Supplementary Information

Engineering Pore Environment of Metal-Organic Framework Membrane via Modification of Secondary Building Units for Improved Gas Separation

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Contents

1. Crystal data and structure refinement for soc-MOF-IM

Table S1. Crystal data and structure refinement of **soc-MOF-IM**

Identification code	soc-MOF-IM (PCN-250-IM)
CCDC number	1956752
Empirical formula	$C_{105}H_{66}Fe_{12}N_{18}O_{61}$
Formula weight	3225.95
Crystal system	cubic
Space group	P-43n
a/Å	21.9666(2)
α/°	90
Volume/Å^3	10599.6(3)
Z	2
ρcalcg/cm^3	1.011
μ/mm^{-1}	6.927
F(000)	3244.0
2Θ range for data collection/°	8.05 to 141.126
Index ranges	-15 ⩽ h ⩽ 19, -17 ⩽ k ⩽ 23,
	-26 ⩽ l ⩽ 23
Reflections collected	8275
Independent reflections	3061 [R_{int} = 0.0441, R_{sigma} = 0.0784]
Data/restraints/parameters	3061/60/167
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0464, wR2 = 0.1216
Final R indexes [all data]	R1 = 0.0588, wR2 = 0.1306
Largest diff. peak/hole / e Å-3	0.41/-0.34

2. Characterizations of crystals

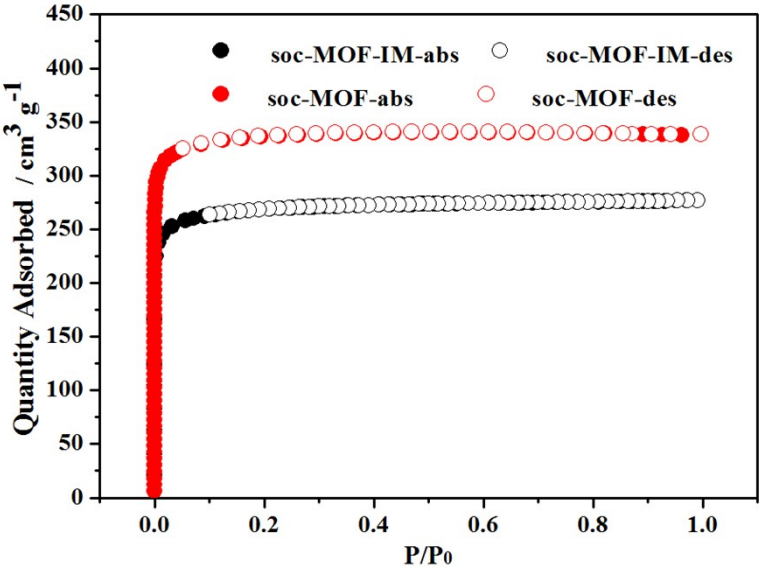

Fig. S1. N_2 adsorption/desorption isotherms of **soc-MOF** and **soc-MOF-IM** at 77 K.

Table S2. The surface area, pore volume, pore size obtained by N_2 (77 K) adsorption–desorption experiment for **soc-MOF** and **soc-MOF-IM**.

Sample	BET SA (m^2/g)	Langmuir SA (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)	
soc-MOF	989.15	1,476.40	0.5232	6.8	9.3
soc-MOF-IM	883.70	1,270.60	0.4403	4.8	5.3

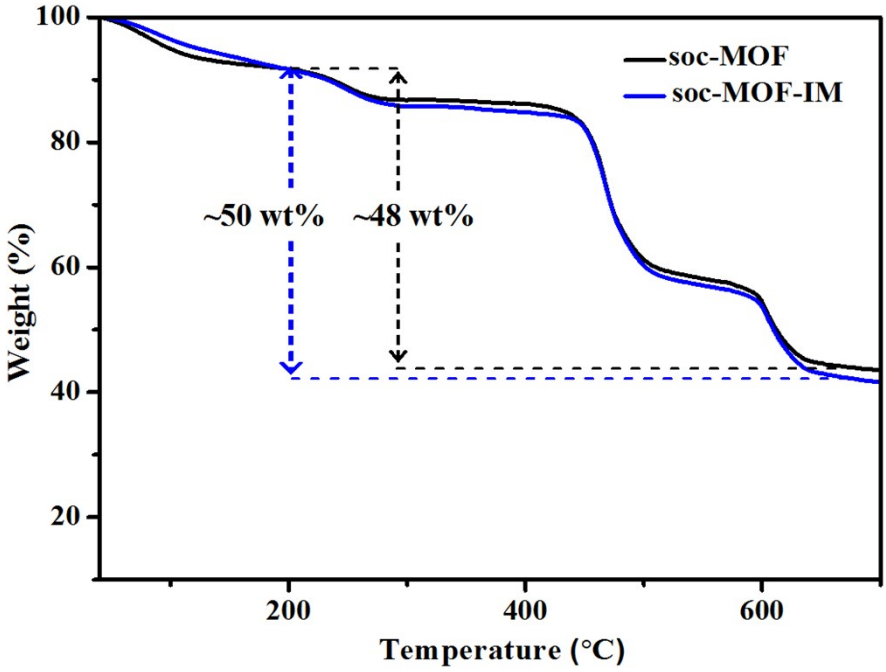

Fig. S2. TGA of **soc-MOF** and **soc-MOF-IM**.

Thermogravimetric Analysis. To explore the thermal stability of **soc-MOF and soc-MOF-IM**, TGA test was performed. And the result proves that both two crystals are stable up to 415 °C. There is a weight loss of 9.40% in the range of 40–200 °C, which could be attributed to the loss of water and solvent molecule. The partial collapse of two MOFs structures occurs above 415 °C, and a plateau is observed before 545 °C for the complete framework collapse.

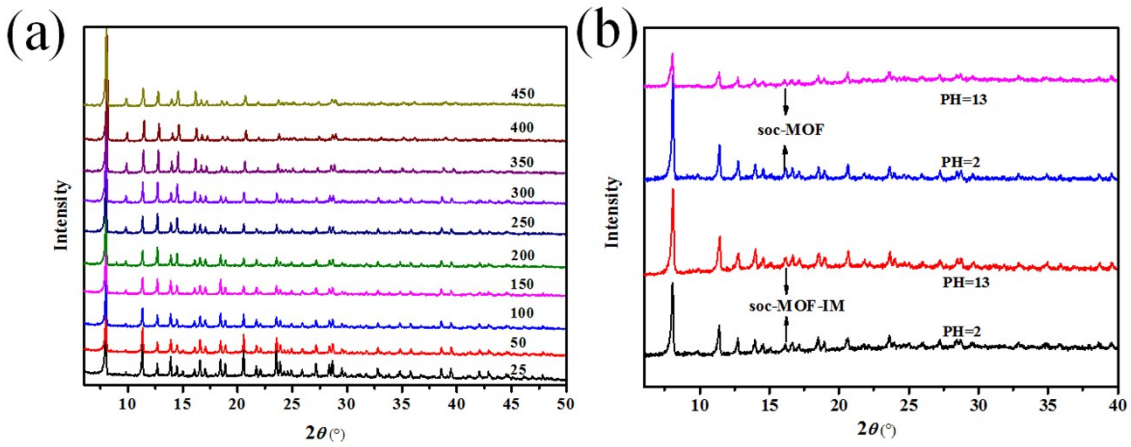

Fig. S3. (a) *in-situ* temperature-dependent (25 – 400 °C) PXRD of **soc-MOF-IM**, (b) PXRD of **soc-MOF** and **soc-MOF-IM** after immersing in aqueous solution with different pH (2 - 13).

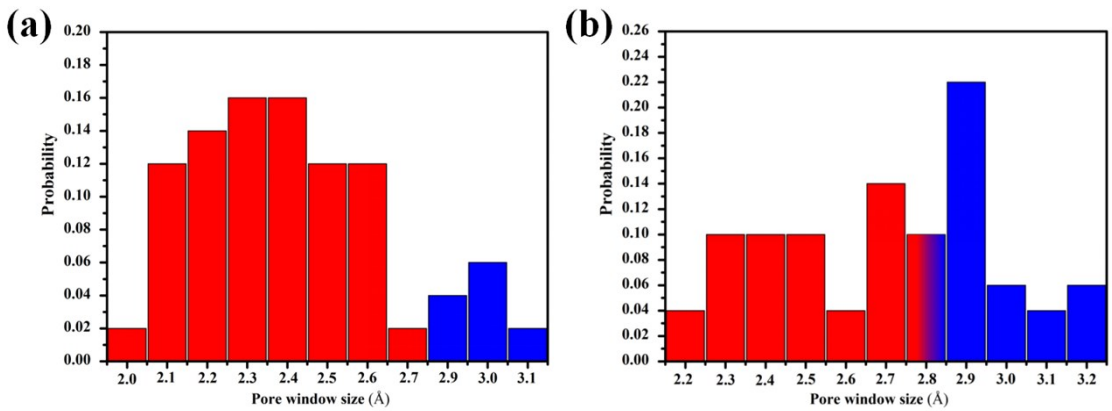

Fig. S4. Distribution probabilities of pore window size of cage 2 in b axis direction at (a) 273 K and (b) 298 K. (Red represents the aperture range which H_2 cannot passed, and blue represents the passable range.)

3. Characterizations of membranes

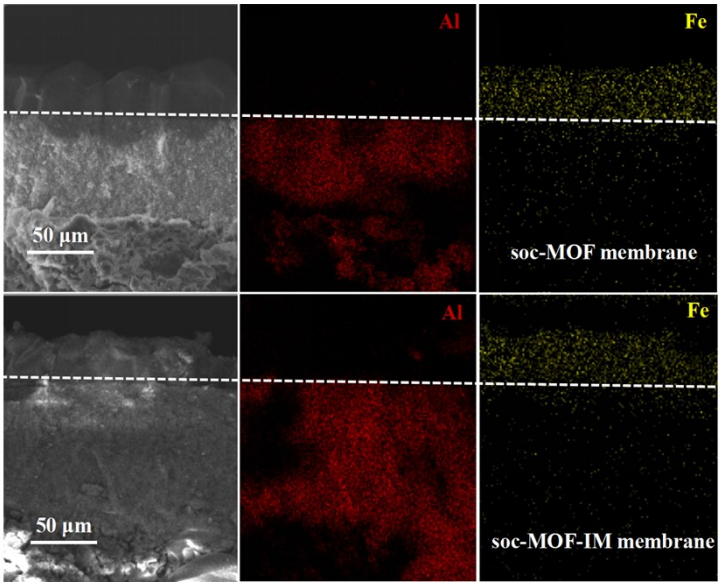

Fig. S5. Cross-section SEM images and EDS mapping of **soc-MOF** and **soc-MOF-IM**.

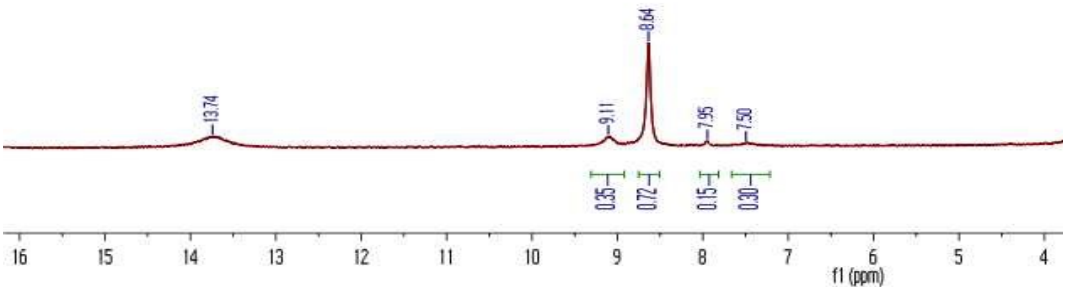

Fig. S6. ^{1}H NMR spectrum of **soc-MOF-IM** (400 MHz, DMSO-d^{6}).

4. Gas separation performances of membranes

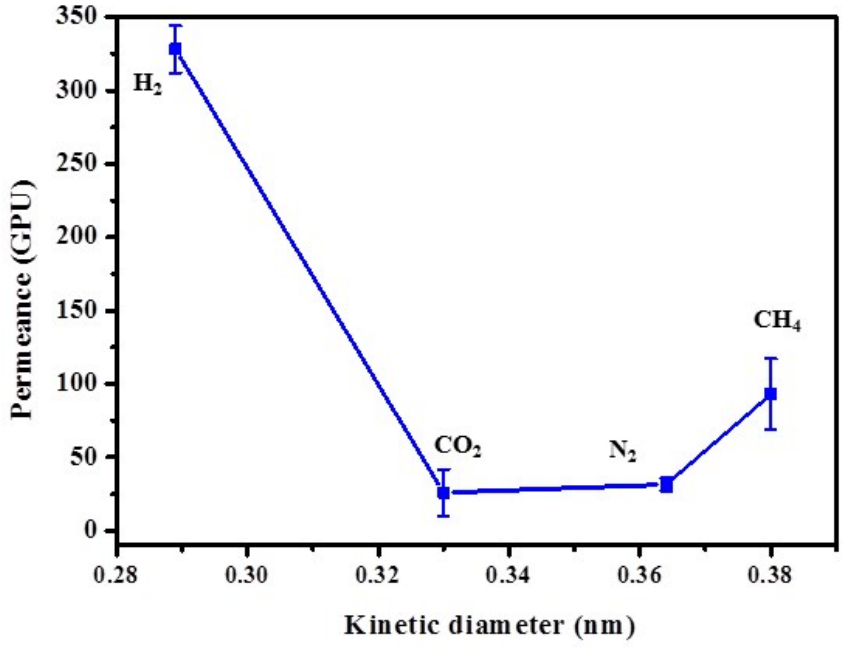

Fig. S7. Single gas permeance for **soc-MOF-IM** at 100 °C under the pressure of 1.8 bar.

Table S3. Single gas permeance for substrate, **soc-MOF** and **soc-MOF-IM**

Membrane	Temperature (°C)	H_2 permeance (GPU)	CO_2 permeance (GPU)	N_2 permeance (GPU)	CH_4 permeance (GPU)
Substrate	25	10873±251	10698±393	10335±79	10379±535
soc-MOF	25	639.5±67.1	107.5±9	284±7	400±19.7
soc-MOF-IM	25	148.3±32.9	2.87±0.29	6.98±0.70	5.76±1.30
soc-MOF-IM	100	328±16	26±16	31.4±4.62	93±24.04

Table S4. The value of solubility (S) and diffusivity (D) of CO_2 and H_2 measured on the **soc-MOF** and **soc-MOF-IM** membrane at 298 K under the pressure of 1.8 bar.

Membrane	S_{H2} (cm^3 (STP) cm^{-3} $cmHg^{-1}$)	S_{CO2} (cm^3 (STP) cm^{-3} $cmHg^{-1}$)	$S_{H2/CO2}$	D_{H2} (cm^2 s^{-1})	D_{CO2} (cm^2 s^{-1})	$D_{H2/CO2}$
soc-MOF	$5.45*10^{-3}$	0.6288	0.00867	$2.93*10^{-4}$	$4.27*10^{-7}$	685
soc-MOF-IM	$4.05*10^{-3}$	0.7532	0.00535	$9.14*10^{-5}$	$1.03*10^{-8}$	8911

Table S5. Mixture gas permeance and selectivity for **soc-MOF** and **soc-MOF-IM** membranes at 25 ^oC under the pressure of 1.8 bar.

Membrane	H_2 permeance (GPU)	CO_2 permeance (GPU)	H_2 / CO_2 Selectivity
soc-MOF	376±41	146±11	2.6±0.3
soc-MOF-IM	84.0±13	4.4±0.1	19.0±2

5. Simulations for gas separation performances

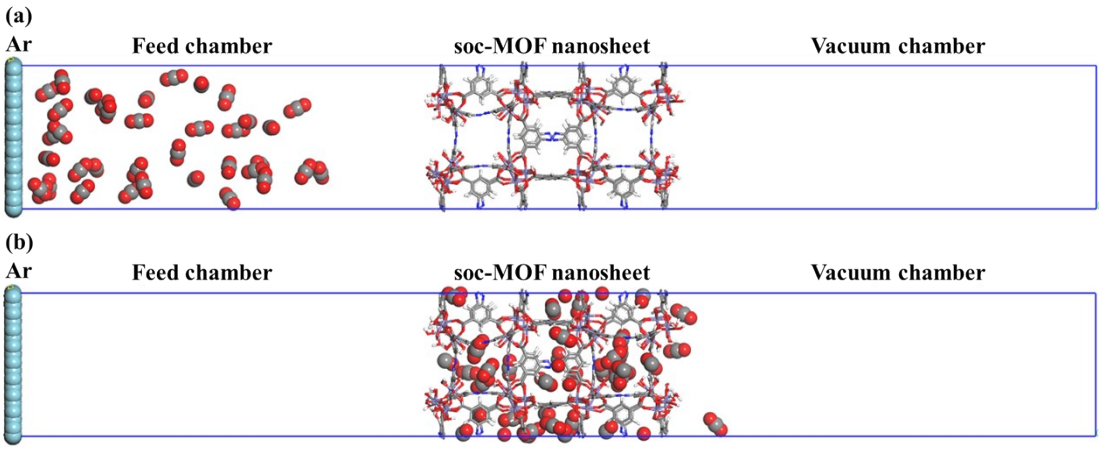

Fig. S8. Simulation study of pure CO_2 (40 molecules) penetrating through a **soc-MOF** nanosheet. (a) Initial structure; (b) snapshot after 10 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.

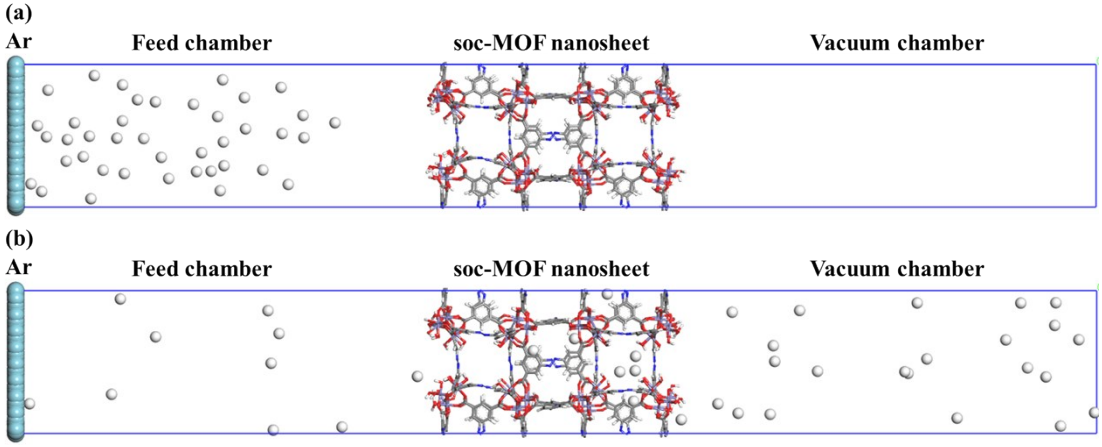

Fig. S9. Simulation study of pure H_2 (40 molecules) penetrating through a **soc-MOF** nanosheet. (a) Initial structure; (b) snapshot after 10 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.

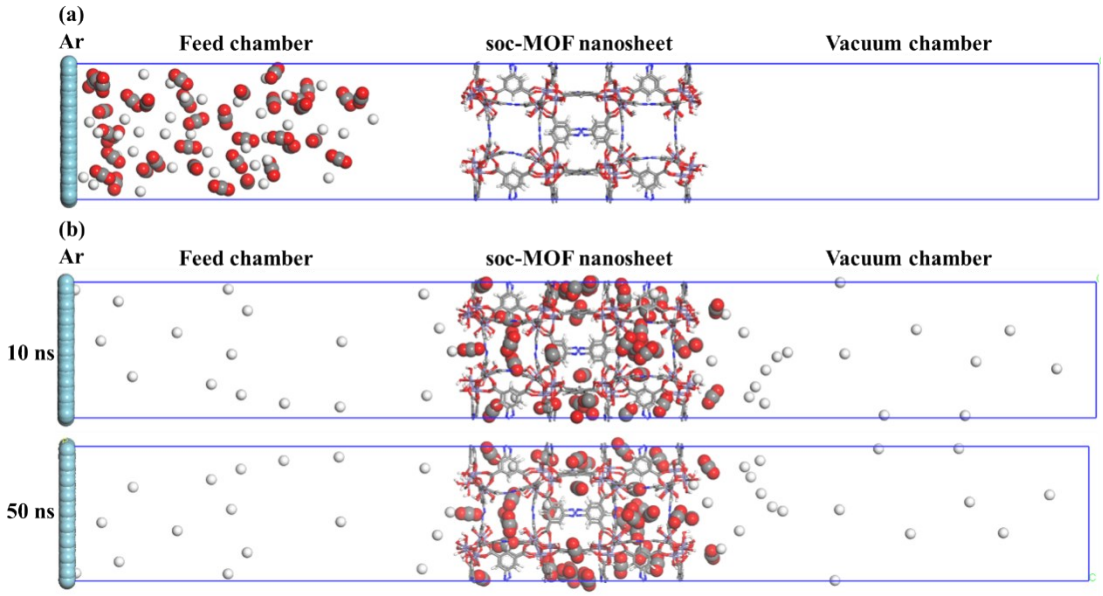

Fig. S10. Simulation study of mixed H_2 (40 molecules) and CO_2 (40 molecules) penetrating through a **soc-MOF** nanosheet. (a) Initial structure; (b) snapshots after 10 ns and 50 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.

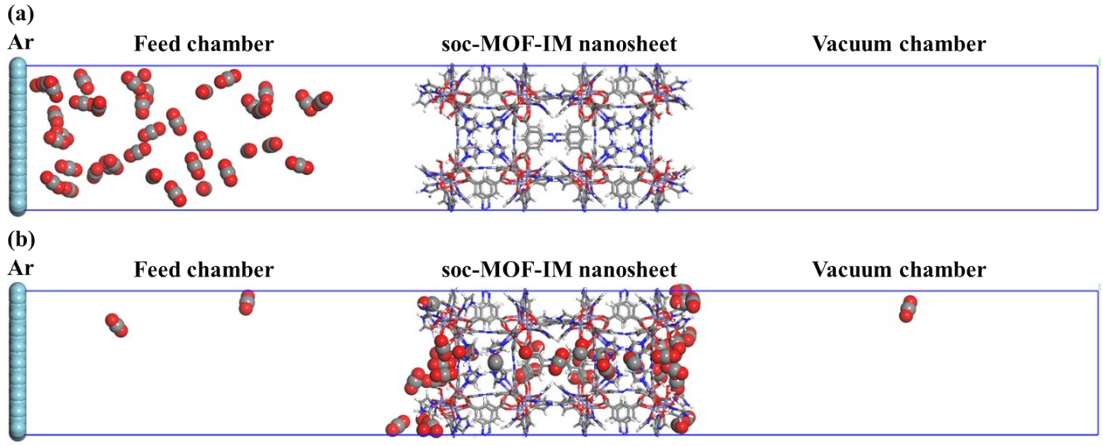

Fig. S11. Simulation study of pure CO_2 (40 molecules) penetrating through a **soc-MOF-IM** nanosheet. (a) Initial structure; (b) snapshot after 10 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.

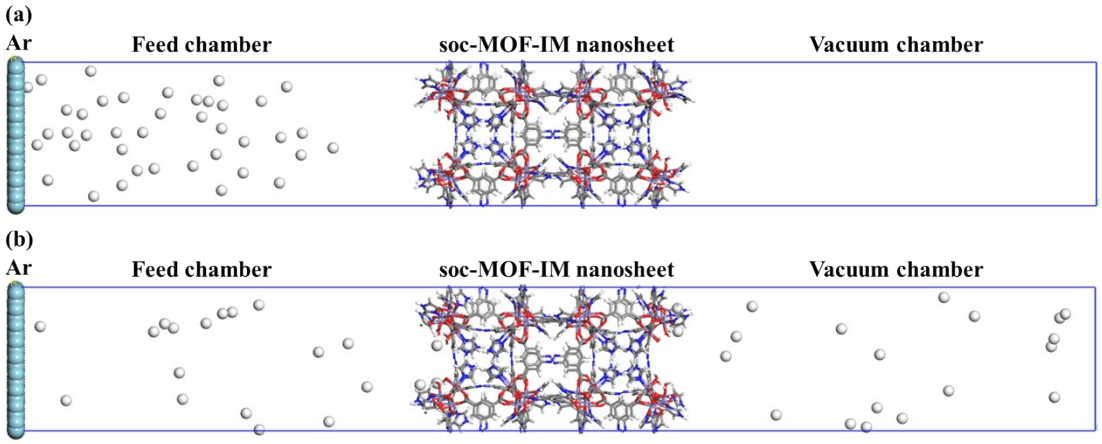

Fig. S12. Simulation study of pure H_2 (40 molecules) penetrating through a **soc-MOF-IM** nanosheet. (a) Initial structure; (b) snapshot after 10 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.

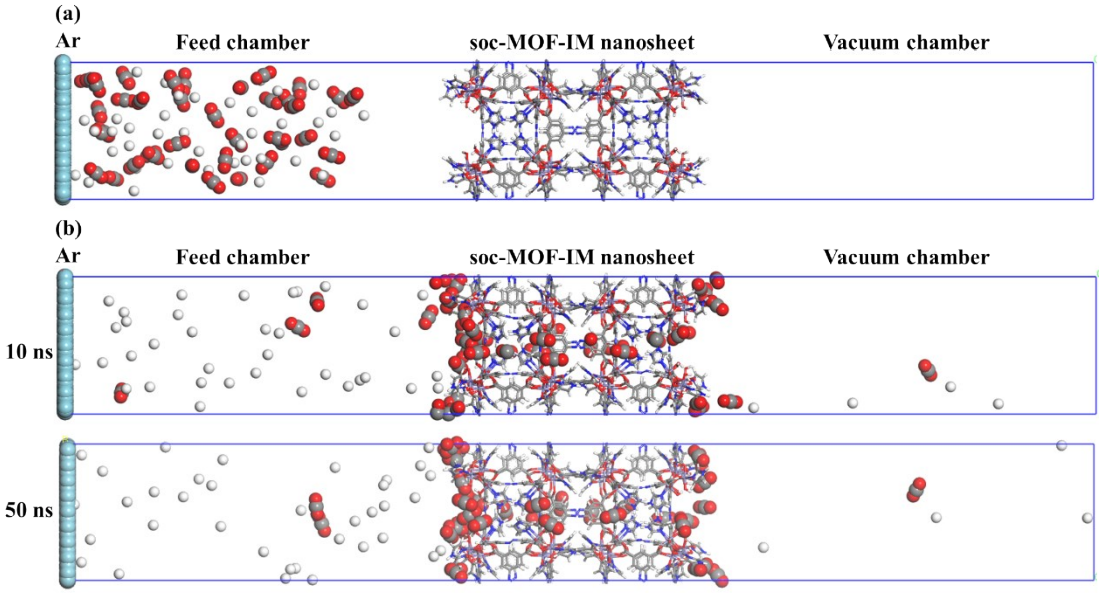

Fig. S13. Simulation study of mixed H_2 (40 molecules) and CO_2 (40 molecules) penetrating through a **soc-MOF-IM** nanosheet. (a) Initial structure; (b) snapshots after 10 ns and 50 ns of simulation. An argon plate is exerted to separate the feed and permeate chambers. Color of the atoms: Ar, cyan; C, gray; O, red; N, blue; Fe, purple; H, white.