Electronic Supplementary Information

Highly selective sieving of small gas molecules by an ultra-microporous metal-organic framework membrance

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1. Setup of the equipment for the gas separation

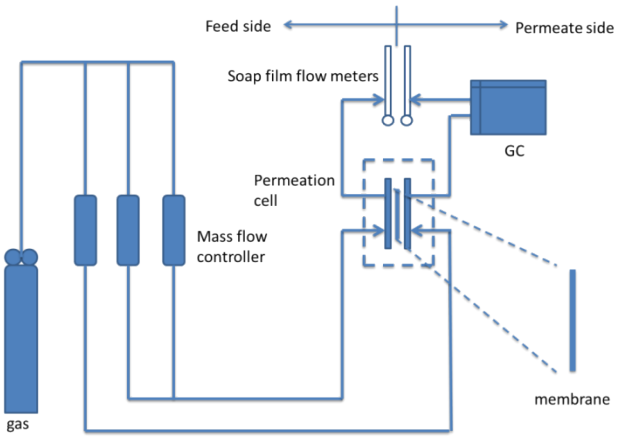

Figure S1. Schematic diagram of gas separation test device.

2. X-ray Structure determination

Table S1 Crystal and Structure Refinement of **JUC-150**

Parameter	$Ni_2(L\text{-}asp)_2pz$ (**JUC-150**)
Empirical formula	$C_6H_5N_2NiO_4$
F_w	227.83
Crystal system	Orthorhombic
Space group	*P*2(1)22(1)
a [Å]	6.5827(6)
b [Å]	7.8919(7)
c [Å]	15.4217(14)
α [deg]	90
β [deg]	90
γ [deg]	90
V [Å^3]	801.16(13)
Z	4
T (K)	293
λ (Å)	0.71073
ρ_{calcd} (Mg/m^3)	1.889
μ (mm^{-1})	2.402
GOF on F^2	1.003
R^a [I>2 σ(I)]	0.0416
$R_w{}^b$	0.0947

[a] R = Σ||Fo| -|Fc||/Σ|Fo|, [b] Rw = [Σw(Fo2 – Fc2)/ Σw(Fo2)2]1/2.

Table S2 Selected bond lengths (Å) and angles (deg) for **JUC-150**[a]

Ni(1)-O(2)#1	2.056(6)	Ni(1)-N(1)	2.060(4)
Ni(1)-O(4)#2	2.064(6)	Ni(1)-O(1)	2.065(5)
Ni(1)-O(3)	2.082(6)	Ni(1)-N(2)	2.109(4)
O(2)#1-Ni(1)-N(1)	98.1(3)	O(2)#1-Ni(1)-O(4)#2	88.74(16)
N(1)-Ni(1)-O(4)#2	98.0(3)	O(2)#1-Ni(1)-O(1)	91.9(2)
N(1)-Ni(1)-O(1)	84.1(3)	O(4)#2-Ni(1)-O(1)	177.7(3)
O(2)#1-Ni(1)-O(3)	177.3(2)	N(1)-Ni(1)-O(3)	84.6(3)
O(4)#2-Ni(1)-O(3)	90.4(3)	O(1)-Ni(1)-O(3)	88.90(17)
O(2)#1-Ni(1)-N(2)	89.4(2)	N(1)-Ni(1)-N(2)	171.29(16)
O(4)#2-Ni(1)-N(2)	86.5(3)	O(1)-Ni(1)-N(2)	91.2(3)
O(3)-Ni(1)-N(2)	87.9(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x-1/2,-y+1,-z+1/2 #2 x-1/2,-y+2,-z+1/2

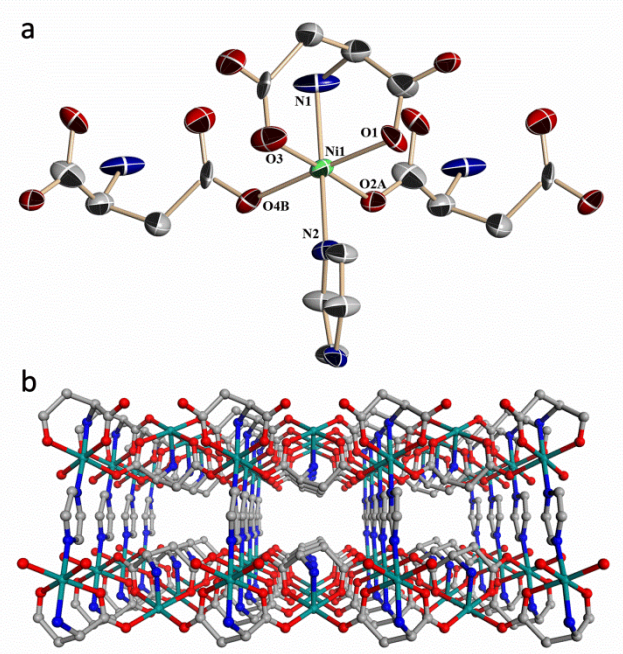

Figure S2. (a) Fundamental building unit of **JUC-150**, (b) 3D structure of **JUC-150** with 1D corrugated channels viewed along the [100] direction, Ni cyan, C gray, N blue, O red; H atoms are omitted for clarity.

3. Morphological characterization

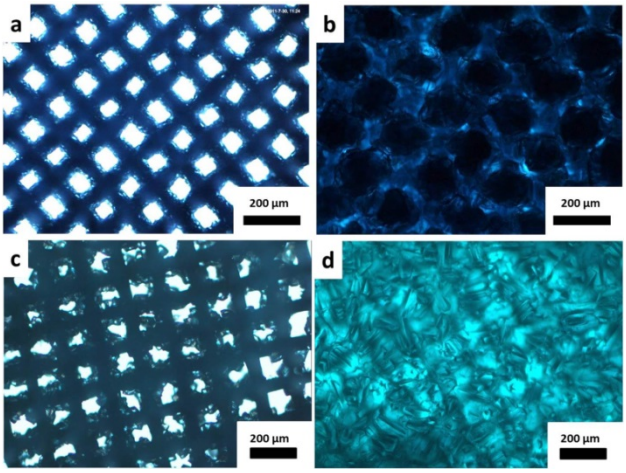

Figure S3. Leica Optic micrographs of the seed layers grown nickel screens for (a) **1** and (c) **JUC-150**; the surfaces of membranes after secondary growth for (b) **1** and (d) **JUC-150**, respectively.

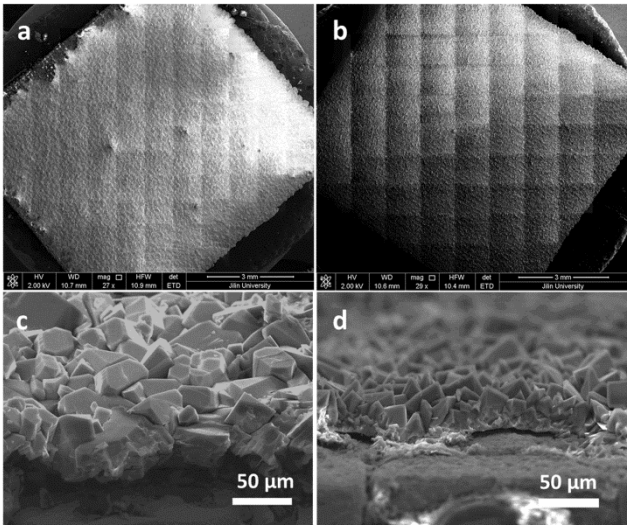

Figure S4. Panoramic view FIB-SEM pictures of (a) **1** and (b) **JUC-150** membranes; cross-section SEM images of (c) **1** and (d) **JUC-150** membranes after secondary growth.

4. Thermogravimetric Analysis

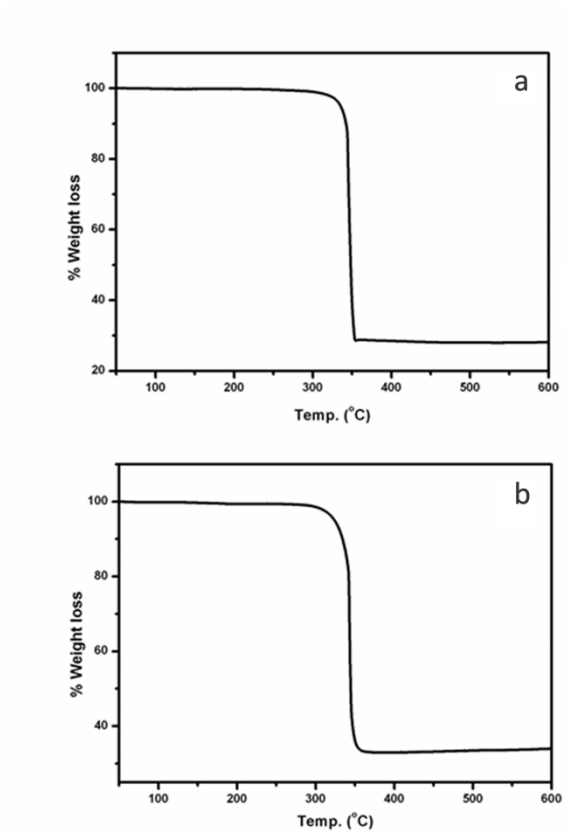

Figure S5. TGA analysis of powder samples scraped from (a) **1** membrane and (b) **JUC-150** membrane after 5 hours activating treatment under vacuum at 150 °C.

5. Gas Adsorption Measurements

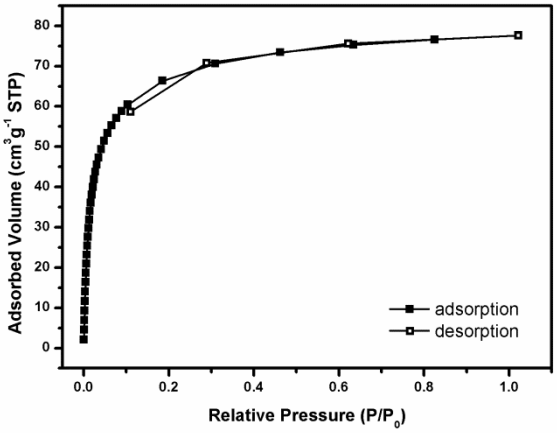

Figure S6. CO_2 sorption isotherm for **1** at 195K, which was used to determine the BET surface area.

6. Single and mixed gas permeation measurements

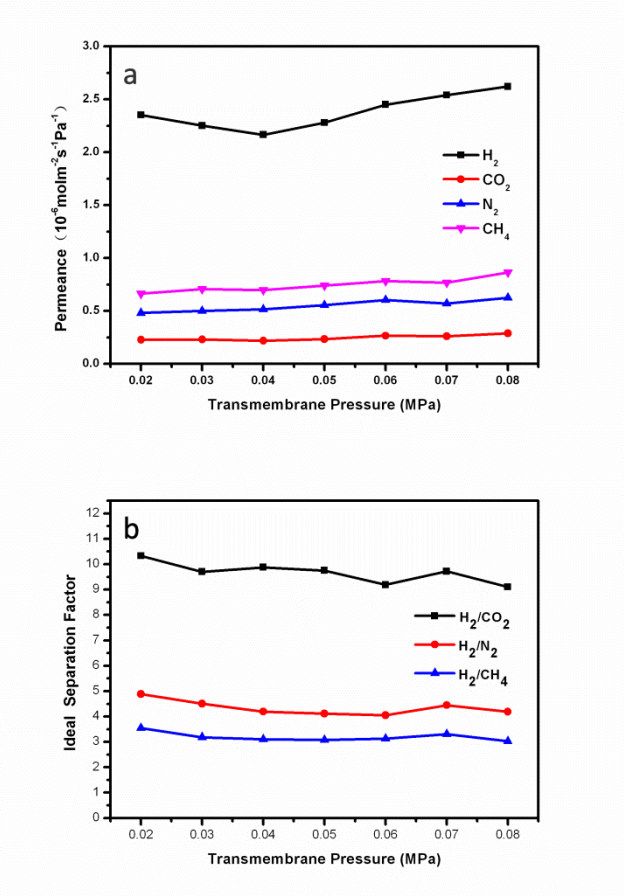

Figure S7. (a) Permeances of H_2, N_2, CH_4 and CO_2 gas molecules and (b) the idea separation factor through **1** membranes at different trans-membrane pressure drops.

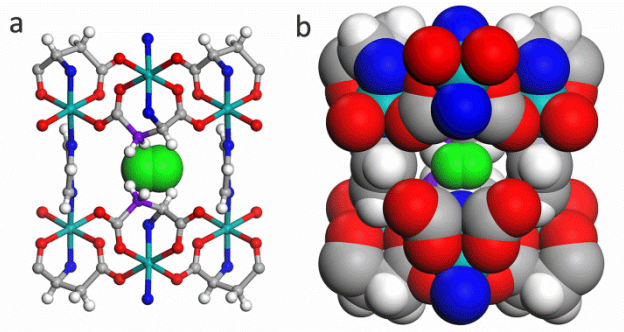

Figure S8. Perspective views of one-dimensional channel in **JUC-150** and there is a 2.5 x 4.5 Å cage for H_2 gas molecules (green ball). (a) Ball and stick representation and (b) CPK representation. The carbon atoms of methylene group from the aspartate amino acid are colored in purple to highlight how their projection into the channels. Ni cyan, C gray, H white, N blue, O red.

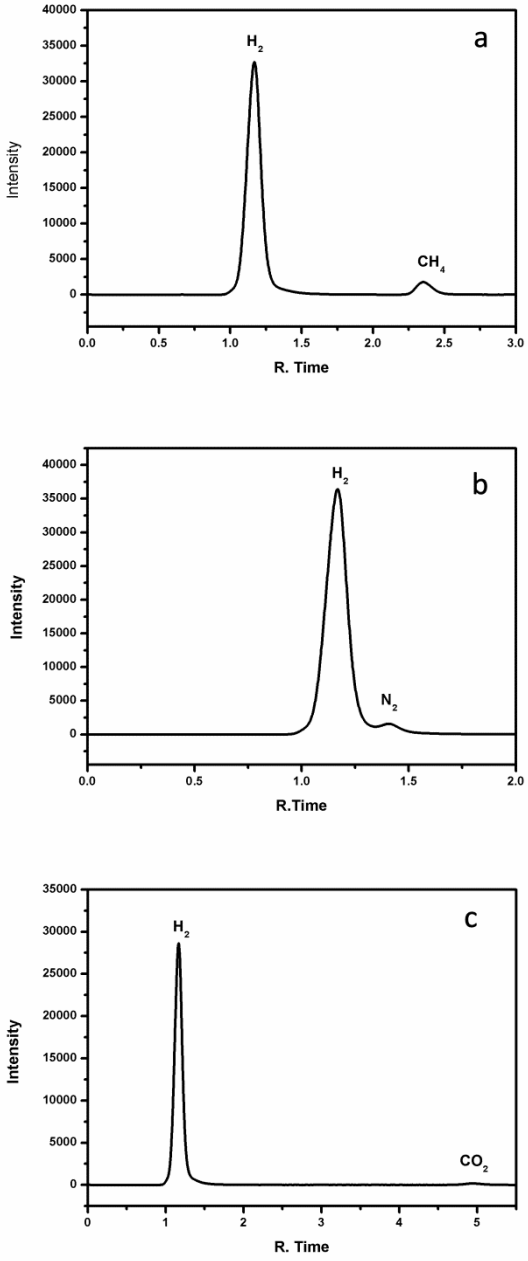

Figure S9. GC spectra of mixture gas separation: (a) H_2/CH_4; (b) H_2/N_2 and (c) H_2/CO_2 on **1** membrane.

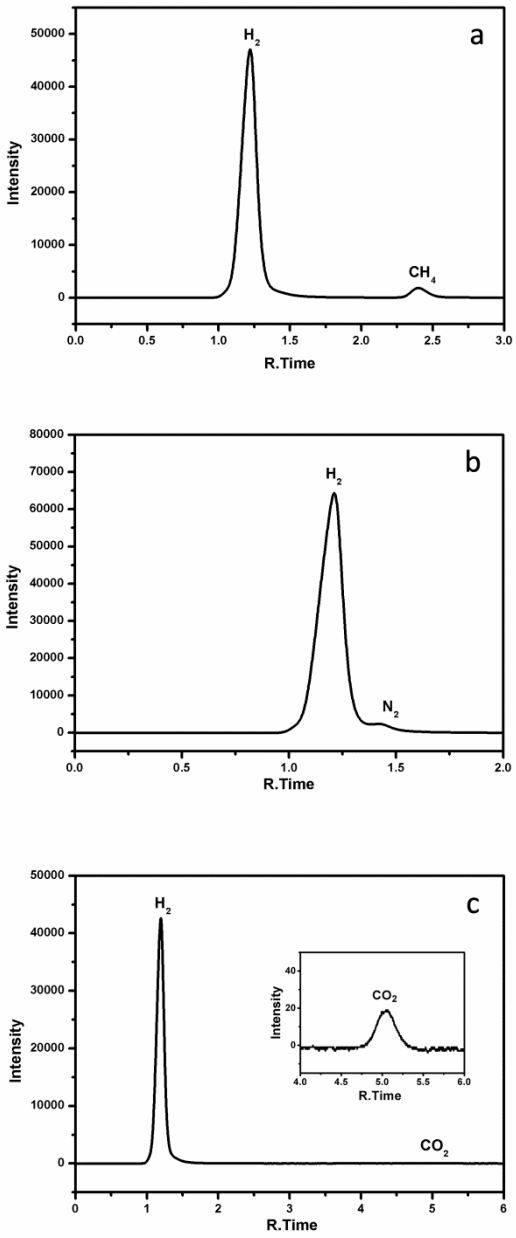

Figure S10. GC spectra of mixture gas separation: (a) H_2/CH_4; (b) H_2/N_2; (c) H_2/CO_2 and inside picture of (c) magnified peak of CO_2 on **JUC-150** membrane.

7. Stability analysis of membrane

Both the 1 and JUC-150 membranes were kept in an oven at 200 °C for more than 1 week after exposure to 40-KHz ultrasonic waves for 2 hours. PXRD revealed that both membranes maintained their crystalline structures (Fig. S11). Studies also showed that these membranes can be utilized repeatedly even after storage in the laboratory for 1 year (Fig. S12).

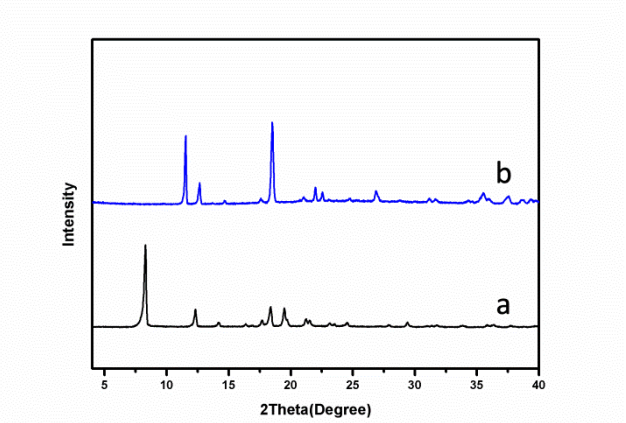

Figure S11. XRD patterns of (a) **1** membrane and (b) **JUC-150** membrane after the test of thermal and mechanical stability.

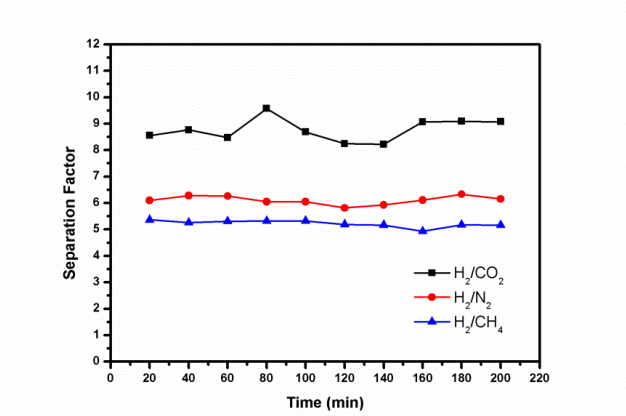

Figure S12. H_2/CO_2, H_2/CH_4 and H_2/N_2 separation factors of **1** membrane exposed to air for more than one year.

8. Permeances and separation factors Data

Table S3 Mixture gas permeances and separation factors for **1** membrane at 25°C and 1×10^{5}Pa.

Gas	H_2	CO_2	H_2	N_2	H_2	CH_4
Permeance×10^{-7}（molm^{-2}s^{-1}Pa^{-1}）	18.2	1.65	19.3	2.47	20.3	3.02
Separation Factor		8.7		6.2		5.2
Ideal Separation Factor		10.2		4.5		3.5

Table S4 Mixture gas permeances and separation factors for **JUC-150** membrane at 25°C and 1×10^{5}Pa.

Gas	H_2	CO_2	H_2	N_2	H_2	CH_4
Permeance×10^{-7}（molm^{-2}s^{-1}Pa^{-1}）	1.83	0.0460	1.84	0.105	1.81	0.0662
Separation Factor		38.7		17.1		26.3
Ideal Separation Factor		36		18.9		26.1