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Electronic Supplementary Information

Regulation on C_2H_2/CO_2 adsorption and separation by molecular rotors in metal-organic frameworks

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1. Experimental Section/Methods

1.1. Synthesis

Synthesis of In-NDC ($[In(OH)(1,4-NDC)]_n$): The synthesis process, as described in the referenced literature S1, involves placing $In(NO_3)_3 \cdot xH_2O$ (1 mmol, 300 mg) and ligand 1,4-NDC (0.5 mmol, 108 mg) in a 20 mL Teflon reaction vessel. After adding 10 mL H₂O, the mixture is stirred for 2 hours, then heated in a 170 °C oven for 1 day. The resulting white powder is collected, and after drying, its yield is calculated to be 80%.

Synthesis of SNNU-118 ([In(OH)(1,4-NDC)]_n): In this synthesis, $In(NO_3)_3 \cdot xH_2O$ (0.1 mmol, 30 mg) and ligand 1,4-NDC (0.1 mmol, 22 mg) are placed in a 20 mL glass bottle. A mixture of solvents (DMF/EG/DMPU/6M HNO₃, v/v/v/v=2/1/1/1, 2.5 mL) is added, and the solution is sonicated for 20 minutes until it becomes a clear and transparent solution. The glass bottle, covered with a PTFE shell, is then heated in a 100 °C oven for 3 days. After several washes with DMF, colorless transparent rod-like crystals are obtained, and the yield is calculated to be 61% after collecting and drying the crystals.

Synthesis of SNNU-128 ([In(OH)(9,10-ADC)(DMA)]_n): In this synthesis, $In(NO_3)_3 \cdot xH_2O$ (0.1 mmol, 30 mg) and ligand 9,10-ADC (0.0375 mmol, 10 mg) are placed in a 20 mL glass bottle. A mixture of solvents (DMA/DMSO/H₂O, v/v/v=2/1/1, 4 mL) is added, and 100µL HBF₄ is added as a modulator. The solution is sonicated for 20 minutes until it becomes a clear and transparent solution. The glass bottle, covered with a PTFE shell, is then heated in a 90 °C oven for 3 days. After several washes with DMA, light green rod-like crystals are obtained, and the yield is calculated to be 75% after collecting and drying the crystals.

1.2. Powder X-ray diffraction (PXRD) and thermogravimetric analyses (TGA)

Powder X-ray Diffraction (PXRD) was carried out employing the MiniFlex 600 X-ray powder diffractometer manufactured by Rigaku, Japan (40 kV, 15 mA). A Cu target was utilized for Ka X-ray emission ($\lambda = 1.5406$ Å). Before testing, the dried samples were ground into powder and uniformly placed in glass or silicon holders. Testing was conducted within the range of 5-50° at a 20 angle of 20.

The TGA analysis utilized the HCT-1 thermogravimetric analyzer produced by Beijing Hengjiu Scientific Instrument Factory. Samples, weighing approximately 8-13 mg and in a fresh, dried state, were meticulously weighed and positioned within pristine quartz crucibles. The experimental process entailed a gradual temperature increase, at a rate of 3 °C per minute, within a nitrogen atmosphere until reaching approximately 900 °C. The outcomes were depicted through a thermogravimetric curve, with temperature delineated on the horizontal axis and mass percentage on the vertical axis.

1.3. Single crystal X-ray diffraction (SCXRD)

The experimentation utilized the D8 Quest instrument manufactured by Bruker, Germany. Prior to analysis, samples of suitable size, transparency, and intactness were meticulously chosen under an optical microscope. These selected samples were immersed in single crystal oil and, after secure placement within a single crystal holder, diffraction data were gathered using Mo-K α as the X-ray source with a variable speed ($\infty \theta$ =20). The obtained diffraction data underwent reduction within the instrument and were subjected to absorption correction using the SADABS program. Subsequently, the collected data were analyzed through Olex2-1.3 and SHELXTS-97 software. Crystal structure refinement was accomplished utilizing the full-matrix least squares method, and the SQUEEZE procedure from the PLATON program was applied to remove disordered solvent molecules from the pores.

1.4. Gas adsorption measurements

The isothermal gas adsorption performance was assessed using the Micromeritics ASAP 2020 HD88 or 3 Flex adsorption analyzers. Prior to testing, the samples underwent immersion in low-boiling-point solvents for 3 days, with solvent exchanges performed every 8 hours. (SNNU-118: CH₃CN, In-NDC and SNNU-128: CH₃OH). Subsequently, the samples were subjected to drying in a nitrogen atmosphere, followed by heating under vacuum conditions to ensure the complete removal of high-boiling-point solvent molecules (SNNU-118: 210 °C, In-NDC and SNNU-128: 120 °C). After the degassing process, the mass of the sample tube was measured, and the sample's mass was calculated.

Subsequently, the sample tubes were placed in the analysis port for testing, with the testing temperature controlled by a circulating water bath. The results were illustrated through isothermal

adsorption-desorption curves, with pressure on the horizontal axis and unit mass adsorbed gas volume on the vertical axis. The specific surface area of the samples was determined through N_2 adsorption testing at a temperature controlled by liquid nitrogen (77 K) or CO₂ adsorption testing at a temperature of acetone/dry ice (195 K). The pore size distribution curves were calculated using the Horvath-Kawazoe method.

1.5. IAST selectivity calculations for binary gas mixtures

Ideal adsorbed solution theory (IAST) was used to predict binary mixture adsorption from the experimental pure-gas isotherms. The isotherm data of the single component adsorption method fit well with the Langmuir-Freundlich (LF) equation:

$$q = q_m * \frac{b * p^c}{1 + b * p^c}$$

where p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mmol g^{-1}), q_m is the saturation capacities of site (mmol g^{-1}), b is the affinity coefficients of site (1/kPa), and c represent the deviations from an ideal homogeneous surface. In addition, the adsorption selectivity is defined by

$$S_{A/B} = \frac{x_A/y_A}{x_B/y_B}$$

Where X_A and Y_B are the mole fraction of A/B components in the adsorbed phase and bulk phase respectively.

1.6. Separation and breakthrough experiments

The self-assembled gas permeation separation devices comprise three key components: a gas distribution unit, a fixed bed, and an analytical detector. Two distinct detectors are employed for this purpose: a mass spectrometer (Hiden, HPR-20) and a gas chromatograph (Fuli Instruments, 9790II).

Before initiating the testing procedure, activated MOFs samples are loaded into stainless steel sample columns with an inner diameter of approximately 4mm and an outer diameter of about 6mm. Deoiled cotton is placed at both the upper and lower ends of the sample column for stabilization. The samples undergo helium purging for a minimum of 3 hours within a helium atmosphere to ensure the thorough activation of the samples (SNNU-118: 396 mg; In-NDC: 696 mg). Various

ratios of C_2H_2/CO_2 (50/50, v=2 mL·min⁻¹) mixed gases are introduced into the sample tube, and the rear end of the sample tube is monitored using a gas chromatograph.

Based on the mass balance, the amount of gas adsorbed i (q_i) is calculated from the breakthrough curve using the following equation:

$$q_i = \frac{C_i}{22.4 \times m} \times \int_0^t (1 - \frac{F}{F_0}) dt$$

Where qi is the equilibrium adsorption capacity of gas i (mmol g⁻¹), Ci is the feed gas concentration, V is the volumetric feed flow rate (cm³ min⁻¹), t is the adsorption time (min), F_0 and F are the inlet and outlet gas molar flow rates, respectively, and m is the mass of the adsorbent (g).

1.7. In-situ infrared spectroscopy characterization

In-situ FT-IR measurements were performed on a Bruker INVENIO S spectrometer using a liquid N_2 -cooled DTGS detector. The sample at the focal point of the infrared beam. The SNNU-118 and In-NDC samples were activated for 12 h. The spectra of the crystals were collected by referencing to the KBr (Spectrography pure) firstly. Then, the gas-loaded spectra were collected by referencing to the corresponding activated crystals respectively.

1.8. Grand Canonical Monte Carlo (GCMC) simulations

To visually present the C_2H_2 and CO_2 molecules loaded in the single unit cell of three MOFs, the Materials Studio (MS) was firstly used to simulate the density distribution of two gas molecules at 298 K and 101 kPa. The simulations were carried out by fixing the pressure to establish the corresponding adsorption and equilibrium steps, with an equilibrium step of 1×10^6 , and the output steps were all set to 1×10^7 . The force field is used with Universal; the charge is set to Use Current, and the Quality is set to Ultra-fine. Further, by fixing the pressure at 101 kPa, we simulated the adsorption sites preferred by a fixed loading of one gas molecule to investigate the interaction force with the framework, with an equilibrium step of 1×10^6 , the Loading steps of 1×10^6 and the output steps were all set to 1×10^7 .

2. Supplementary Figures and Tables

MOF	[In(OH)(1,4-NDC)] _n (SNNU-118)	[In(OH)(9,10-ADC)(DMA)] _n (SNNU-128)		
Empirical formula	$C_{48}H_{28}In_4O_{20}$	C ₂₀ H ₁₇ InNO ₆		
Formula weight	1383.98	482.17		
Crystal system	orthorhombic	trigonal		
Space group	Imma	P421c		
a(Å)	17.3685	22.0053(7)		
$b(\text{\AA})$	7.2287	22.0053(7)		
$c(\text{\AA})$	13.4781	7.3962(4)		
$\alpha(\text{deg})$	90	90		
β (deg)	90	90		
γ(deg)	90	90		
Volume (Å ³)	1692.2	3581.5(3)		
Ζ	1	8		
$d_{\text{calcd.}}$ (g·m ⁻³)	1.358	1.788		
Wavelength	0.71073 Å	0.71073 Å		
F(000)	672.0	1928.0		
R _{int}	0.0624	0.0526		
Reflections collected/unique	9568/971	19408/5335		
Data/restraints/parameters	971/39/79	5335/15/256		
GOF on F^2	1.204	1.021		
$R_1^{\mathrm{a}}, wR_2^{\mathrm{b}}[I > 2\sigma(I)]$	0.0481, 0.1366	0.0472, 0.0841		
R_1^a , wR_2^b (all data)	0.0603, 0.1426	0.1033, 0.0983		
CCDC Number	2327387	2327388		

 Table S1. Crystal data and structure refinements for SNNU-118 and SNNU-128.

Table S2. Selected bond lengths (A) and angles (*) of SNNO-118.				
In1-O1	2.072(5)	In1-O2	2.155(5)	
O1 In1 O1 ^{#1}	180.0	O2 ^{#1} -In1-O2 ^{#2}	88.5(5)	
O1 ^{#1} -In1-O2	90.6(2)	O2 ^{#1} -In1 O2 ^{#3}	91.5(5)	
O1-In1-O2	89.4(2)	In1-O1-In1 ^{#4}	121.2(4)	

Table S2. Selected bond lengths (Å) and angles (°) of SNNU-118.

^{#1} 1-X, 1-Y, 1-Z; ^{#2} 1-X, +Y, +Z; ^{#3} +X, 1-Y, 1-Z; ^{#4} 1-X, 3/2-Y, +Z.

Table S3. Selected bond lengths (Å) and angles (°) of SNNU-128.

In1-O ^{#1}	2.108(5)	In1 O1	2.113(5)
In1 O4 ^{#2}	2.187(5)	In1-O16 ^{#3}	2.190(5)
In1 O5#4	2.155(5)	In1-O2	2.152(5)
O1#1-In1-O1	176.36(17)	O1-In1-O4#2	93.65(18)
O1 ^{#1} -In1-O4 ^{#2}	89.96(17)	O1-In1-O16 ^{#3}	88.89(17)
O1 ^{#1} -In1-O16 ^{#3}	87.49(18)	O1-In1-O5#4	88.96(18)
O1 ^{#1} -In1-O5 ^{#4}	90.87(18)	O1-In1-O2	89.63(18)
O1#1-In1-O2	90.95(18)	O4#2-In1-O16#3	177.4(2)
O5 ^{#4} -In1-O4 ^{#2}	85.1(2)	O5 ^{#4} -In1-O16 ^{#3}	94.2(2)
O2-In1-O4#2	88.4(2)	O2-In1-O16 ^{#3}	92.3(2)
O2-In1-O5 ^{#4}	173.3(2)	In1 ^{#3} -O1-In1	122.44(19)

^{#1} 3/2-Y, 3/2-X, 1/2+Z; ^{#2} 1-Y, +X, 1-Z; ^{#3} 3/2-Y, 3/2-X, -1/2+Z; ^{#4} 3/2-X, 1/2+Y, 1/2-Z.

	$-Q_{st}\left(C_{2}H_{2}\right)\left(kJ\ mol^{-1}\right)$	-Q _{st} (CO ₂) (kJ mol ⁻¹)	ΔQ _{st} (kJ mol ⁻¹)	Ref
SNNU-118	41.37	23.2	18.17	This work
FJU-90	25.2	20.7	4.5	S2
FeNi-M'MOF	27	24.5	2.5	S 3
UTSA-74a	31	25	6	S4
CAU-10-H	32.8	21.4	11.4	S5
JCM-1	36.9	33.4	3.5	S 6
DICRO-4-Ni-i	37.7	33.9	3.8	S 7
SIFSIX-21-Ni	37.9	19.8	18.1	S 8
SIFSIX-Cu-TPA	39.1	25.7	13.4	S9
SNNU-45	39.9	27.1	12.8	S10
UPC-200(Al)-F- BIM	20.5	14.2	6.3	S11
BSF-3	42.7	22.4	20.3	S12
CPL-1	45.5	36.6	8.9	S13
TIFSIX-2-Cu-i	46.3	35.8	10.5	S14
ZNU-1	54	44	10	S15
ZJU-74a	65	30	35	S18
Ni(4-DPDS) ₂ CrO ₄	75.4	37	38.4	S17

Table S4. The comparison of Q_{st} values for top-level MOF adsorbents at 298 K.

	C_2H_2 uptake at 0.1 bar	CO_2 uptake at 0.1 bar	uptake ratio	Ref
SNNU-118	46.36	3.8	12.2	This work
In-NDC	26.18	6.8	3.9	This work
CPL-1	29.12	2.24	13	S13
CPL-1-NH ₂	35.84	0.9	38.8	S13
САИ-10-Н	30	30	3	S5
ZJU-280a	70.6	33.6	2.1	S19
ZJU-74a	80	20	4	S18
NKMOF-1-Ni	51.2	32	1.6	S20
DICRO-4-Ni-i	23.4	6	3.9	S7
JCM-1	61.5	15	4.1	S6
UTSA-74a	70	16.7	4.2	S4
SNNU-45	60	17.64	3.4	S10
TIFSIX-2-Cu-i	63.8	33.6	1.9	S14
FJU-90	58	20	2.9	S2
FeNi-M'MOF	105	25	4.2	S 3
SIFSIX-Cu-TPA	110	50	2.2	S9
SIFSIX-21-Ni	16.8	4	4.2	S8
BSF-3	50.4	11.2	4.5	S12
Cul@UiO-66-(COOH) ₂	29.68	5.6	5.3	S16
UPC-200(Fe)-F-BIM	20.2	5	4	S11
ZNU-1	57	10	5.7	S15
Ni(4-DPDS) ₂ CrO ₄	63.95	22.84	2.8	S17
Ni(4-DPDS) ₂ MoO ₄	35.43	31.36	1.1	S17
Ni(4-DPDS) ₂ WO ₄	29.3	22.2	1.3	S17

Table S5. The comparison of C_2H_2/CO_2 uptake ratios at 298 K and 0.1 bar for top-level MOFs.



Figure S1. The asymmetric unit (a), coordination environments (b) and 1D zigzag chain (c) in SNNU-118



Figure S2. The 3D structure and (4,6)-connected topological net of SNNU-118



Figure S3. The coordination environments and 3D structure of In-NDC



Figure S4. The coordination environments and 3D structure of SNNU-128.



Figure S5. PXRD patterns of SNNU-118 after soaking in H₂O for one week.



Figure S6. PXRD patterns of SNNU-118 after soaking in different pH solutions for three days.



Figure S7. TGA curves of In-NDC, SNNU-118 and SNNU-128.



Figure S8. PXRD patterns of In-NDC (a) and SNNU-118 (b) synthesized at different temperatures.



Figure S9. PXRD patterns of SNNU-118 and In-NDC synthesized by switching the primary solvent.



Figure S10. PXRD patterns for SNNU-118 with altered synthesis conditions, DMF (a), DMPU (b), 6M HNO₃ (c) and EG (d).



Figure S11. The structure transformation indicated by PXRD patterns between In-NDC and SNNU-118.



Figure S12. Summary of structure transformation for SNNU-118 and In-NDC.



Figure S13. Gas adsorption curves of C_2H_2 and CO_2 for In-NDC at 273 K (a), 283 K (b) and 298 K (c).



Figure S14. Gas adsorption curves of C_2H_2 and CO_2 for SNNU-118 at 273 K (a), 283 K (b) and 298 K (c).



Figure S15. Gas adsorption curves of C_2H_2 and CO_2 for SNNU-128 at 273 K (a), 283 K (b) and 298 K (c).



Figure S16. Virial fitting of the C_2H_2 (a, b) and CO_2 (c, d) adsorption isotherms at 273 K, 283 K and 298 K of In-NDC.



Figure S17. Virial fitting of the C_2H_2 (a, b) and CO_2 (c, d) adsorption isotherms at 273 K, 283 K and 298 K of SNNU-118.



Figure S18. Langmuir-Freundlich (LF) fit of C₂H₂ and CO₂ at 273 K, 283 K and 298 K of In-NDC.



Figure S19. Langmuir-Freundlich (LF) fit of C_2H_2 and CO_2 at 273 K, 283 K and 298 K of SNNU-118.







Figure S20. Simulated C_2H_2 (a) and CO_2 (b) density distributions at 298 K and 1 bar in In-NDC.





Figure S21. Simulated C_2H_2 (a) and CO_2 (b) density distributions at 298 K and 1 bar in SNNU-118.







Figure S22. Simulated C_2H_2 (a) and CO_2 (b) density distributions at 298 K and 1 bar in SNNU-128.

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