SUPPORTING INFORMATION

Unusual pore structure and sorption behaviour in a hexanodal zinc-organic framework material

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Table of Contents

Section S1. General Experimental Procedures S2-S3

Section S2. Single-Crystal X-ray Crystallography S4-S5

Section S3. Additional Structural and Topological Figures S6-S9

Section S4. Topological Analysis Results S10-S12

Section S5. Powder X-Ray Diffraction S13

Section S6. TGA Plots S13

Section S7. Gas Sorption Test S14-S17

Section S8. IAST adsorption selectivity calculation S18-S19

Section S9. References S20

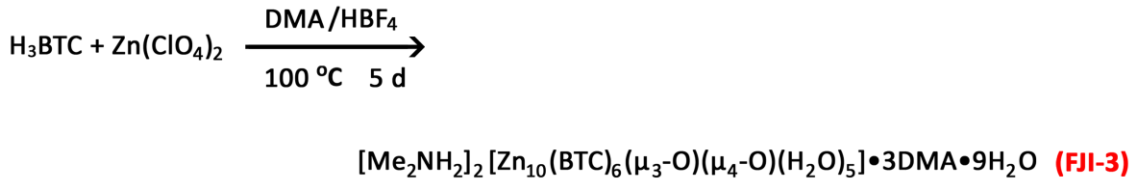
S1. General Experimental Procedures

1.1. Materials and Methods.

Reactions were carried out in 23 ml glass vials under autogenous pressure. All the reactants are of reagent-grade quality and used as commercially purchased without further purification. The power X-ray diffraction patterns (PXRD) were collected by a Rigaku D using Cu Kα radiation (λ = 0.154 nm). Single gas adsorption measurements were performed in the Accelerated Surface Area and Porosimetry 2020 (ASAP2020) System. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. Thermogravimetric analyses (TGA) were recorded on a NETZSCH STA 449C unit at a heating rate of 10 $^{o}C\cdot min^{-1}$ under flowing nitrogen atmosphere. SEM images were taken by Phenom G2.

1.2. Synthesis of $[Me_2NH_2]_2[Zn_{10}(BTC)_6(\mu_3\text{-}O)(\mu_4\text{-}O)(H_2O)_5]\bullet 3DMA\bullet 9H_2O$ (**FJI-3**)

A mixture of $Zn(ClO_4)_2\cdot 6H_2O$ (0.10 mmol, 37 mg), H_3BTC (0.10 mmol, 21 mg, H_3BTC = 1,3,5-benzenetricarboxylate) in N,N'-dimethylacetamide (DMA) (5 ml) with an additional HBF_4 (0.1 ml, Tetrafluoroboric acid, 40% in water) was sealed in a 23 ml glass vial, which was heated at 100 ^{o}C for 5 days, and cooled down to room temperature. It is worth pointing here is that the distorted $Me_2NH_2^+$ cations locate inside the large solvent accessible void, which is the byproduct of *in situ* decomposition of the DMA solvent, thus leading to the charge equilibrium. After washed by fresh acetonitrile, the colorless crystals of **FJI-3** were obtained in *ca*. ~50% yield based on the BTC ligand. Elemental analysis was calculated for **FJI-3**: C, 33.17%; H, 3.54%; N, 2.76%. Found: C, 33.43%; H, 3.78%; N, 2.96%. The phase purity of the sample was confirmed by powder X-ray diffraction (PXRD) and more details are shown below in Section S5.



Scheme S1. The synthesis of **FJI-3**.

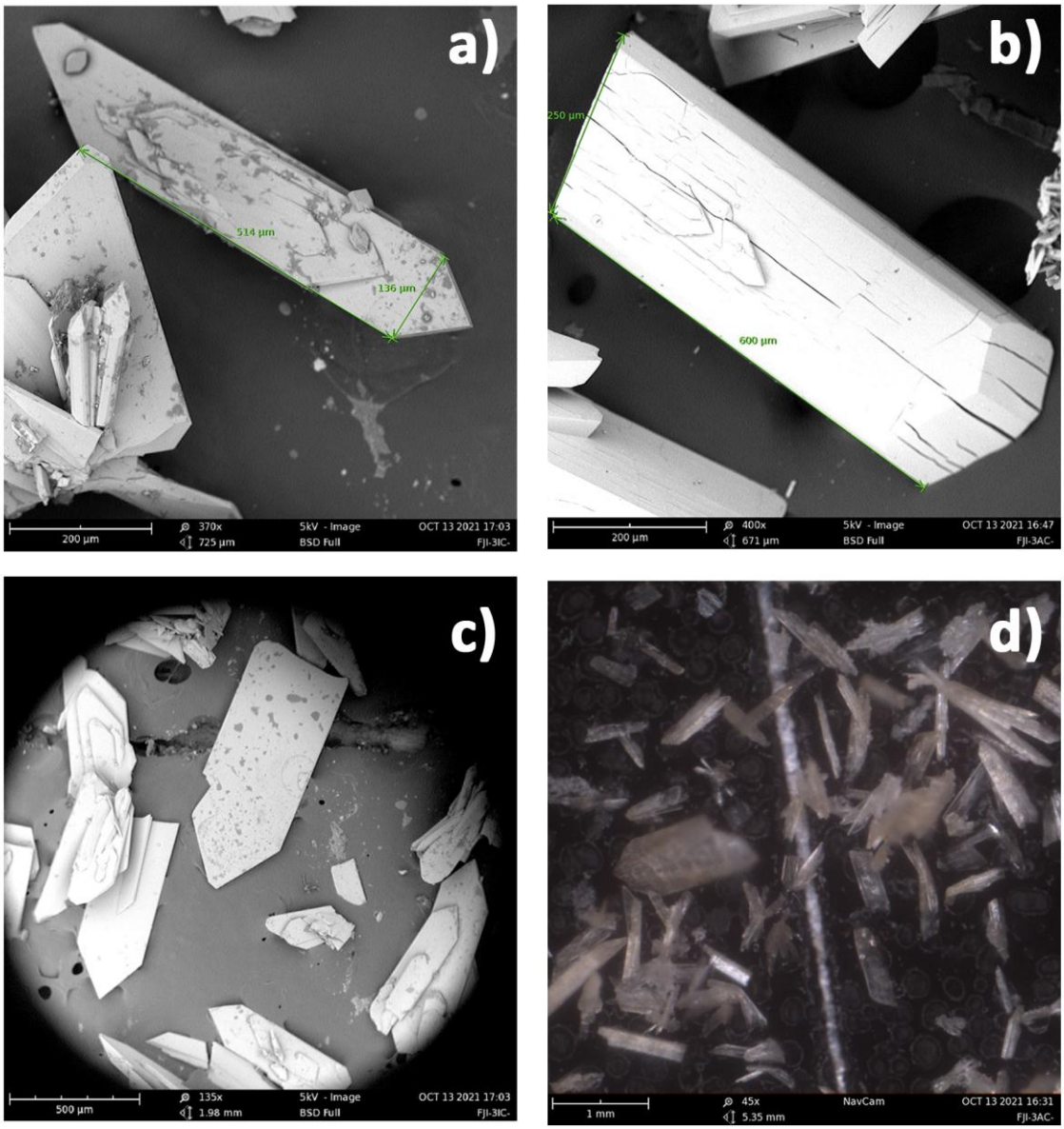


Figure S1. SEM images of the **FJI-3** before (a, c) and after the activation process (b, d).

S2. Single-Crystal X-ray Crystallography

The structure data of **FJI-3** was collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073Å) at room temperature and the structure was resolved by the direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[S1] Crystallographic data and structure refinement parameters at 173 (2) K for **FJI-3** are listed in Table S1. We employed PLATON/SQUEEZE[S2] to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formula of **FJI-3** was calculated from the SQUEEZE results combined with elemental analysis data and TGA data. More details on the crystallographic studies as well as atomic displacement parameters are given in Supporting Information as CIF files. Crystallographic data for the structure reported in this paper has been deposited. The following crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number (CCDC No.) 967656 for **FJI-3**.

Table S1. Crystal Data and Structure Refinement for FJI-3 at 173 (2) K.

Items	**FJI-3-T173K**
chemical formula	$C_{27}H_9O_{22}Zn_5$
formula mass	1012.19
crystal system	Orthorhombic
space group	***I***bam (#. 72)
a (Å)	19.7757(2)
b (Å)	44.7064(5)
c (Å)	28.6303(3)
α (°)	90.00
β(°)	90.00
γ(°)	90.00
unit cell volume ($Å^3$)	25312.1(5)
temperature (K)	173 (2)
Z	16
F(000)	7952
no. of reflections measured	26679
no. of independent reflections	10953
R_{int}	0.0960
final R1 values (I>2σ(I))	0.0850
final wR (F^2) values (I>2σ(I))	0.2709
goodness of fit on F^2	1.072
flack parameter	0.00(2)

S3. Additional X-ray Crystal Structural and Topological Figures

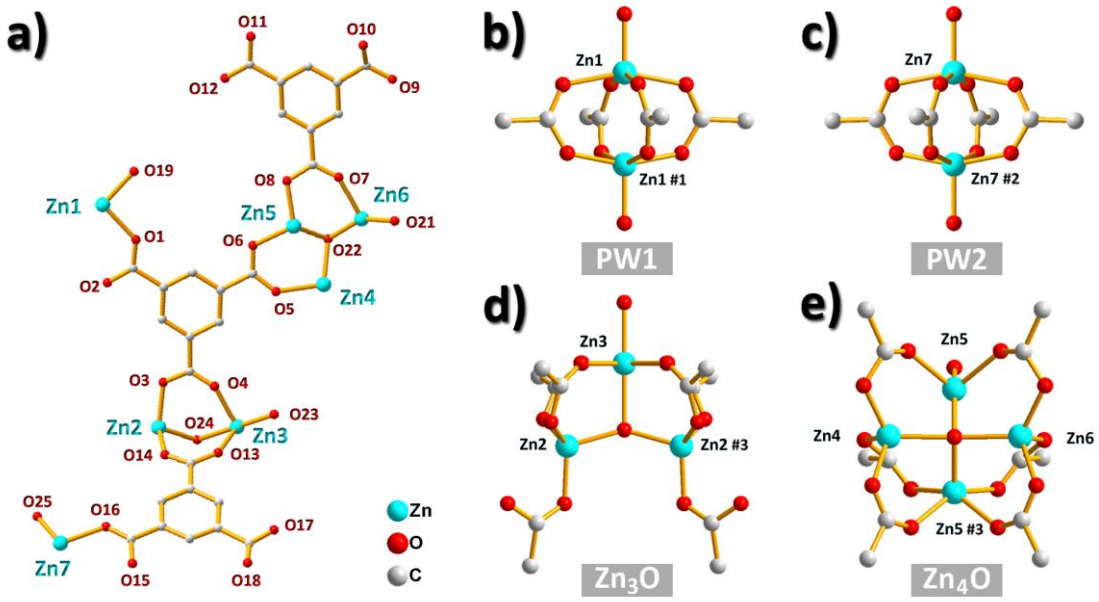


Figure S2. Coordination condition of Zn(II) centers and BTC(III) ligands in the asymmetric unit of **FJI-3**, secondary building units (SBUs), symmetry codes: #1 = 1-x, y, 0.5-z; #2 = -x, 1-y, z; #3 = x, y, 1-z.

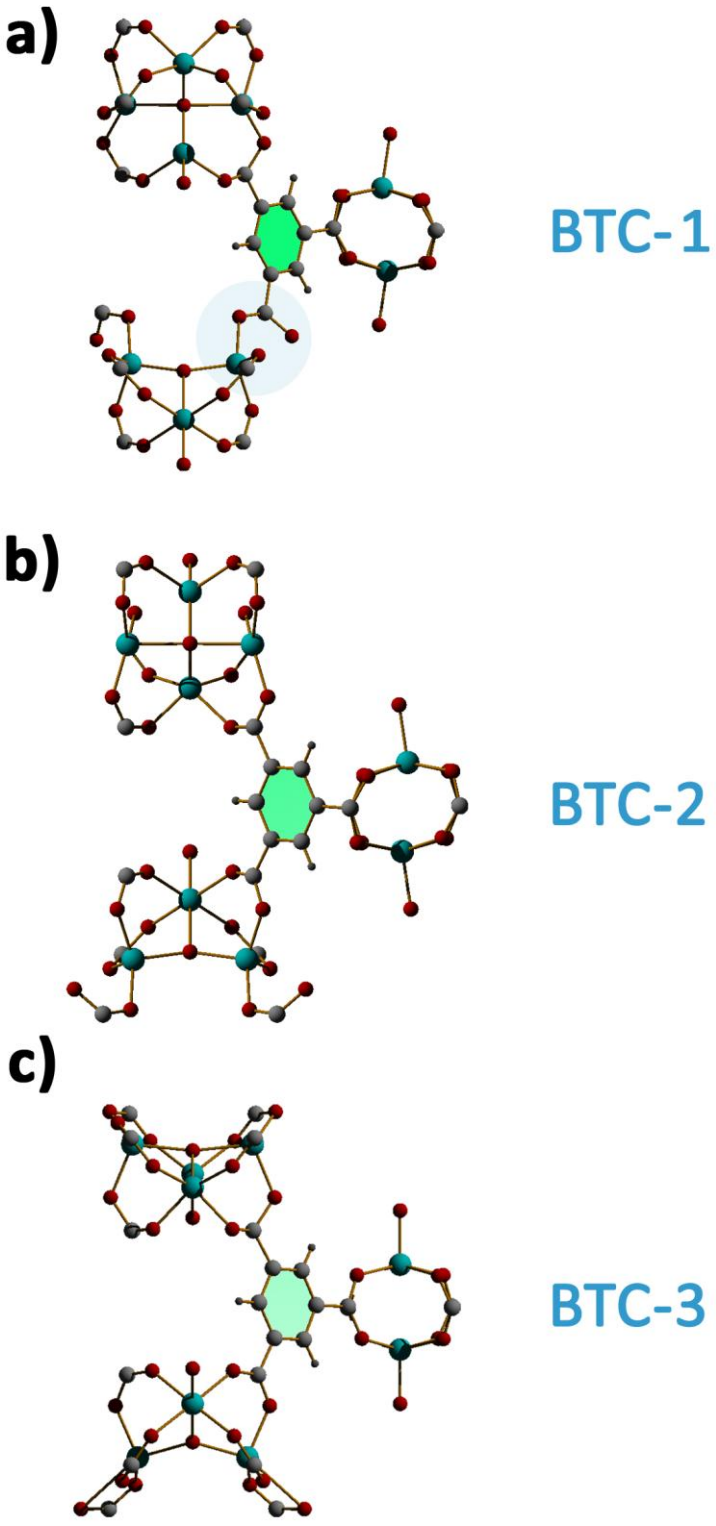


Figure S3. Coordination environment of BTC ligands in **FJI-3**, namely BTC-1 (a), BTC-2 (b) BTC-3 (c).

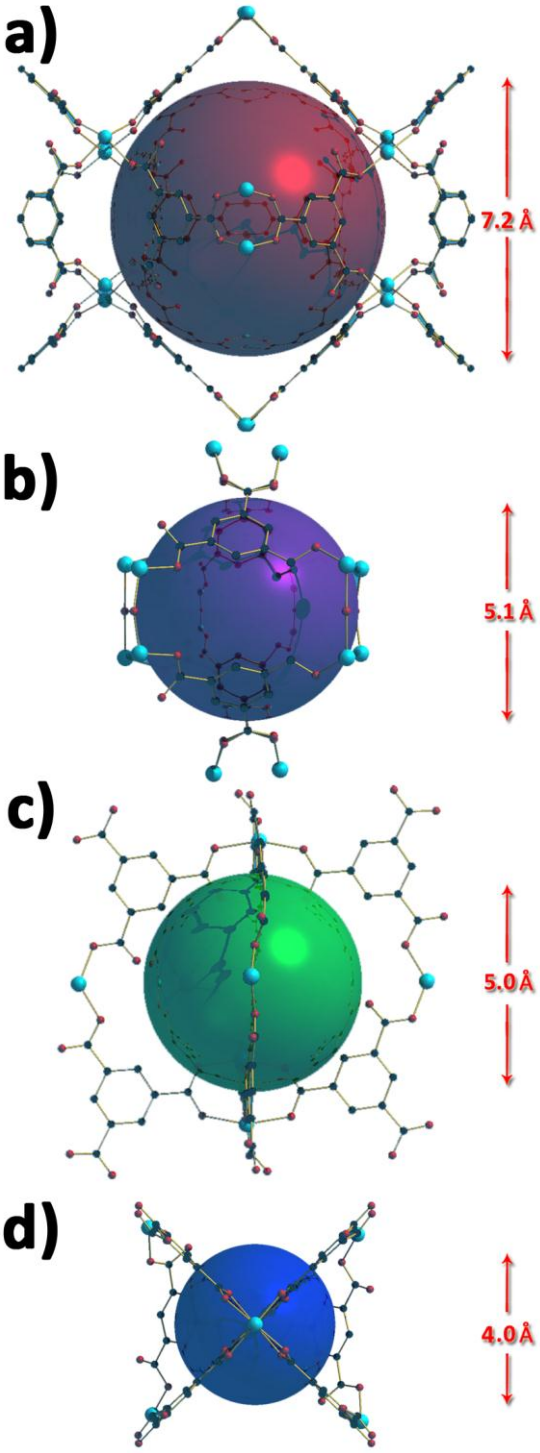


Figure S4. Four kinds of microporous cages in **FJI-3** with different sizes.

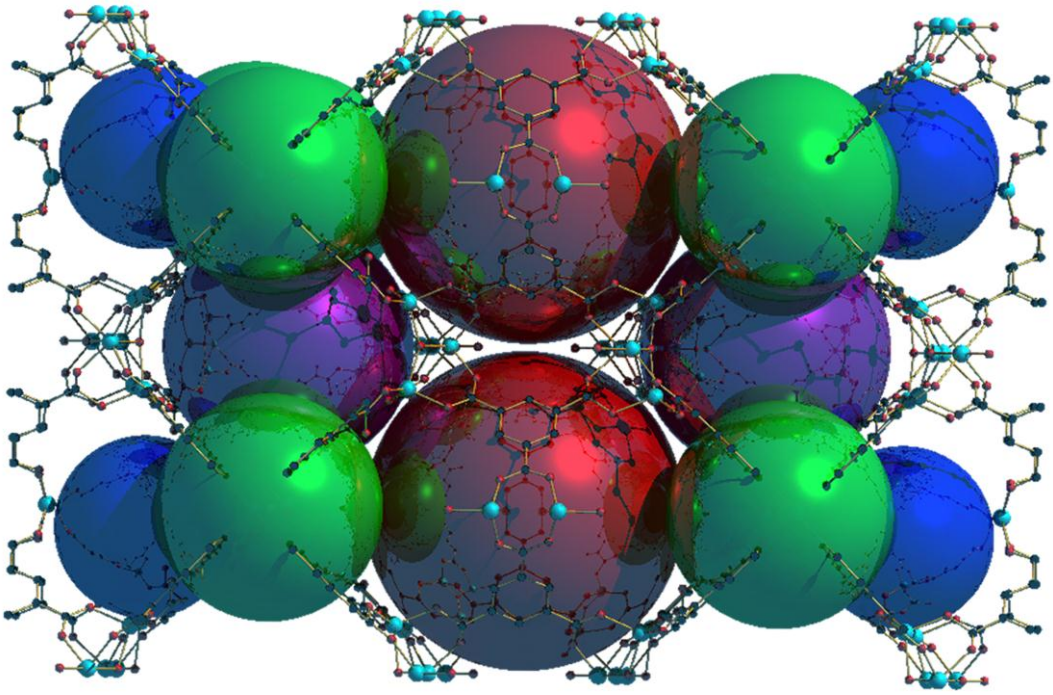


Figure S5. Four kinds of microporous cages packed in **FJI-3**.

S4. Topological Analysis Results by TOPOS 4.0

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Name: FJI-3

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Topology for **BTC-1:** Atom **BTC-1** links by bridge ligands and has

Common vertex with					R(A-A)	
PW1	0.0000	0.2333	0.2500	(0 0 0)	5.453A	1
Zn_4O	-0.2211	0.3907	0.5000	(-1 0 0)	6.562A	1
Zn_3O	0.2694	0.3915	0.5000	(0 0 0)	6.824A	1

Topology for **BTC-2:** Atom **BTC-2** links by bridge ligands and has

Common vertex with					R(A-A)	
PW1	0.5000	0.2667	0.2500	(0 0-1)	5.462A	1
Zn_3O	0.2694	0.3915	0.5000	(0 0 0)	5.937A	1
Zn_4O	0.7789	0.3907	0.5000	(0 0 0)	6.545A	1

Topology for **BTC-3:** Atom **BTC-3** links by bridge ligands and has

Common vertex with					R(A-A)	
PW2	0.0000	0.5000	0.2500	(0 0 0)	5.437A	1
Zn_4O	0.2211	0.6093	0.5000	(1 1 0)	5.830A	1
Zn_3O	0.2694	0.3915	0.5000	(0 0 0)	6.139A	1

Topology for **PW1:** Atom **PW1** links by bridge ligands and has

Common vertex with					R(A-A)	
BTC-1	0.0156	0.3213	0.3814	(0 0 0)	5.453A	1
BTC-1	-0.0156	0.3213	0.1186	(0 0 0)	5.453A	1
BTC-2	-0.0048	0.1487	0.1124	(0 0 0)	5.462A	1
BTC-2	0.0048	0.1487	0.3876	(-1 0-1)	5.462A	1

Topology for **PW2:** Atom **PW2** links by bridge ligands and has

Common vertex with					R(A-A)	
BTC-3	0.1932	0.5024	0.3851	(0 0 0)	5.437A	1
BTC-3	-0.1932	0.5024	0.1149	(0 0 0)	5.437A	1
BTC-3	0.1932	0.4976	0.1149	(0 1 0)	5.437A	1
BTC-3	-0.1932	0.4976	0.3851	(0 1 0)	5.437A	1

Topology for **Zn_3O:** Atom **Zn_3O** links by bridge ligands and has

Common vertex with					R(A-A)	
BTC-2	0.5048	0.3513	0.3876	(0 0 0)	5.937A	1
BTC-2	0.5048	0.3513	0.6124	(0 0 1)	5.937A	1
BTC-3	0.1932	0.5024	0.6149	(0 0 1)	6.139A	1

BTC-3	0.1932	0.5024	0.3851	(0 0 0)	6.139A	1
BTC-1	0.0156	0.3213	0.6186	(0 0 1)	6.824A	1
BTC-1	0.0156	0.3213	0.3814	(0 0 0)	6.824A	1

Topology for **Zn_4O:** Atom **Zn_4O** links by bridge ligands and has

Common vertex with					R(A-A)	
BTC-3	0.8068	0.4976	0.6149	(1 1 1)	5.830A	1
BTC-3	0.8068	0.4976	0.3851	(1 1 0)	5.830A	1
BTC-2	0.5048	0.3513	0.6124	(0 0 1)	6.545A	1
BTC-2	0.5048	0.3513	0.3876	(0 0 0)	6.545A	1
BTC-1	1.0156	0.3213	0.3814	(1 0 0)	6.562A	1
BTC-1	1.0156	0.3213	0.6186	(1 0 1)	6.562A	1

Structural group analysis, Coordination sequences

BTC-1:	1	2	3	4	5	6	7	8	9	10
Num	3	12	17	49	50	116	93	213	167	342
Cum	4	16	33	82	132	248	341	554	721	1063

BTC-2:	1	2	3	4	5	6	7	8	9	10
Num	3	12	19	53	48	116	101	219	165	344
Cum	4	16	35	88	136	252	353	572	737	1081

BTC-3:	1	2	3	4	5	6	7	8	9	10
Num	3	12	17	47	49	124	100	211	156	328
Cum	4	16	33	80	129	253	353	564	720	1048

PW1:	1	2	3	4	5	6	7	8	9	10
Num	4	8	36	33	80	74	168	128	284	217
Cum	5	13	49	82	162	236	404	532	816	1033

PW2:	1	2	3	4	5	6	7	8	9	10
Num	4	8	28	28	76	74	176	122	256	208
Cum	5	13	41	69	145	219	395	517	773	981

Zn_3O:	1	2	3	4	5	6	7	8	9	10
Num	6	9	28	33	88	74	166	135	282	195
Cum	7	16	44	77	165	239	405	540	822	1017

Zn_4O:	1	2	3	4	5	6	7	8	9	10
Num	6	9	28	33	88	74	166	135	282	195
Cum	7	16	44	77	165	239	405	540	822	1017

Vertex symbols for selected sublattice

BTC-1 Point (Schlafli) symbol:{4.8^2}
Extended point symbol:[4.8(8).8(8)]

BTC-2 Point (Schlafli) symbol:{4.8^2}
Extended point symbol:[4.8(7).8(7)]

BTC-3 Point (Schlafli) symbol:{4.6^2}
Extended point symbol:[4.6(2).6(2)]

PW1 Point (Schlafli) symbol:{8^6}
Extended point symbol:[8(2).8(2).8(4).8(6).8(8).8(8)]

PW2 Point (Schlafli) symbol:{6^2.8^4}
Extended point symbol:[6(4).6(4).8(2).8(2).8(4).8(4)]

Zn_3O Point (Schlafli) symbol:{4^3.6^4.8^8}
Extended point symbol:[4.4.4.6.6.6.6.8.8.8(3).8(3).8(4).8(4).8(5).8(5)]

Zn_4O Point (Schlafli) symbol:{4^3.6^4.8^8}
Extended point symbol:[4.4.4.6.6.6.6.8.8.8(3).8(3).8(4).8(4).8(5).8(5)]

Point (Schlafli) symbol for net: {4.6^2}4{4.8^2}8{4^3.6^4.8^8}4{6^2.8^4}{8^6}2
3,3,3,4,4,6-c net with stoichiometry (3-c)4(3-c)4(3-c)4(4-c)2(4-c)(6-c)4; 6-nodal net

New topology

S5. Powder X-Ray Diffraction

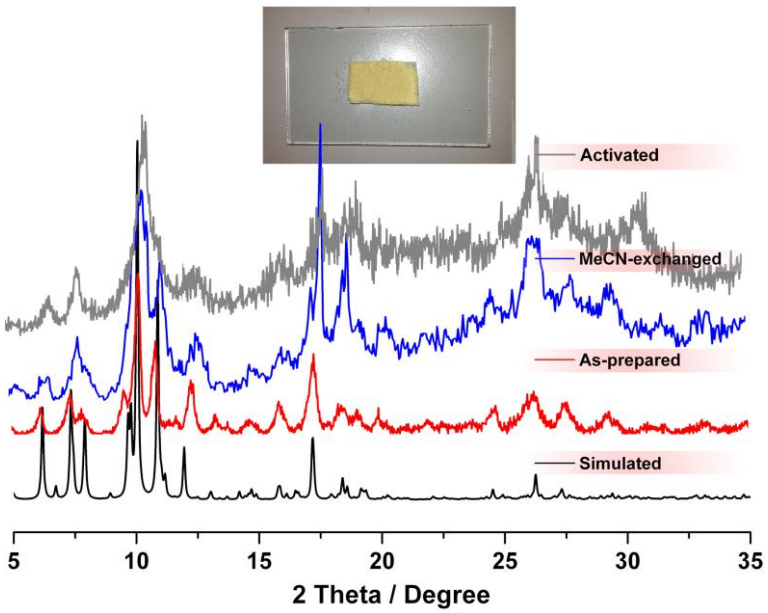

Figure S6. PXRD patterns of **FJI-3**: a) simulated from the crystallographic information file; b) from the as-prepared sample; c) from the MeCN-exchanged sample; d) from the desolvated sample.

S6. Thermal Gravimetric Plots

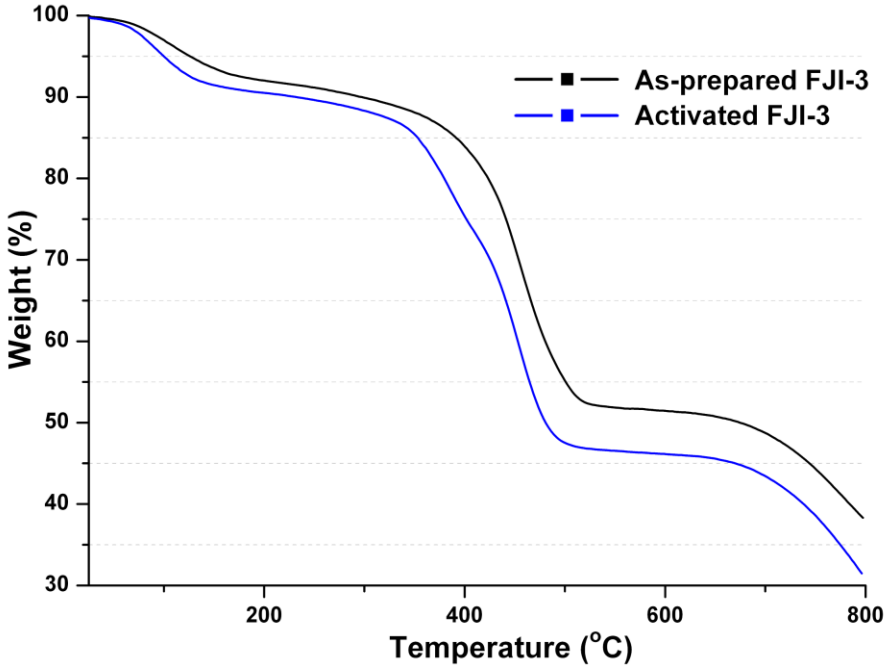

Figure S7. TGA curves for fresh and desolvated **FJI-3** samples.

S8 Gas Sorption Test

N_2, H_2 and CO_2 Isotherms. N_2, H_2 and CO_2 isotherms were determined using an IGA gravimetric adsorption apparatus at the Fujian Institute of Research on the Structure of Matter in a clean ultra high vacuum system. Before measurements, about 100 mg MeCN-exchanged samples were loaded into the sample basket within the adsorption instrument and then degassed under dynamic vacuum for 10 h to obtain the fully desolvated samples.

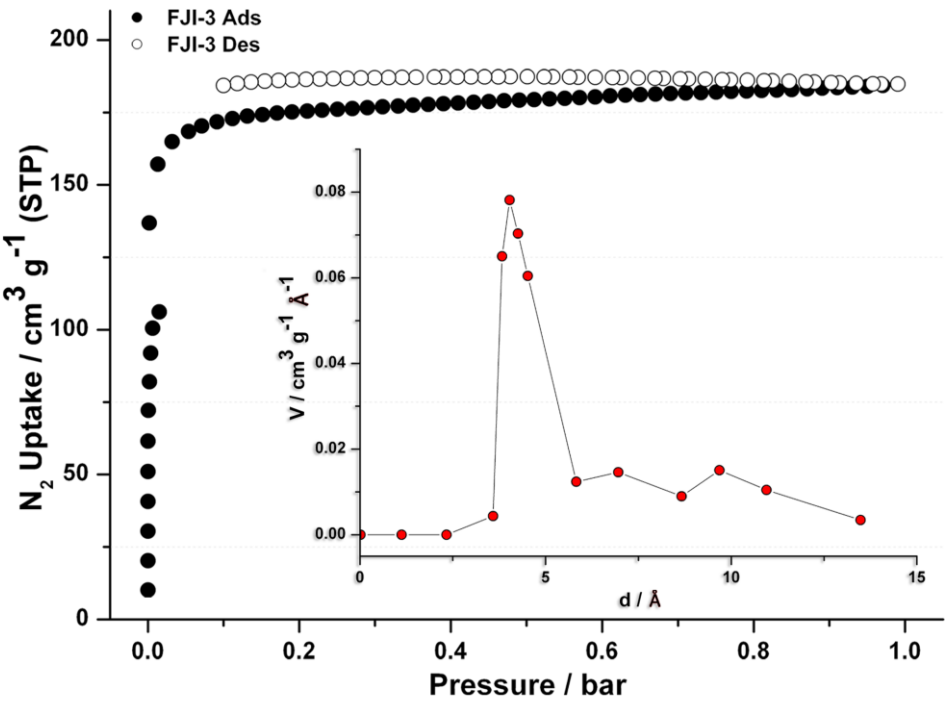

Figure S8. N_2 adsorption-desorption isotherms for activated **FJI-3** at 77 K.

H_2 isotherms measured at 77 K and 87 K for **FJI-3** were fit to the following Equation

In Fig. S11, the adsorption heat (Q_{st}) of hydrogen for the desolvated **FJI-3** is fitted by Virial method using the data obtained from 77 K and 87 K.

$$\ln(p) = \ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i * N_i + \frac{1}{T}\sum_{j=0}^{m} a_j * N_j$$

N: adsorbed quantity (mg/g);

p: pressure (mmHg);

T: Temperature (K);

ai、bj: Constant;

R: 8.314 $J \cdot mol^{-1} \cdot K^{-1}$;

The isosteric enthalpy of adsorption (Q_{st})：

$$Q_{st} = \ln(p) = -R * \sum_{i=0}^{m} a_i * N_i$$

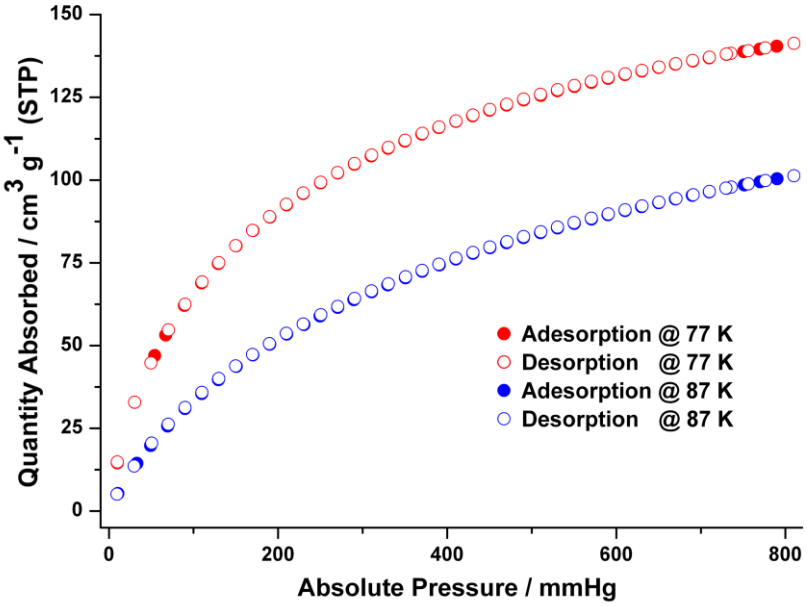

Figure S9 H_2 sorption isotherms for **FJI-3** at 77 and 87 K.

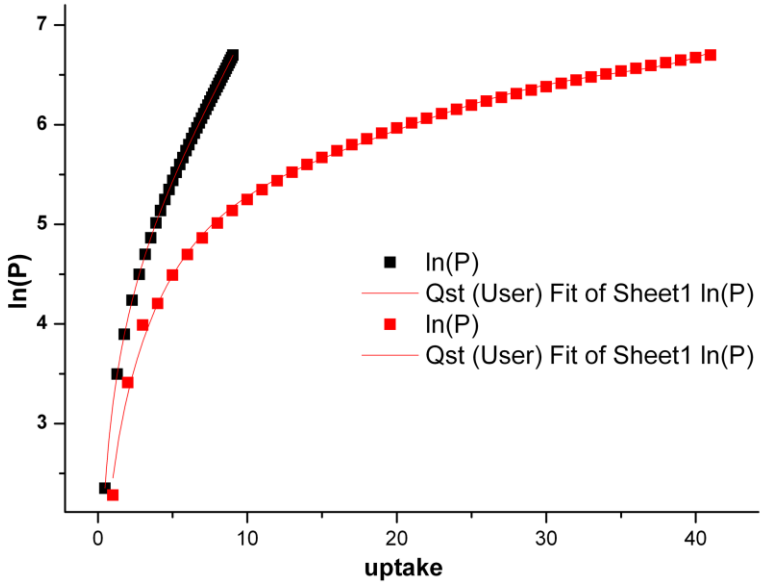

Figure S10 Nonlinear curve fitting of H_2 adsorption isotherms for **FJI-3** at 77 K and 87 K.

$$y=\ln(x)+1/k*(a0+a1*x+a2*x^2+a3*x^3+a4*x^4+a5*x^5)+(b0+b1*x+b2*x^2)$$

		Value	Standard Error
ln(P)	a0*	-500.34342	29.43741
	a1*	14.32361	11.08673
	a2*	-8.55931	0.97831
	a3*	0.0905	0.0118
	a4*	-0.00207	3.08327E-4
	a5*	1.75898E-5	2.92473E-6
	b0*	8.76101	0.35181
	b1*	0.02873	0.13087
	b2*	0.08754	0.01096
	k	77	0
	k	87	0

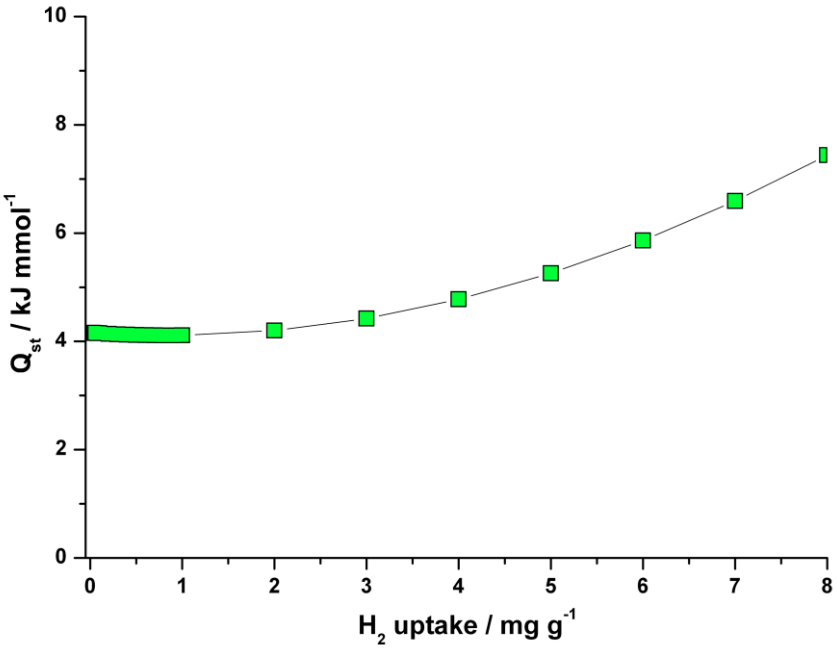

Figure S11 Heats of adsorption for H_2 in **FJI-3**.

S9 IAST adsorption selectivity calculation

We adopt the ideal adsorbed solution theory (IAST)[S7] based upon the experimental single gas adsorption measurements as listed in the following pages, including carbon dioxide, methane and nitrogen at 273 K and 295 K, which is commonly used to predict binary mixture adsorption selectivity. Using the pure component isotherm fits, the adsorption selectivity is defined by

$$S_{ads} = (q_1/q_2)/(p_1/p_2),$$

where q_i is the amount of i adsorbed and p_i is the partial pressure of i in the mixture.

We us the following written codes to simulate the adsorption selectivity of CO_2 over CH_4 or N_2 in Fig. 3d,

28 # No. of Pressure Point

y1, y2 # Molar fraction of binary mixture (y1 and y2, y1 + y2 = 1)

1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 101, 102, 103,

104, 105, 106, 107, 108, 109 #The unit is same parameter b, kPa

a1, a1 # fitting parameter Nsat1(A1) for both component (Unit: mmol/g)

b1, b1 # fitting parameter b1 for both component (Unit: kPa^{-1})

c1, c1 # fitting parameter c1 for both component

0, 0 # fitting parameter Nsat2(A2) for both component(Unit: mmol/g)

0, 0 # fitting parameter b2 for both component (Unit: kPa^{-1})

1, 1 # fitting parameter c2 for both component

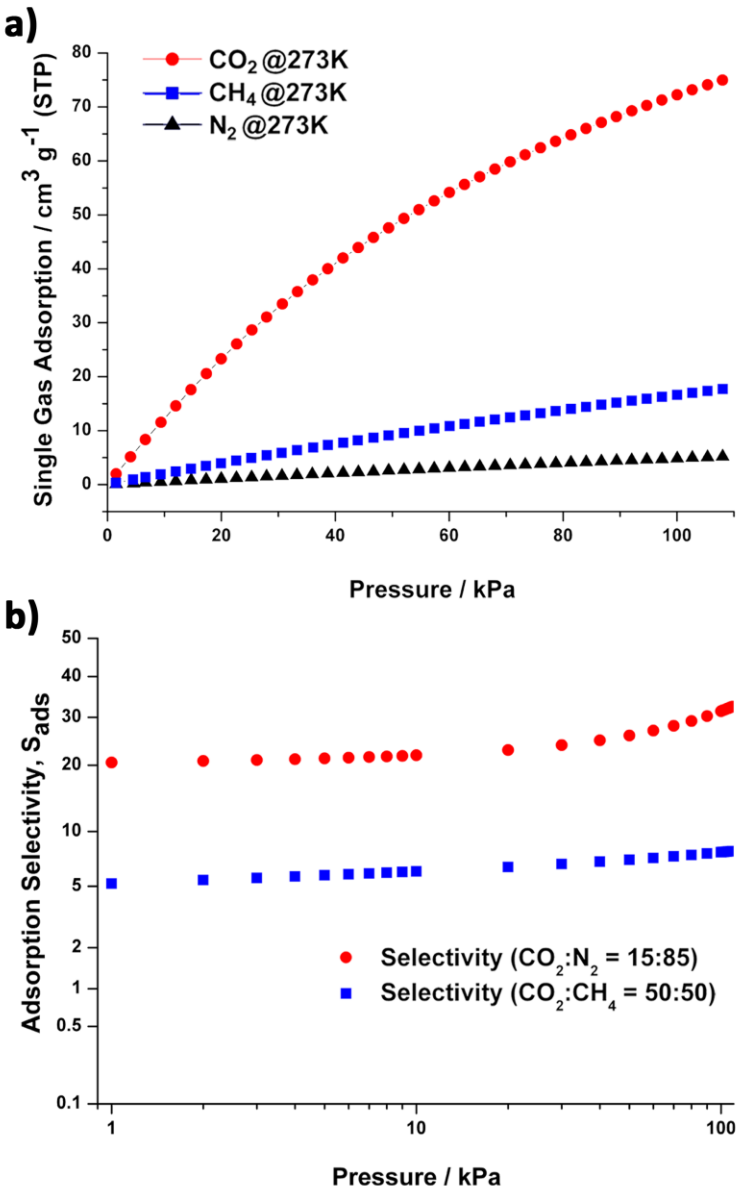

Figure S12: (a) CO_2, CH_4 and N_2 adsorption isotherm curves in the range of 0 ~ 110 kPa at 273 K. (b) Adsorption selectivity of CO_2 over CH_4 or N_2.

S9. References.

[S1] Sheldrick, G. M. SHELXS-97, Programs for X-ray Crystal Structure Solution; University of Göttingen: Germany, **1997**.

[S2] (a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; (b) P. v.d. Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, **1990**, *46*, 194.