Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

A Metal-Organic Framework with Coordinatively Unsaturated Metal Centers and Microporous Structure

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1. Synthesis: All the reagents and solvents were purchased from commercial sources and used without further purification. Solvothermal reactions were carried out in digestion bomb reactors. Exact amounts of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1g) and 1,3,5-Tris(4-carboxyphenyl)benzene acid (0.1g) were dissolved in a 50mL digestion bomb reactor using diethylformamide (DEF). The mixture solution was heated at 110□ for 35 hours. Then the light plate-like crystal $[Cd_3(BTB)_2(DEF)_4]_n \cdot 3nDEF$ (**1**) was obtained. The as-synthesized sample was obtained by filtration, and dried in air. Activated samples for nitrogen gas adsorption measurements were prepared by solvent exchanging with the mixture of acetone and dichloromethane, and then heating compound at 210□ for 2 hrs in vacuum oven.

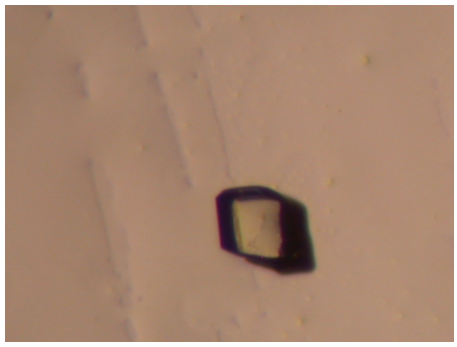


Fig. S1 Crystal particle used to obtain the single-crystal structure

2. **Single-crystal X-ray crystallography**: Single-crystal XRD data of compound **1** (CCDC) was collected on a Rigaku Mercury CCD area-detector single crystal diffraction system with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods with the help of SHELX-97 and refined by full-matrix least-squares techniques using SHELXL-97. Due to highly disordered solvent pockets, the data were corrected by PLATON Squeeze program. All non-hydrogen atoms were refined with anisotropic temperature parameters. The hydrogen atoms were positioned geometrically and refined using a riding model.

Empirical formula	$C_{74}Cd_3O_{16}N_4H_{74}$
Molecular weight	1612.57
Temperature (K)	193(2)
Crystal system	triclinic
Space group	P-1
a(Å)	10.4595(9)
b(Å)	14.3920(13)
c(Å)	14.7634(13)
α(°)	69.608(1)
β(°)	82.476(1)
γ(°)	88.043(1)
V(A^3)	2065.0(3)
Z	1
D_{calcd}(g cm^{-3})	1.297
F(000)	818
μ (mm^{-1})	0.825
Reflection (collected/unique)	22830 / 11602
R_{int}	0.03
Goodness-of-fit on F^2	1.04
Final *R* indices [I>2σ(*I*)]	$R_1 = 0.0562$, $wR_2 = 0.1389$
R indices (all data)	$R_1 = 0.0698$, $wR_2 = 0.1471$
Max, min Δρ (e $Å^{-3}$)	1.528, -0.546

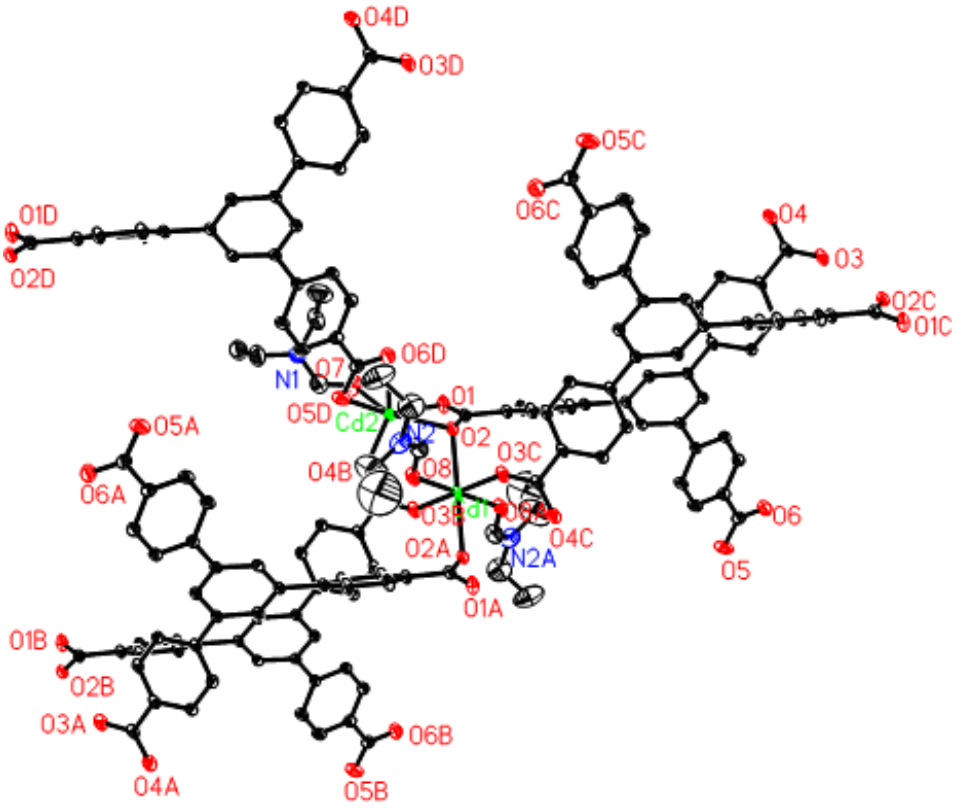


Fig. S2 The coordination environments of metal ions in **1**. Displacement ellipsoids are plotted at 30% probability level. Symmetry codes: A: -x, -y, -z; B: x, 1+y, z-1; C: -x, -y-1, 1-z, D: 1+x, y, z-1, respectively.

3. **Powder X-ray diffraction:** The powder-XRD pattern of samples were collected on a Bruker D8 powder diffraction system with Cu radiation (λ = 1.5406 Å).

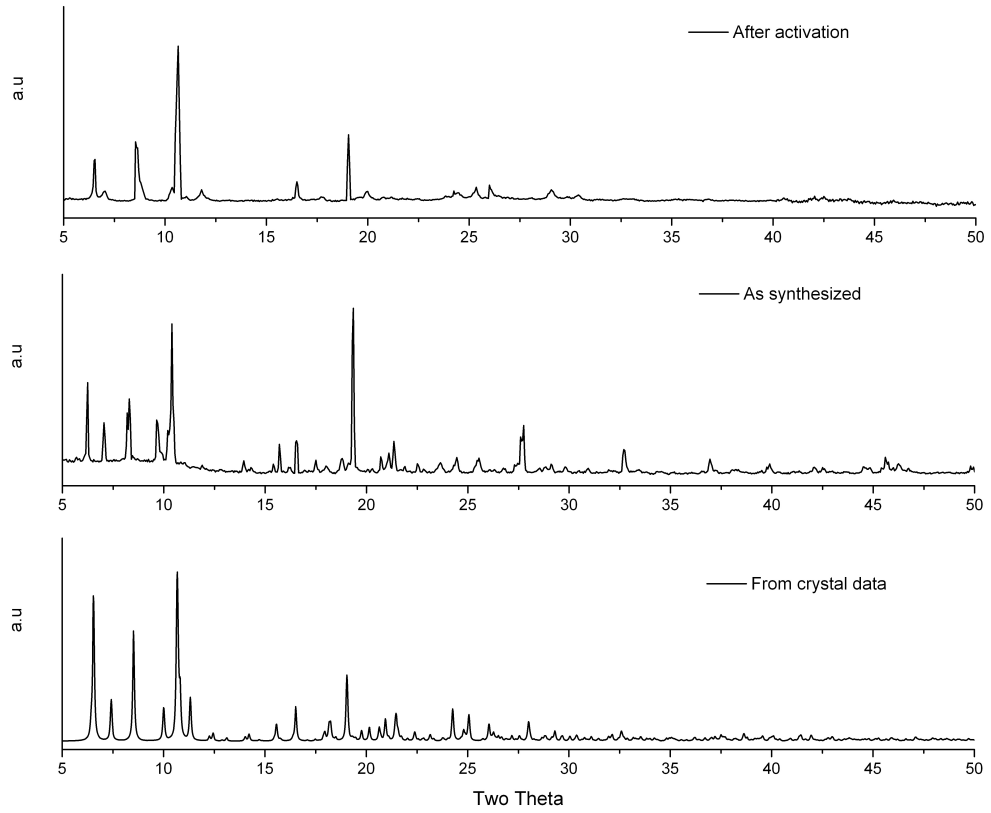
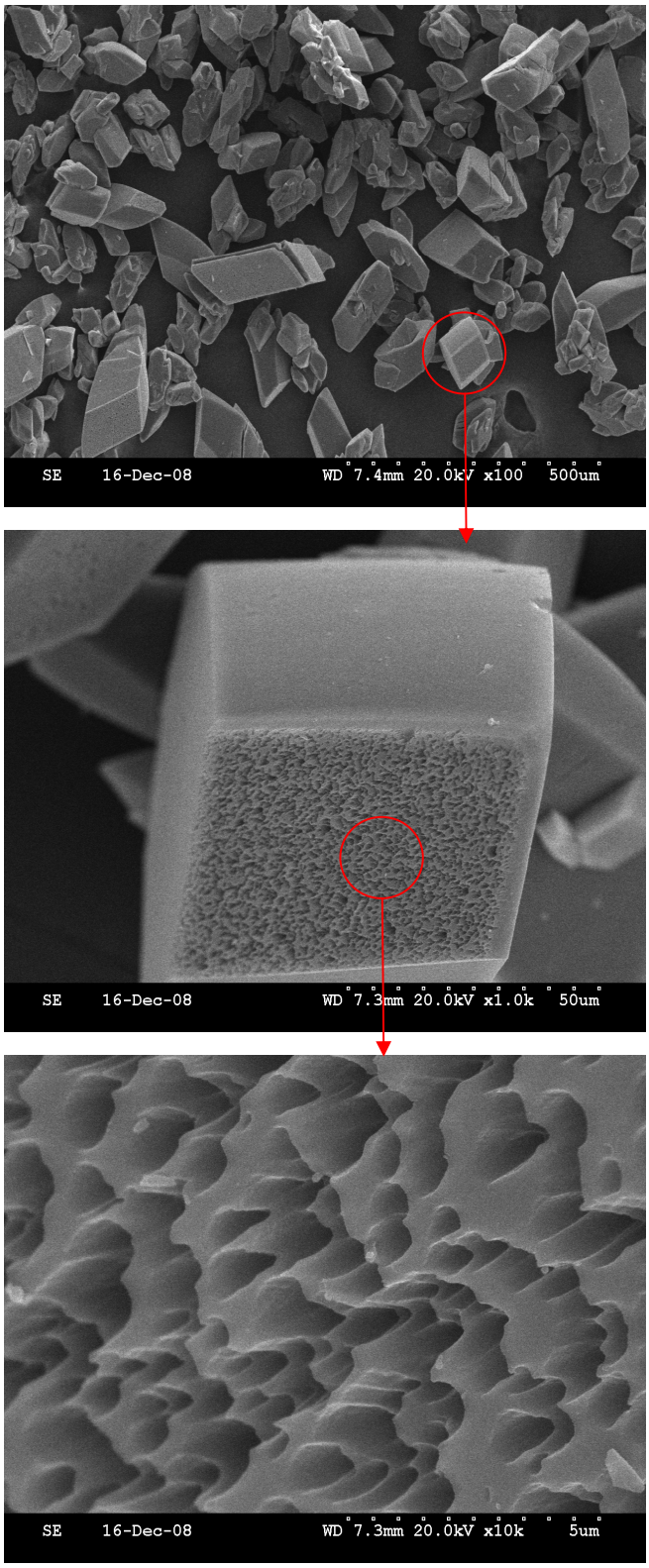


Figure S3. A comparison of experimental powder-XRD pattern of **1** after activations to remove guest molecules (top), as synthesized (middle) and theoretical pattern from the single crystal data (bottom).

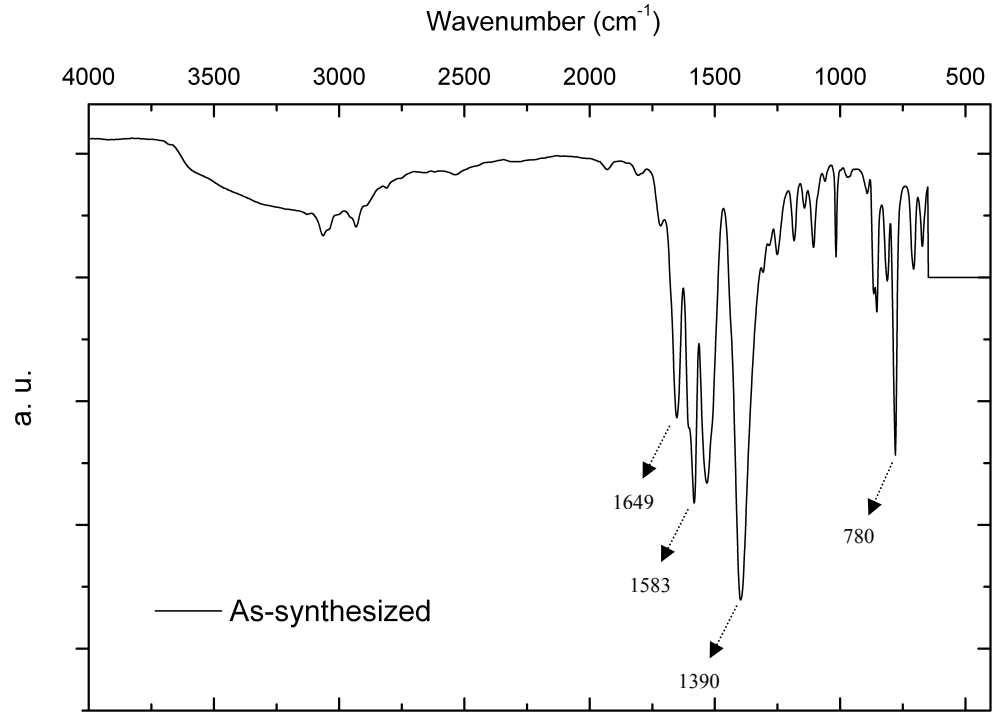
4. Scanning electron microscope (SEM) characterization: The SEM images were conducted on a Hitachi SEM S-3500N equipped with a model S-6542 absorbed electron detector.



5. TGA analysis: Thermogravimetric analyses were carried out with a SHIMADZU TGA-50 at a heating rate of 5°C/min under helium atmosphere with 25 mL/min flow rate.

6. Elemental analysis: Elemental analyses were carried out on an Elementar Vario EL III analyzer. According to the result of TGA analysis, there are one and half DEF molecules associated in an asymmetric unit. Therefore, the molecular formula with associated DEF will be $C_{89}Cd_3O_{19}N_7H_{107}$: C, 55.79%; Cd, 17.62%; O, 15.88%; N, 5.12%; H, 5.59%. Found: C, 55.81%; Cd, 17.60%; O, 15.89%; N, 5.10%; H, 5.60%.

7. FTIR: Infrared (IR) spectra were recorded with PerkinElmer Spectrum One as KBr pellets in the range 4000 – 400 cm^{-1}.



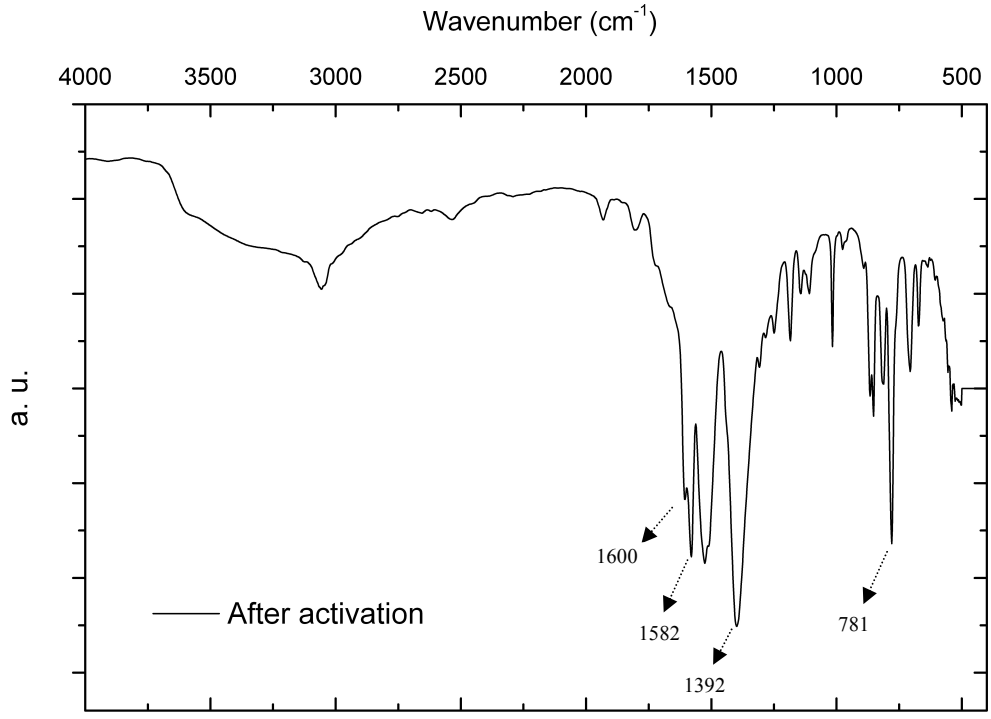


Fig. S4 FT-IR pattern of compound **1** (top, as-synthesized; bottom, after activation).

8. Specific surface area characterization: Nitrogen adsorption isotherm of activated product at 77 K was measured with Autosorb-1 from Quantachrome Corporation to calculate the surface area. The BET surface area is calculated to be 504 m^2/g. The Langmuir surface area is calculated to be 661 m^2/g.

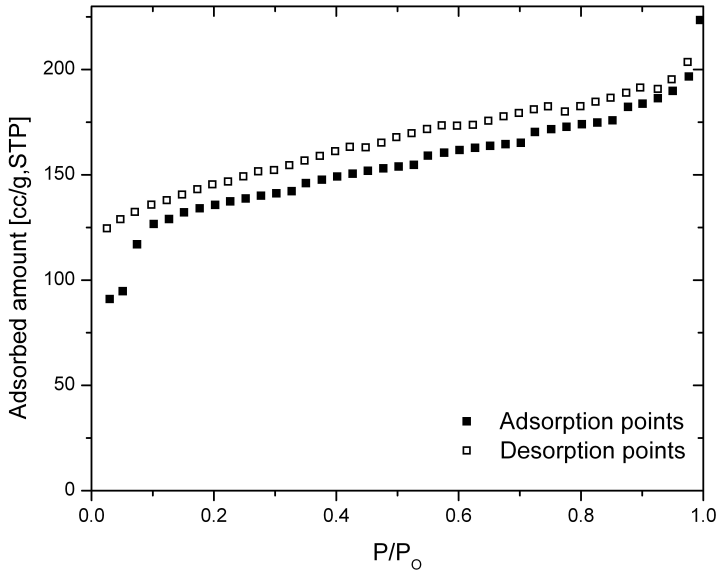


Fig. S5 N_2 isotherm of activated compound **1** at 77 K.

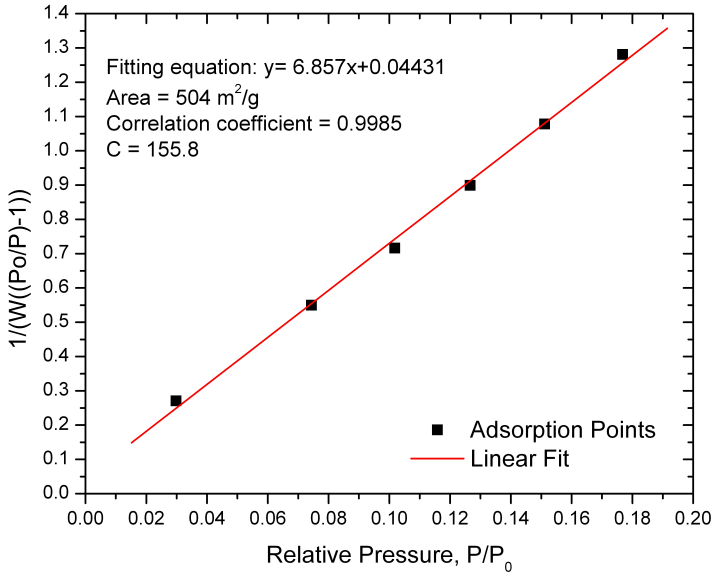


Fig. S6 Multipoint BET analysis of N_2 isotherm at 77 K.