Supplementary Information

A flexible microporous framework with temperature-dependent gate-opening behaviours for C2 gases†

Zhenyu Ji, [a,b] Yerong Fan, [a] Mingyan Wu*, Maochun Hong*

[a] College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China

Materials and Instrumentation

All reagents and solvents used in synthetic studies were commercially available and used as supplied without further purification. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. Single crystal X-ray diffraction experiments were carried on a Synergy Custom (Liquid MetalJet D2+) diffractometer, with Ga Kα radiation (λ = 1.34050 Å) by using a ω scan mode. PXRD patterns were collected by an Empyrean X-ray diffractometer using CuKα radiation. Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10 °Cmin^{-1} under nitrogen atmosphere. Gas sorption isotherms of activated $\mathbf{1_{des}}$ were measured on a Micromeritics 2020 surface area analyzer.

Synthesis of 1 and 1_{des}

$Co(NO_3)_2 \cdot 6H_2O$(0.1mmol,0.0291g), DMIPM(0.05mmol, 0.0106g) and H_2BDC(0.1mmol, 0.0166g) were dissolved in 6ml DMF. The mixed solution was stirred at room temperature until it became clear. Then the resulted solution was sealed in a 10 ml Pyrex vial and heated at 85 °C for 3days. After cooling to room temperature, the plate-like black crystals of **1** were collected at the bottom of the bottle with a yield of ca 40% based on DMIPM.

As-synthesized $\mathbf{1_{des}}$ (200mg) was washed three times with DMF and acetone, and then the sample was exchanged in acetone for 7 days. During the solvent exchange, fresh acetone was used to replace the exchanged acetone, three times a day. After the solvent exchange was complete, filter out the **1**, then place the sample under vacuum for 12 hours, and then place the sample under vacuum at 80 °C for

10 hours to obtain $\mathbf{1_{des}}$. Element analysis (%) for $\mathbf{1_{des}}$. Calculated: C, 48.99; H, 2.94; N, 12.24. Experiment: C, 49.24; H, 2.91; N, 12.27.

Single-Crystal X-ray Crystallography

Single crystal X-ray diffraction experiments were carried on a Synergy Custom (Liquid MetalJet D2+) diffractometer, with GaKα radiation (λ = 1.34050 Å) at 273k and 298K. The crystal structure was resolved by direct methods and refined by full-matrix least squares fitting on F_2 using the SHELXL-2016 software package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the aromatic rings were located at geometrically calculated positions and refined by riding. In **1** the diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE routine of PLATON.

Table S1. Summary of crystal data and structure refinements for **1** and $\mathbf{1_{des}}$

Compounds	**1**	$\mathbf{1_{des}}$
CCDC	2053355	2053456
Empirical formula	$C_{28}H_{20}N_6O_8Co_2$	$C_{28}H_{20}N_6O_8Co_2$
Formula weight	686.36	686.36
T (K)	298	298
Crystal system	*monoclinic*	*monoclinic*
Space group	C2/c	$P2_1/n$
a (Å)	16.23320(10)	10.0100(4)
b (Å)	14.59330(10)	18.7883(5)
c (Å)	31.8280(8)	16.0273(5)
α (°)	90	90
β (°)	93.5300(10)	95.972(3)
γ (°)	90	90
V (Å^3)	7525.62(10)	2997.91(17)
Z	8	4
Size/mm^3	0.2×0.2×0.25	0.1×0.1×0.1
Density(g/cm^3)	1.395	1.525
Radiation	GaKα	GaKα
ρ_{calcd} (g/cm^3)	1.212	1.525
μ (mm^{-1})	5.106	6.409
F(000)	2784.0	1392.0
T (K)	173	293
Measured refls.	27478	21835
Independent refls.	8376	6636
R_{int}	0.0240	0.045
R1/wR2 [I > 2σ(I)]	0.0294/ 0.0706	0.039/0.103
GOF on F^2	1.032	1.004

$^{a}R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. $^{b}wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

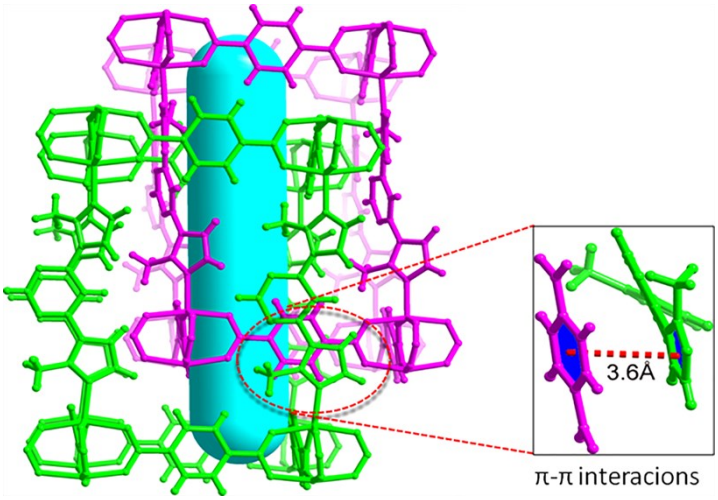

Figure S1. A representation of the two interpenetrating frameworks in **1** with the large channel along *c* direction. The pyrimidine and imidazole groups are arranged by π–π interactions (3.6 Å).

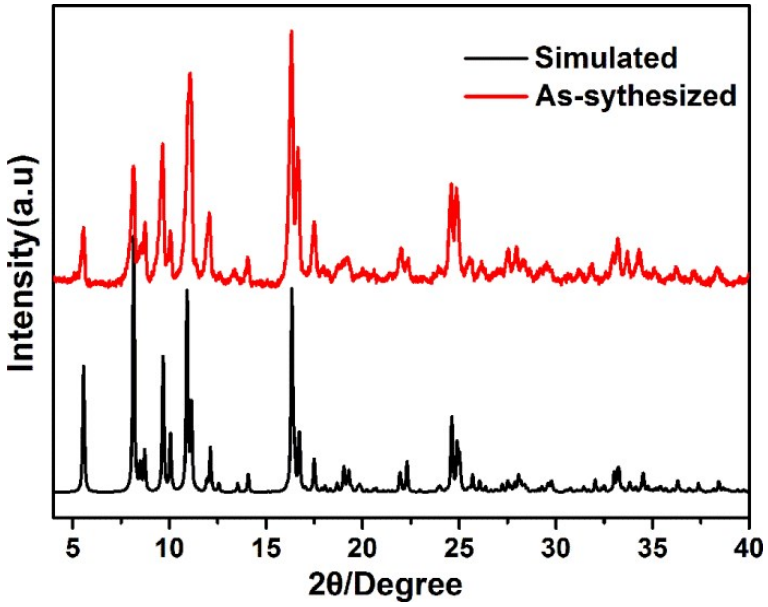

Figure S2. The PXRD patterns of **1**.

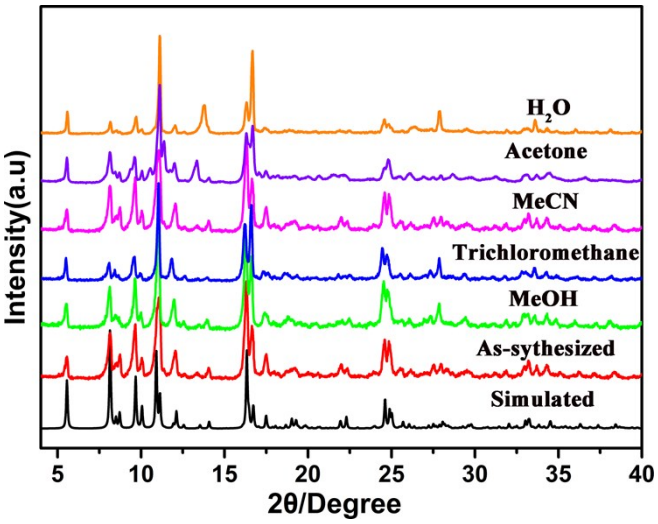

Figure S3. PXRD patterns of **1** after treatment with MeOH, $CHCl_3$, MeCN, Acetone and H_2O

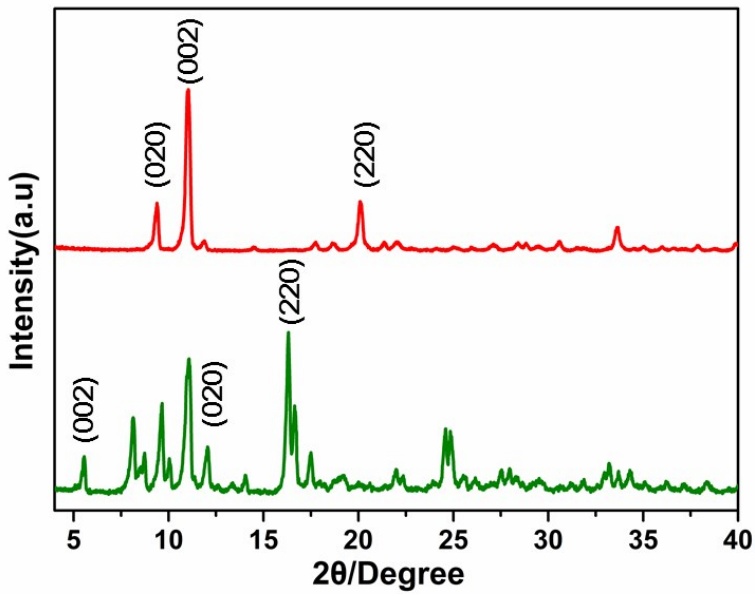

Figure S4 Comparison of the PXRD patterns of **1** (green) and $\mathbf{1}_{des}$ (red).

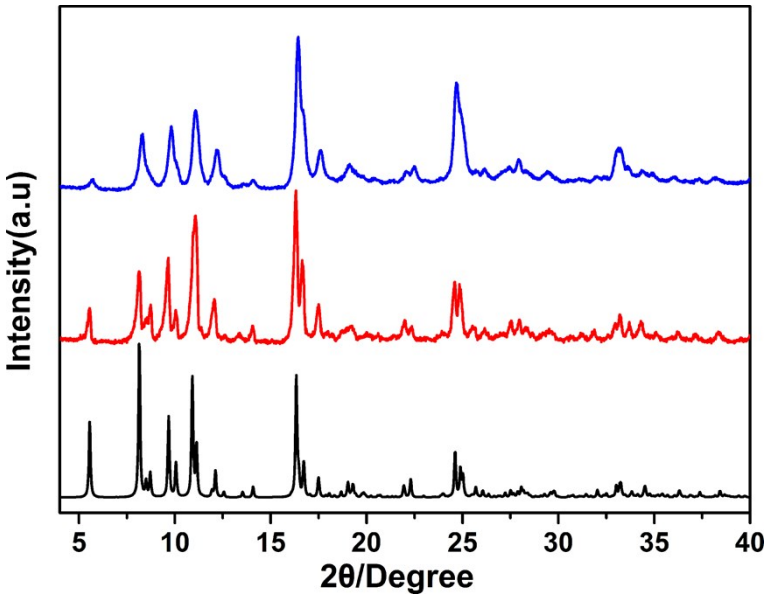

Figure S5. The PXRD patterns of **1** simulated (black), **1** as synthesized (red) and $\mathbf{1}_{\mathbf{des}}$ soaked in DMF.

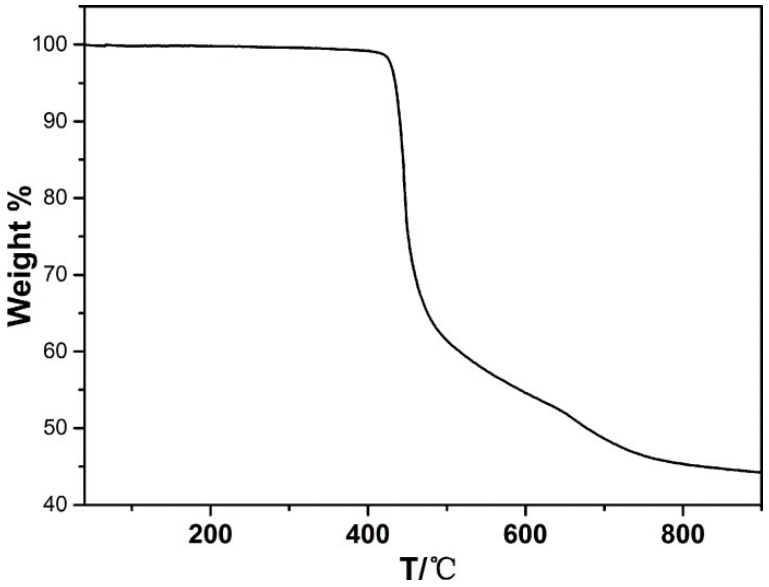

Figure S6. The thermogravimetric analysis of as-synthesized $\mathbf{1}_{\mathbf{des}}$.

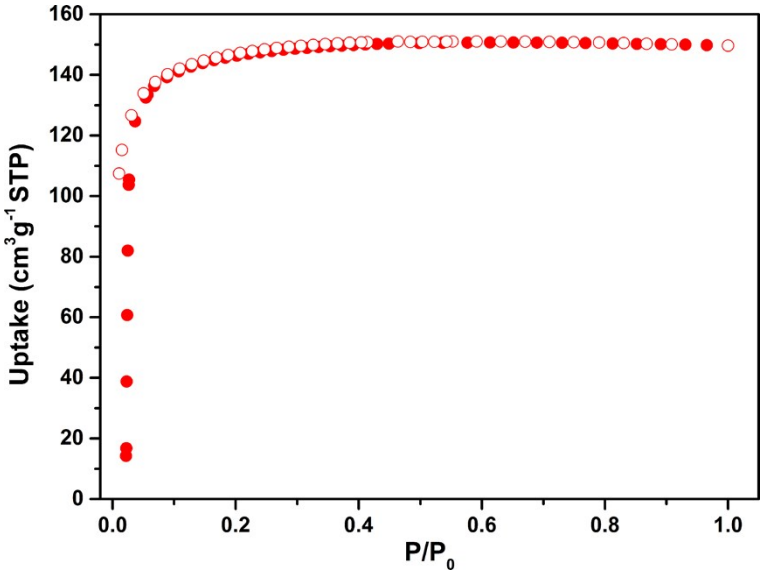

Figure S7. The CO_2 sorption isotherms of $\mathbf{1}_{des}$ at 195K.

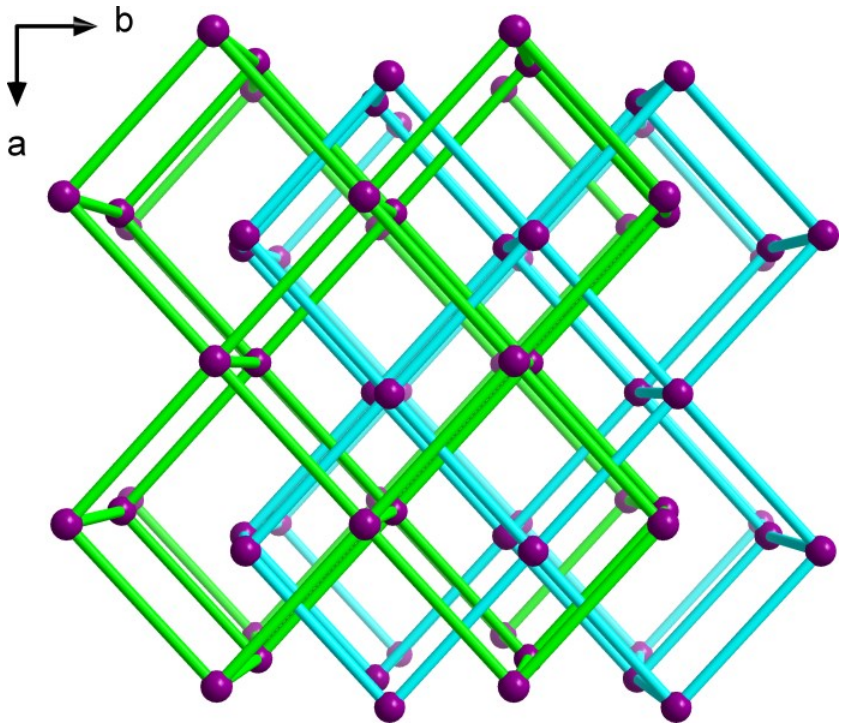

Figure S8. The two interpenetrated topology are shown in green and light blue respectively.

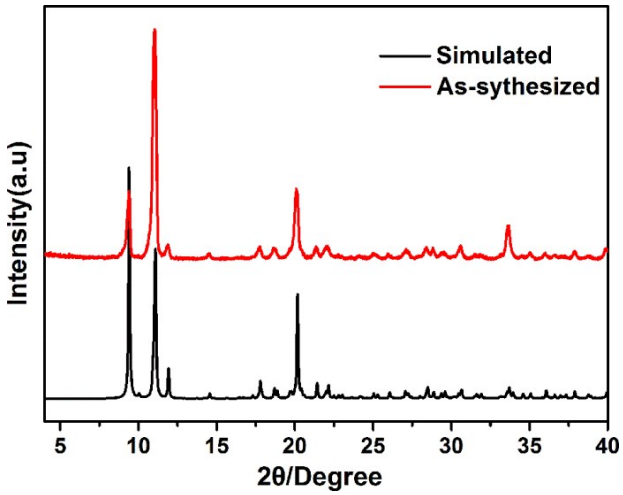

Figure S9. The PXRD patterns of $\mathbf{1}_{des}$.

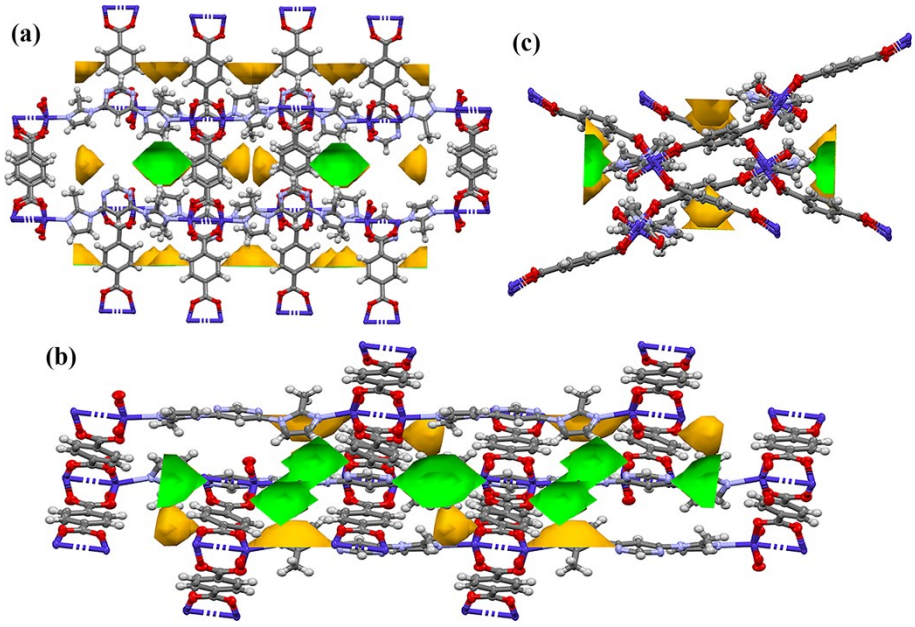

Figure S10. A representation of the non-porosity of $\mathbf{1}_{des}$ in different directions.(a) *a* axis, (b) *b* axis, (c) *c* axis

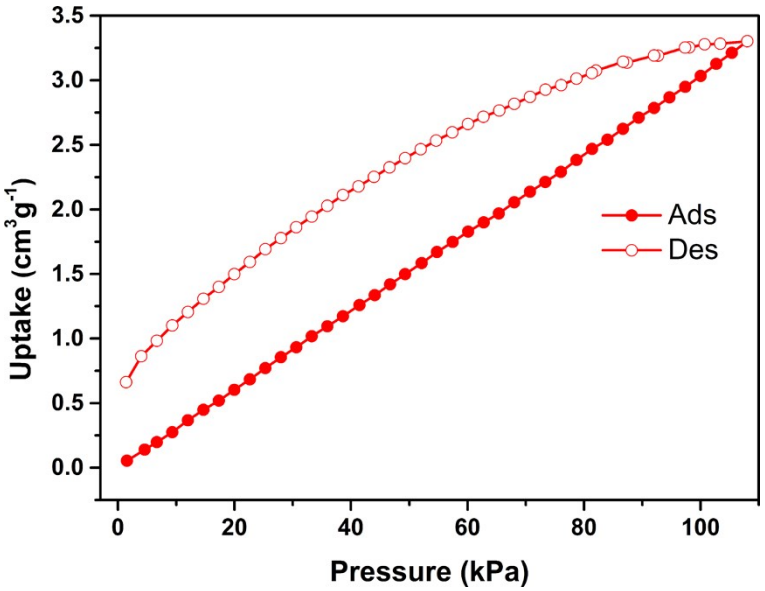

Figure S11. The adsorption isotherm of $\mathbf{1}_{des}$ for CO_2 at 298 K.

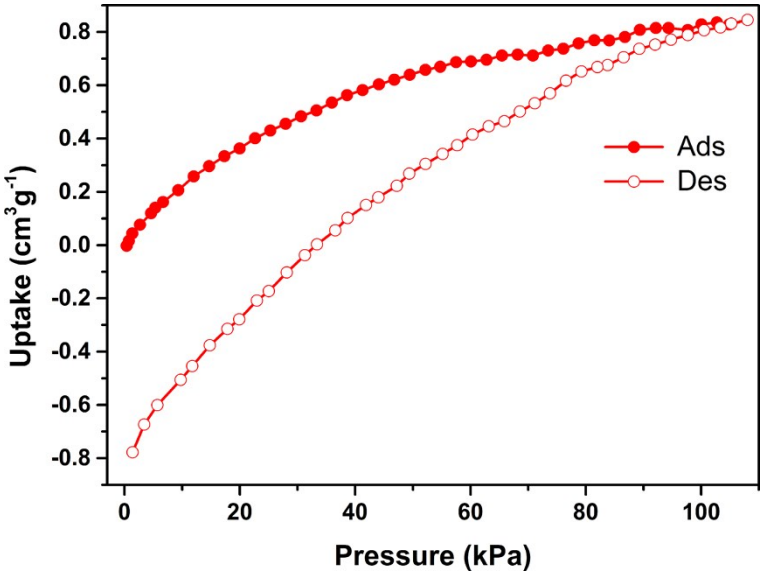

Figure S12. The adsorption isotherm of $\mathbf{1}_{des}$ for N_2 at 298 K.

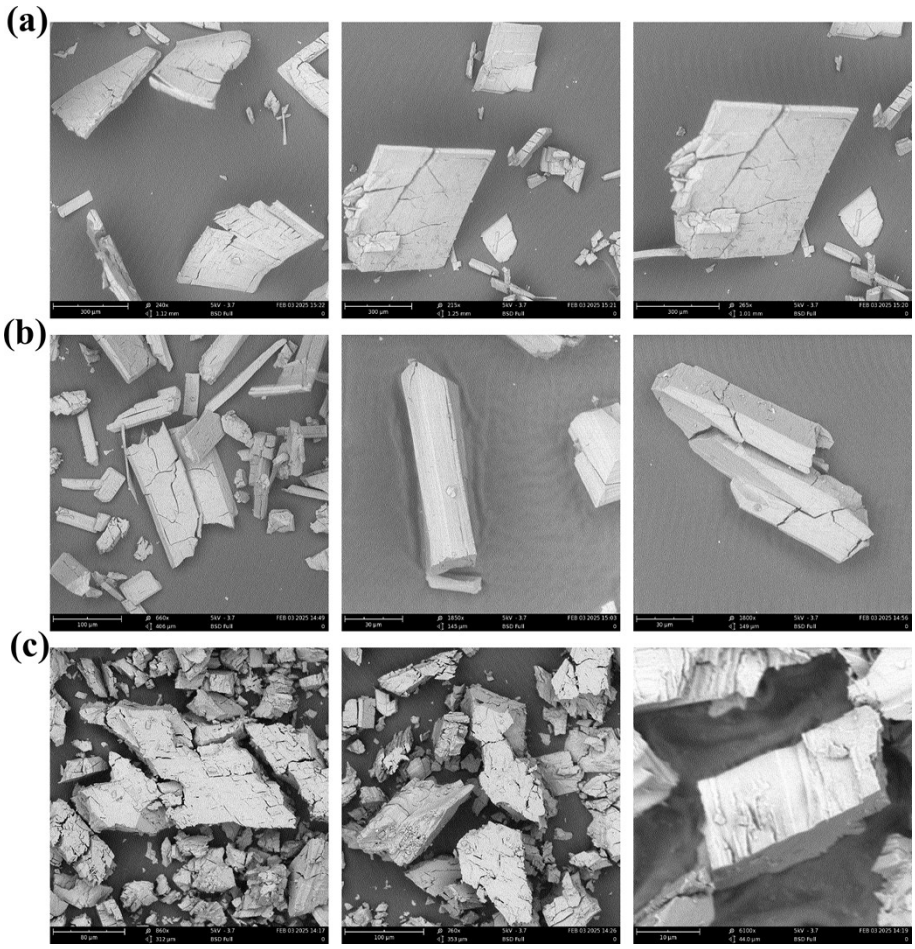

Figure S13. The SEM images of **1** (a), $\mathbf{1}_{\mathbf{des}}$ (b), and the sample after adsorption (c)**.**