A Non-interpenetrated Porous Metal-Organic Framework with High Gas-Uptake Capacity

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Supporting Information:

Synthesis of FJI-1:

All the solvents and reagents for synthesis were commercially available and used as received. A mixture of $Zn(ClO_4)_2 \cdot 6H_2O$ (0.223g, 0.6mmol), H_3BTB (0.175g, 0.4mmol), 4,4'-bipy (0.047g, 0.3mmol) and fluoboric acid 100μL in DMF (10 mL) in a Pyrex tube was dissolved by ultrasonic waves 10 minutes and heated at 85℃ for 3 days. Then the mixture was cooled to room temperature, yielding colorless transparent cubic crystals which were collected and repeatedly washed with DMF three times. Phase purity was confirmed by powder X-ray diffraction (PXRD). Using a combination of elemental analysis, thermogravimetric analysis (TGA) and single-crystal X-ray diffraction analysis, the compound was formulated as $[Zn_6(btb)_4(4,4'\text{-bipy})_3(dmf)_{55}(H_2O)_{32}]$ (FJI-1). Elemental analyses calcd (%) for $C_{276}H_{168}O_{48}N_{12}Zn_{12}$ (After activation with supercritical CO_2): C 63.69, H 3.25, N 3.23; found: C 63.71, H 3.30, N 3.29.

Thermogravimetric Analysis (TGA) of FJI-1:

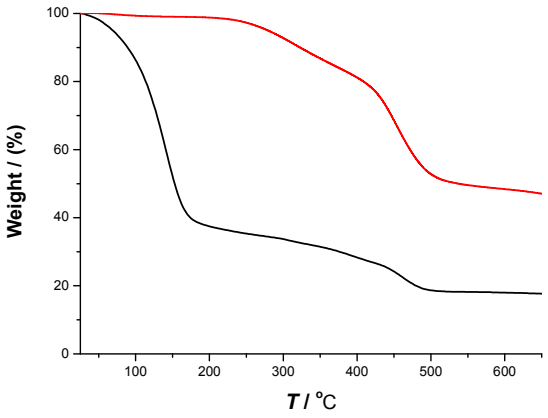

Figure S1. Synthesized product (black), after SCD activation (red).

TGA was performed with FJI-1 under a constant flow of nitrogen gas. The sample (10.230 mg) was loaded and the temperature was increased by 2℃/min from 30℃ to 700℃. TGA analysis showed that FJI-1 lost 62.6% of its mass in the range of 30~200℃, corresponding to the loss of all solvent molecules. Above 200℃, framework decomposed. For the sample after SCD activation, the flat remained until about 220℃, demonstrating that the solvents were removed completely.

X-ray Data Collection and Structure Determination of FJI-1:

The single crystal of FJI-1 sealed in a glass capillary with DMF was performed on a Rigaku 70-CCD diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ=0.71073Å) using the ω-scan mode at 293 K.

Powder X-Ray Diffraction of FJI-1

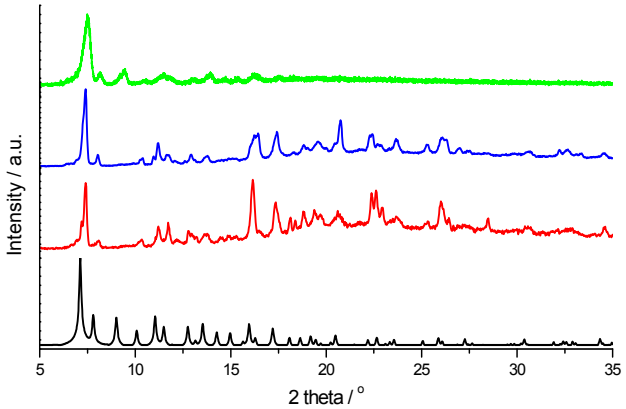

Figure S2. Measured powder X-Ray diffraction for synthesized product (red), after SCD activity (blue), after repeating absorption and desorption 6 times (green), and calculated (black) from single crystal data of FJI-1.

Powder X-ray diffraction data were collected on a MiniFlex II diffractometer with Cu-$K_{\alpha 1}$ radiation (λ = 1.5405 Å) at room temperature.

Treating sample:

When the guest molecules in the sample of FJI-1 were exchanged with conventional organic solvents, due to the presence of tremendous gas-liquid interface capillary tension, the treated sample lose luster and turned into powder. At the same time, the Powder X-ray diffraction data showed that this sample was amorphous implying the framework collapse.

Finally, the sample was treated with supercritical carbon dioxide (SCD). The PXRD, TGA and Elemental analyses all confirmed that this method was able to remove guest solvent molecules from the sample of FJI-1 without damaging its framework, while crystal images also revealed that the activated sample retained its crystalline (Figure 2). The reason may be that supercritical drying avoids the gas-liquid two-phase equilibrium process, which can eliminate the

frameworks collapse caused by capillary tension.

Detailed procedure in SCD activation as follows:

The SCD processing was performed with SFT-10 Pump linkup pressure vessel and the Rxtrol Jr^{TM} reactor temperature control system. Before SCD drying, the as-synthesized fresh sample was immersed in $CHCl_3$ for 3 days with fresh $CHCl_3$ added every 24 h. After the first exchange, the $CHCl_3$-containing samples were immersed in hexane for 3 days with fresh hexane added every 24 h. The hexane-containing sample was placed inside the pressure vessel. The CO_2 was injected into the pressure vessel with the temperature 40℃ and pressure 1600psi for one hour. Then, exhaust supercritical state CO_2 was rapidly released. Repeating the process of injecting CO_2 and exhaust supercritical state CO_2 twelve times afforded the CO_2-activated sample. And the sample was placed in a sealed container and stored in a glove box or tested for gas adsorption immediately.

Hydrogen Heats of Adsorption

By applying the Clausius–Clapeyron equation to two sets of hydrogen adsorption data collected at 77K and 87K, the isosteric heat of adsorption ($\triangle H_{ads}$) can be deduced. This is an important criterion in judging how strongly hydrogen binds the MOFs.

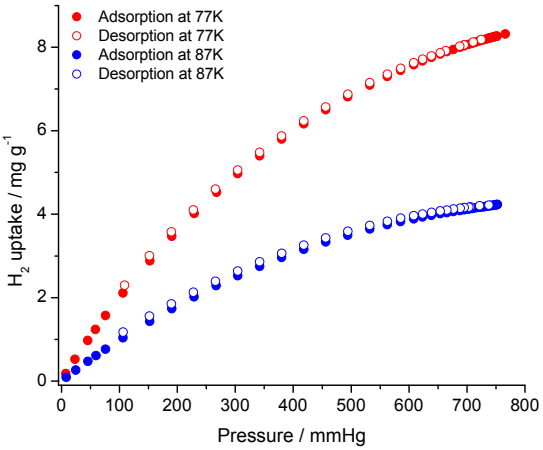

Figure S3. Hydrogen adsorption isotherm at 77K and 87 K for FJI-1, respectively (●, excess adsorption; ○, excess desorption).

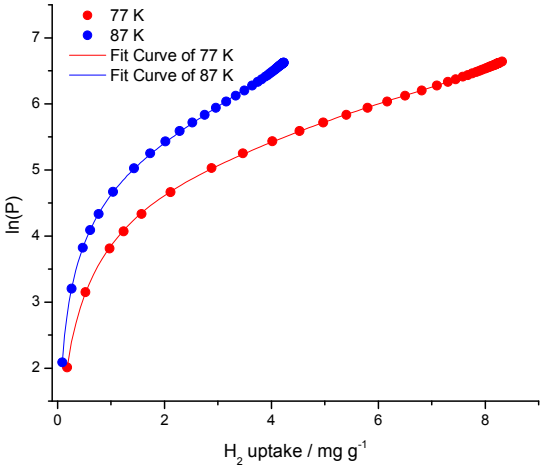

Figure S4. Fit curve for FJI-1 at 77K and 87 K respectively.

Table 1. Fit curve equation and factor

Equation	y=ln(x)+1/k*(a0+a1*x+a2 *x^2+a3*x^3+a4*x^4+a5 *x^5)+(b0+b1*x+b2*x^2)		
Reduced Chi-Sqr			8.7992E-5
Adj. R-Square			0.99992
		Value	Standard Error
	a0*	-555.93314	6.47897
	a1*	74.75206	6.5005
	a2*	-36.19156	1.66682
	a3*	3.03041	0.34194
	a4*	-0.35881	0.04447
	a5*	0.01598	0.00207
	b0*	10.88888	0.0773
	b1*	-0.67392	0.07565
	b2*	0.32228	0.01461
	k	77	0
	a0*	-555.93314	6.47897
	a1*	74.75206	6.5005
	a2*	-36.19156	1.66682
	a3*	3.03041	0.34194

	a4*	-0.35881	0.04447
	a5*	0.01598	0.00207
	b0*	10.88888	0.0773
	b1*	-0.67392	0.07565
	b2*	0.32228	0.01461
	k	87	0

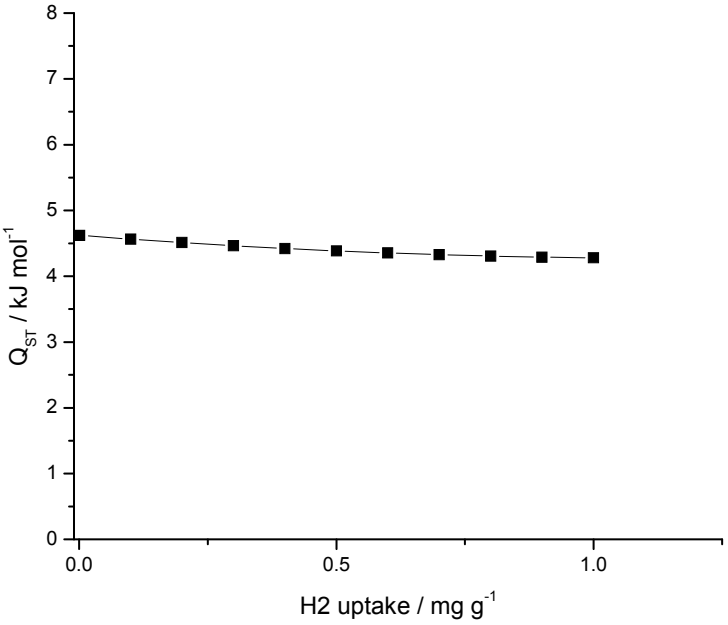

Figure S5. Heat of adsorption: 4.62kJ/mol at low coverage.

Low-Pressure N_2 Sorption Measurements

N_2 sorption isotherms measurements were performed on an ASAP 2020 Surface Area and Pore Size Analyzer. After SCD activation, the sample was tested for nitrogen absorption immediately. The sample was degassed by using the "degas" function of the surface area analyzer for 6h at 40℃. A sample of 100 mg and UHP-grade nitrogen (99.999%) gas source were used in the nitrogen sorption measurement at 77K. The temperature was maintained at 77K with liquid

nitrogen throughout the whole measurement. Oil-free vacuum pumps and the molecule pump were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

High-Pressure H_2, CH_4 and CO_2 Sorption Measurements

High-pressure hydrogen sorption isotherm measurements on FJI-1 were performed using Hydrogen Storage Analyser HTP1-V (Hiden). UHP-grade hydrogen was used for the high-pressure measurements with a purity of 99.9999%. After SCD activation, the sample was tested for H_2 and CH_4 sorption immediately. The sample was degassed under vacuum (~10^{-6}torr) overnight at room temperature, followed by heating at 40℃ for at least 6h.

High-pressure carbon dioxide storage capability was evaluated at 298K. The gas adsorption isotherm was collected using Intelligent Gravimetric Sorption Analyser IGA100B (Hiden) in the pressure range of 1 to 20 bar. Before the measurements, about 50 mg FJI-1 sample was degassed at 40℃ for 6 h under dynamic vacuum.

Measurements of *n*-pentane vapor adsorption isotherms

The liquid *n*-pentane adsorption isotherms were measured at 298 K using Intelligent Gravimetric Sorption Analyser IGA100B (Hiden) adsorption analyzer with about 50mg FJI-1 sample which was activated at 40℃ for 6h under dynamic vacuum.

FT-IR Analysis of FJI-1:

IR spectra were recorded on Spectrum One spectrophotometer with crystals as samples with preparing KBr pellets.

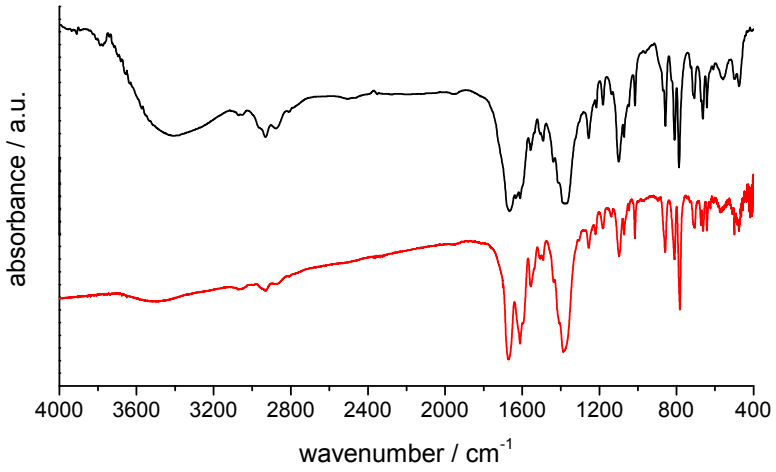

Figure S6. The as-synthesized product (black), after SCD activity (red)

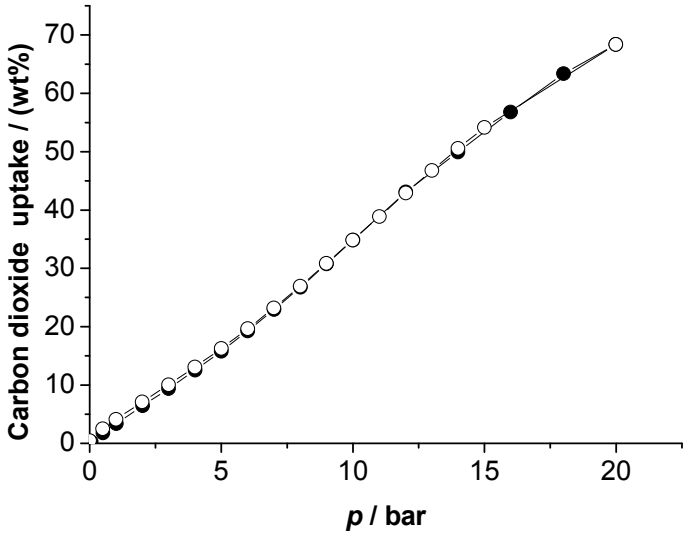

Figure S7. Carbon dioxide sorption isotherm at 298K for FJI-1 (●, adsorption; ○, desorption)

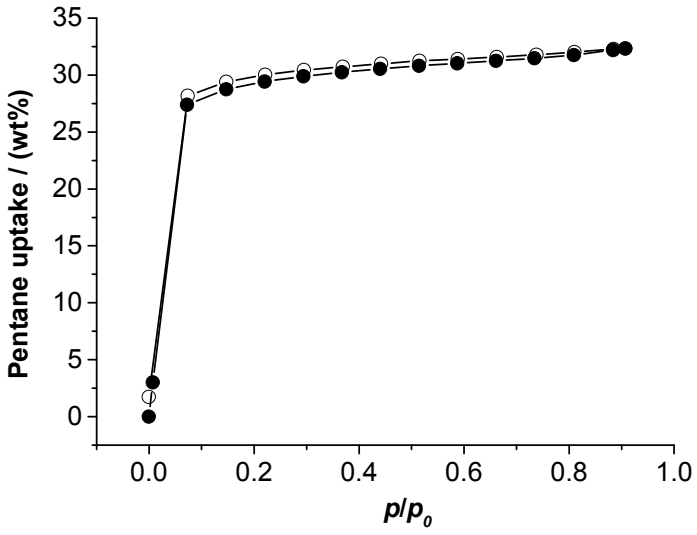

Figure S8. Pentane sorption isotherm at 298K for FJI-1 (●, adsorption; ○, desorption)

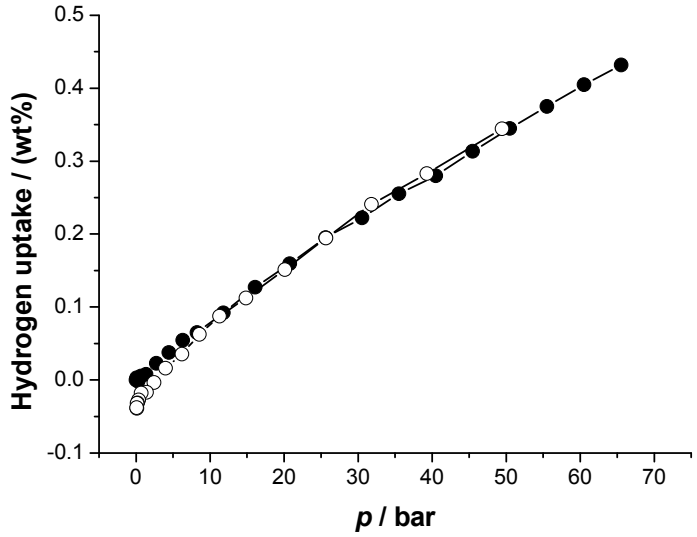

Figure S9. High-pressure hydrogen adsorption isotherm at 298 K for FJI-1 (●, excess adsorption; ○, excess desorption)

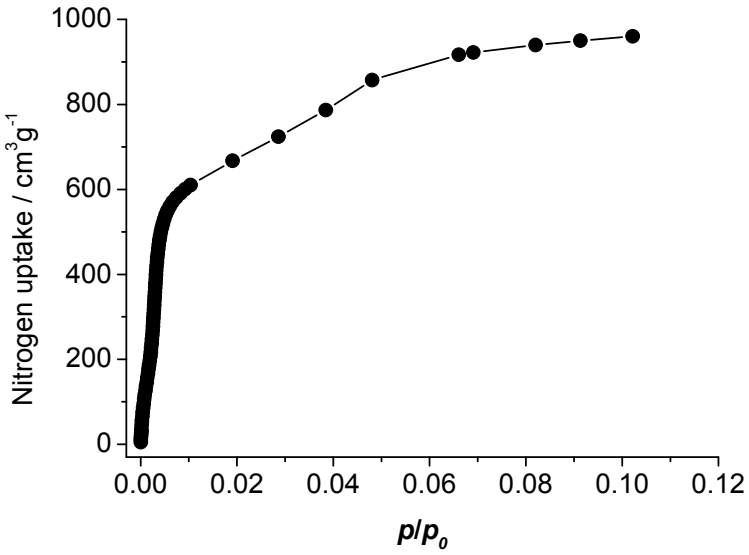

Figure S10. Low pressure nitrogen adsorption isotherm at 77K for FJI-1

Table 2. Surface Area Tabular Report

BET Surface Area Report	Langmuir Tabular Report
BET Area: 4043.3806±59.8596 $m^2 \cdot g^{-1}$	Langmuir Surface Area: 4624.5349±84.4619 $m^2 \cdot g^{-1}$
Slope: 0.023951±0.000357 $g \cdot mmol^{-1}$	Slope: 0.021099±0.000385 $g \cdot mmol^{-1}$
Y-intercept: 0.000180±0.000022 $g \cdot mmol^{-1}$	Y-intercept: 0.179278±0.018650 $mmHg \cdot g \cdot mmol^{-1}$
C: 133.846710	b: 0.117689 $mmHg^{-1}$
Qm: 41.43953 $mmol \cdot g^{-1}$	Qm: 47.39562 $mmol \cdot g^{-1}$
Correlation Coefficient: 0.9991148	Correlation Coefficient: 0.998668
Molecular Cross-Section Area: 0.1620 nm^2	Molecular Cross-Section Area: 0.1620 nm^2