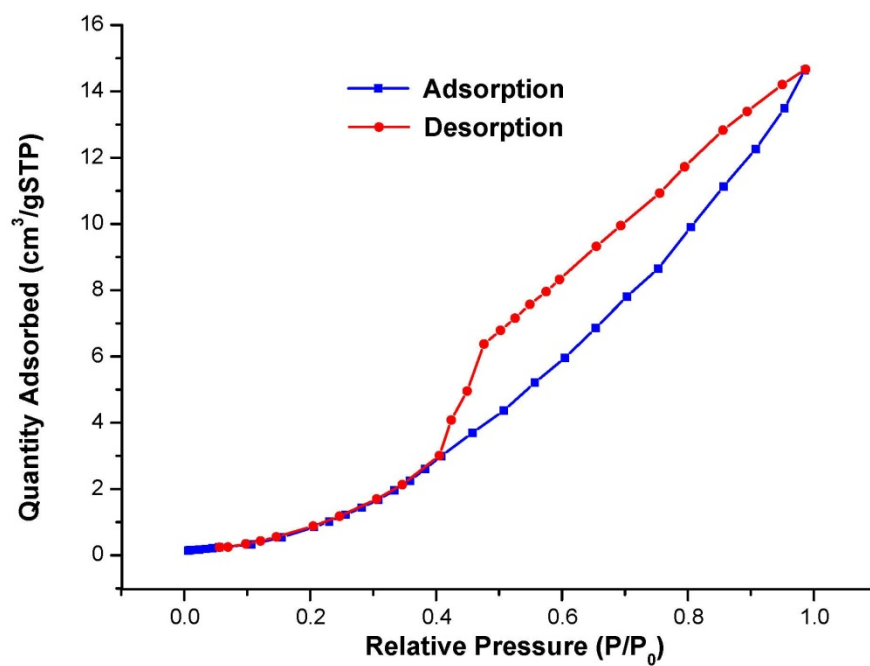
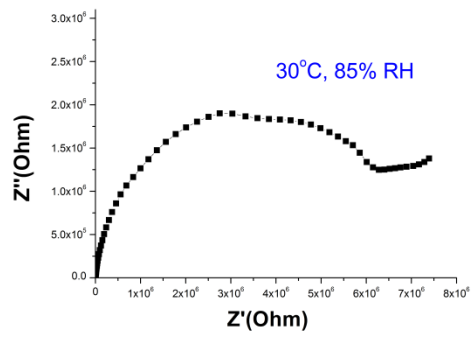
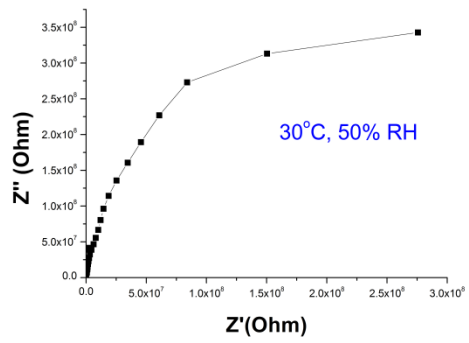
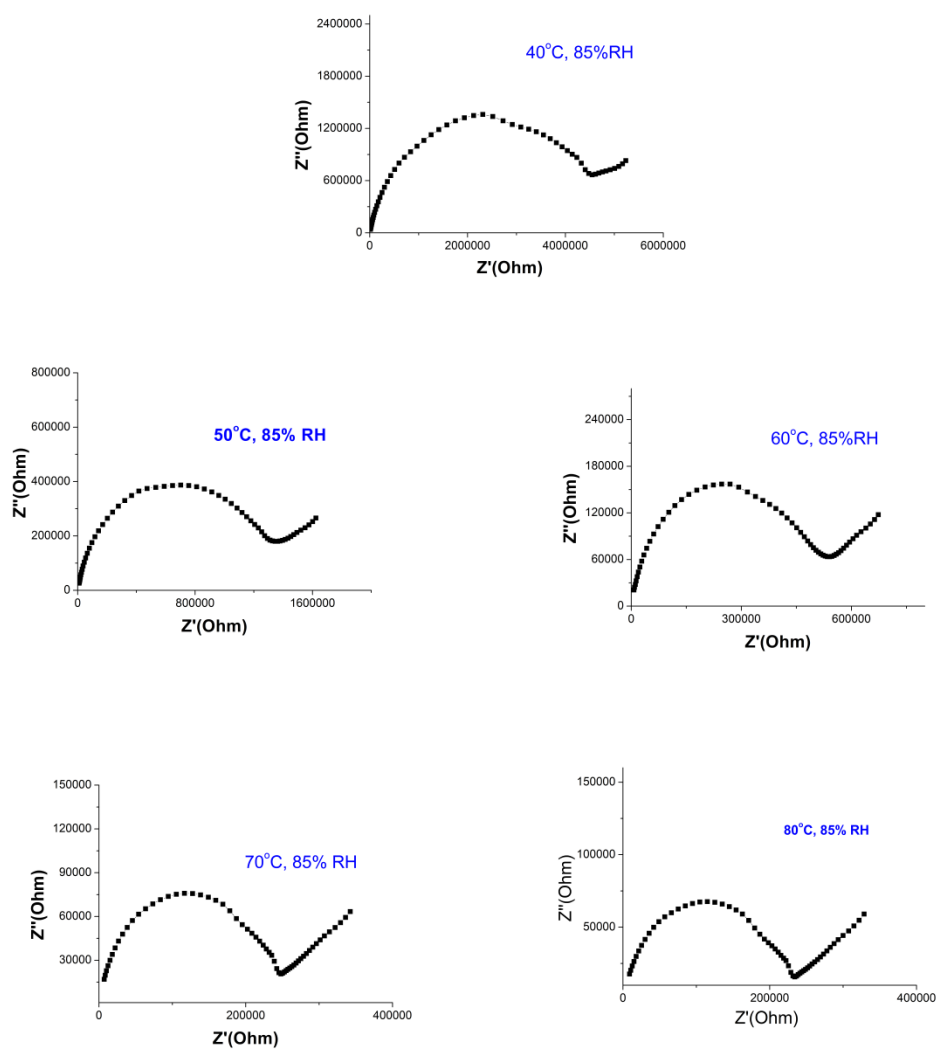


Fig. S6: The N<sub>2</sub> adsorption-desorption isotherm of **1**.



**Fig. S7:** Nyquist plot of 1 at 30°C with 50% RH (left) and 85% RH (right).



**Fig. S8:** Nyquist plots of **1** at the temperature of 40-80°C with 85% RH.