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To cite this version:

Sheng Zhou, Osama Shekhah, Adrian Ramírez, Pengbo Lyu, Edy Abou-Hamad, et al.. Asymmetric pore windows in MOF membranes for natural gas valorization. Nature, 2022, 606 (7915), pp.706-712. 10.1038/s41586-022-04763-5 . hal-03752951

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Item Type	Article
Authors	Zhou, Sheng;Shekhah, Osama;Ramírez, Adrian;Lyu, Pengbo;Abou-Hamad, Edy;Jia, Jiangtao;Li, Jiantang;Bhatt, Prashant;Huang, Zhiyuan;Jiang, Hao;Jin, Tian;Maurin, Guillaume;Gascon, Jorge;Eddaoudi, Mohamed
Citation	Zhou, S., Shekhah, O., Ramírez, A., Lyu, P., Abou-Hamad, E., Jia, J., Li, J., Bhatt, P. M., Huang, Z., Jiang, H., Jin, T., Maurin, G., Gascon, J., & Eddaoudi, M. (2022). Asymmetric pore windows in MOF membranes for natural gas valorization. Nature, 606(7915), 706–712. https://doi.org/10.1038/s41586-022-04763-5
Eprint version	Post-print
DOI	10.1038/s41586-022-04763-5
Publisher	Springer Science and Business Media LLC
Journal	Nature
Rights	Archived with thanks to Nature
Download date	2024-04-15 08:42:22
Link to Item	http://hdl.handle.net/10754/679289

Asymmetric pore windows in MOF membranes for natural gas valorization

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In order to use natural gas as a feedstock alternative to coal and oil, its main constituent, methane, needs to be isolated with high purity[1]. In particular, nitrogen (N_2) dilutes the heating value of natural gas, and therefore is of prime importance for removal[2]. However, the inertness of nitrogen and its similarities to methane (CH_4) in terms of kinetic size, polarizability and boiling point pose particular challenges for the development of energy-efficient N_2-removing processes[3]. Here, we report a mixed-linker metal-organic framework (MOF) membrane based on fumarate (*fum*) and mesaconate (*mes*) linkers, Zr-*fum*$_{67}$-*mes*$_{33}$-fcu**-MOF, with a pore aperture shape specific for effective nitrogen removal from natural gas. The deliberate introduction of asymmetry in the parent trefoil-shaped pore aperture induces a shape irregularity, blocking the transport of tetrahedral CH_4 while allowing linear N_2 to permeate. Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu-MOF membranes exhibit record-high N_2/ CH_4 selectivity and N_2 permeance under practical pressures up to 50 bar, removing both carbon dioxide (CO_2) and N_2 from natural gas. Technoeconomic analysis shows our membranes offer potential to reduce CH_4 purification costs by ~66% for N_2 rejection and ~73% for simultaneous removal of CO_2 and N_2, relative to cryogenic distillation and amine-based CO_2 capture.**

Natural gas contributes to at least a quarter of the global energy supply, and this proportion is expected to exceed that of coal by ~2032[1]. This growth presents challenges to conventional technologies for natural gas purification[2], because natural gas reservoirs are contaminated with N_2 and CO_2[2]. Indeed, approximately 50% of the world's volume of natural gas reserves, known as sub-quality reservoirs, exceed the maximum 4% N_2 pipeline specification[2], necessitating the exploration of energy- and cost-efficient technologies for N_2/CH_4 separation.

In contrast to the diverse routes for CO_2 capture, e.g., liquid-based absorbers[4], solid-state adsorbents[5,6] and membranes[7], for N_2 removal at the plant scale, cryogenic distillation is currently the only available technology[2]. Despite either N_2-selective membranes or CH_4-selective membranes can discriminate N_2 from CH_4, N_2-selective membranes are preferred because CH_4 is rejected to the retentate at high pressures, saving the significant cost of recompression[8]. However, due to the minor size difference, ideal N_2/CH_4 selectivities, even for state-of-the-art polymeric membranes, remain below 3[8]. Zeolite membranes with narrow pore-apertures (~3.8 Å), e.g. SSZ-13[9], SAPO-34[10], AlPO-18[11], and ETS-4[12], could perform better with some N_2/CH_4 selectivities above 10[8]. This however comes at the price of low productivities due to the small pore-apertures, and a trade-off behavior between the permeance and selectivity also exists (Supplementary Fig. 1).

By contrast, the molecular shape disparity between N_2 and CH_4 is more significant because N_2 is linear, while CH_4 is tetrahedral (Fig. 1a). Side views of these two molecules reveal a trefoil-shaped profile for CH_4 and circular circumference for N_2 (Fig. 1a). Metal–organic frameworks (MOFs) present a highly tunable platform for structural design[13], allowing the precise editing of pore-aperture shape and size. Among MOFs, Zr-*fum*-**fcu**-MOF, which is assembled from a hexanuclear cluster $[Zr_6O_4(OH)_4(O_2C\text{-})_{12}]$ and a ditopic linker fumarate (*fum*) with face-centered cubic (**fcu**) topology, presents the desired narrow pore-apertures with the special trefoil shape[14] (Fig. 1b). Typically, a CH_4 tetrahedron is expected to penetrate by aligning its edges parallel to the triangular entrance borders in order to precisely fit well with the trefoil-shaped pore-apertures (Fig. 1b). In principle, such a penetration of CH_4 could be blocked by altering the pore apertures so as to disrupt the original match for tetrahedral CH_4. The remaining space would be still wide enough for linear N_2 to diffuse (Fig. 1c).

The shape-irregularity is induced by partially substituting the fumarate edge of the triangular windows with 2-methylfumarate, namely mesaconate (*mes*) encompassing protruding methyl groups (Supplementary Fig. 2). Our experimental explorations reveal the optimal molar ratio of *fum* to *mes* for N_2/CH_4 separation is 2:1, e.g. Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF, corresponding to two fumarates and one mesaconate encompassing circumference of the triangular window.

Membrane fabrication

We present the electrochemical synthesis of MOF membranes using water as a solvent, where external current is applied to deprotonate the ligands[15,16]. We first explored the optimal conditions for pure fumarate Zr-*fum*-**fcu**-MOF membranes, and a defect-free layer of 30-nm thickness was obtained after 2 hours with a current density of 0.05 mA cm^{-2}, using a preformed $[Zr_6O_4(OH)_4(O_2C\text{-})_{12}]$ cluster concentration of ~8.5 mM and fumaric acid concentration of ~50 mM. This successful practice implies the achievement of an ideal concentration of the deprotonated ligand ($[L^{2-}]_{ideal}$) during the reaction, which is critical to the formation of continuous MOF layers[14]. We found that required ligand concentration ($[H_2L]$) correlated with its pK_a during the fabrication of **fcu**-MOF membranes (Fig. 2a): $[H_2L]_{\text{Zr-}\mathbf{fcu}\text{-MOF,a.q.}} = 2.23 \times 10^{(\mathrm{p}K\mathrm{a}-5)}$. However, to construct mixed-linker Zr-*fum*$_{(100-x)}$-*mes*$_x$-**fcu**-MOF membranes (x is *mes* molar percentage), two prerequisites should be considered: the maintenance of a total concentration of $[L^{2-}]_{ideal}$ for the deprotonated ligands and controllable ligand incorporation percentages. Hence, the input concentration of each ligand can be calculated based on its targeted molar percentage: $[H_2\mathrm{fum}]_{mixed} = (100-x)\% \times 0.05$; $[H_2\mathrm{mes}]_{mixed} = x\% \times 0.109$ (Fig. 2b, Supplementary Note 1).

We targeted four different *mes* percentages, namely 20%, 33%, 40%, and 60%, and prepared the corresponding membranes. As determined by

^{1}H nuclear magnetic resonance (NMR) of acid-digested samples, the targeted *mes* percentages agree well with experimental results of 21%, 33%, 40% and 59% (Fig. 2c, Supplementary Fig. 3). All membranes supported on Anodisc display well-intergrown layers, similar crystal morphology, and ultrathin thickness of ~30 nm (only ~17 unit cells; Figs. 2d-2h; Supplementary Fig. 4). The phase purity, confirmed by X-ray diffraction (XRD), matches well with the parent **fcu**-MOF structures (Supplementary Fig. 5). Some floating particles might deposit loosely on the top of continuous layers or inside Anodisc channels. Nevertheless, those particles can be easily cleaned by using compressed air flow, indicating they cannot contribute to separation. The ultrathin selective layer is proved quite homogeneous by the large-area cross-section images and element distributions. The XRD patterns of membranes after removing the floating particles still match with those of simulated structures (Supplementary Figs. 6-10). Additionally, as a proof-of-concept to reduce membrane cost, we demonstrated the same synthesis of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes on inexpensive support of stainless steel nets (SSN) modified by carbon nanotubes, exhibiting a similar layer thickness and intactness (Fig. 2i; Supplementary Figs. 4-5).

The ligand distribution in the resulting mixed-linker structure is critical for realizing the targeted pore-aperture editing, since the fumarate and mesaconate linkers are required to co-locate in exactly one triangular window so as to transform the trefoil-shaped pore aperture into desired irregular entrance. Two-dimensional (2D) magic-angle spinning solid-state NMR (ssNMR) measurements were applied to the Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF, because the atoms from the two linkers are expected to provide correlation signals when they are co-located within a single window (Supplementary Fig. 11). We acquired the 2D ^{13}C–^{13}C correlation spectra using proton-driven spin diffusion by phase-alternated recoupling irradiation schemes (Fig. 2j)[17,18]. The correlation between the 13.2 and 136.2 ppm peaks can be clearly observed; these peaks originate from the carbon atom of the methyl group in mesaconate and the double-bond carbon atoms in fumarate, respectively (Fig. 2j). The strong correlation indicates the two linkers are in close physical proximity, namely co-locating within one window. Moreover, the double-bond carbon atoms from both linkers also gave detectable correlations at (128.0 ppm, 136.2 ppm) and (145.3 ppm, 136.2 ppm), again indicating that pore-aperture editing was indeed realized. Ultimately, because the molar ratio of *fum*/*mes* for Zr-*fum*$_{67}$-

mes$_{33}$-**fcu**-MOF membranes is 2:1, the obtained triangular windows are circumscribed by one mesaconate and two fumarate edges (Fig. 2j).

N_2 removal and natural gas purification

We measured the single-gas permeation of membranes with different *mes* loadings. All the gas permeances decreased as the *mes* loading increased, owing to the associated narrowed pore-aperture sizes and thus increased transport resistance (Fig. 3a; Supplementary Fig. 12, table 1). The permeance cutoff gradually moved toward smaller gas pairs as revealed by changes in ideal selectivities (Supplementary Fig. 13). Subsequently, all membranes were evaluated for N_2/CH_4 mixed-gas separation, among which Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes with *fum*/*mes* ratios of 2:1 offered the highest N_2/CH_4 selectivity of 15 and an average N_2 permeance of 3057 GPU (Fig. 3b; Supplementary table 2). For the parent Zr-*fum*$_{100}$-*mes*$_0$-**fcu**-MOF membranes, both N_2 and CH_4 could freely permeate, showing selectivities close to those governed by Knudsen diffusion. Steadily increasing the proportion of mesaconate led to a drastic decrease in CH_4 permeance, and a slight decrease in N_2 permeance when *mes*% ≤ 33%, thus enhancing the N_2/CH_4 selectivity (Fig. 3b). The enhanced separation is mainly attributed to the pore-aperture irregularity and its mismatch with CH_4 tetrahedron rather than size exclusion. This is because ethylene (C_2H_4) molecule with a larger kinetic diameter than that of CH_4 but a pseudo-linear shape showed higher permeance than CH_4 for Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes (Fig. 3a). The separation driven by kinetic diameter difference would favor the diffusion of smaller CH_4 molecules, while configuration-mismatch favors the faster diffusion of pseudo-linear C_2H_4 (Fig. 3c). However, further increase in *mes*%, e.g. beyond 33%, cannot afford higher selectivity; instead, selectivity decreased. Apparently, when the *fum*/*mes* ratio is higher than 2:1, more than one mesaconate might be present in some triangular windows, leading to a significant narrowing of pore apertures and a decrease in N_2 permeance (Fig. 3b). Consequently, a Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membrane composition represents a sweet spot that optimally performs the mismatch-induced separation with both high permeance and selectivity.

Molecular simulations revealed, after replacing one fumarate by mesaconate in the triangular window, the diffusion energy barrier for CH_4 increased by more than 150%, whereas that for N_2 increased by only 33%, leading to enhanced N_2/CH_4 selectivity (Fig. 3d-3j; Supplementary Fig. 14, table 3, Note 2).

Additionally, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes offer excellent thermal stability. Both the N_2 permeance and the N_2/CH_4 selectivity increased at elevated temperatures, with apparent activation energies for the N_2 and CH_4 permeation at 6.8 and 4.4 kJ mol^{-1}, respectively (Supplementary Fig. 15). Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes show a superior performance than other membranes in terms of both N_2 permeance and N_2/CH_4 selectivity, surpassing the upper bounds for polymeric and zeolite membranes (Fig. 4a).

For practical applications, N_2/CH_4 separation at high pressures (30-60 bar[19]) is preferred. For zeolite membranes, e.g. state-of-the-art SSZ-13 membranes, high feed pressure leads to severe selectivity loss, decreasing by a half to only ~6 for a 25 bar feed[9] (Fig. 4b). By contrast, when the feed pressure is elevated to 50 bar and the permeate side is maintained at 1 bar without sweep gas, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes still maintain excellent N_2/CH_4 separation performance (Fig. 4b). The N_2 permeance decreases at higher pressures due to the nonlinear adsorption behavior of the Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF, but without notable effect on selectivity (Supplementary Fig. 16)[20].

In terms of absolute N_2 flux and N_2/CH_4 selectivity, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes exhibit a N_2 flux more than two orders of magnitude bigger than those of other membranes with reasonable selectivity (i.e., approximately 10) (Fig. 4c; Supplementary Fig. 17). Additionally, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes suggest exceptional robustness and the separation performance does not degrade after continuous permeation for 150 days (Fig. 4d). We further mimicked the complex feed streams with trace amounts of impurities, e.g. water vapor, hydrocarbons, and corrosive hydrogen sulfide (Supplementary Fig. 18). The occurrence of hydrocarbons led to a slight fluctuation in N_2/CH_4 separation, while water vapor and hydrogen sulfide occurrence resulted in decreased permeance owing to their strong affinities to the MOFs, blocking other species. However, once the feed was switched back to normal, N_2/CH_4 separation always reverted back to its initial benchmark values, indicating the excellent membrane stability.

Considering the variability of N_2 concentrations across different natural gas fields, we evaluated the N_2/CH_4 separation performance with varying N_2 concentrations from 5% to 15% in the feed stream. In contrast to zeolite membranes, for which lower N_2 concentration cause reduced N_2 permeance and N_2/CH_4 selectivity[9], both N_2 permeance and N_2/CH_4 selectivity of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes increased at lower N_2 concentrations (Supplementary Fig. 19). The slightly enhanced permeance is attributed to the nonlinear adsorption behavior for nanoporous membrane materials (Supplementary Fig. 16)[14,20]. Notably, this pressure-resistant behavior is maintained at low N_2 feed concentrations at elevated pressures of 50 bar, as exemplified by the use of a 15%N_2/85%CH_4 feed stream (Supplementary Fig. 20).

The excellent performance at low N_2 concentrations inspired us to explore the possibility of purifying natural gas from ternary mixtures, namely simultaneously removing CO_2 and N_2 from CH_4, given that CO_2 molecule also shows a linear configuration. When a ternary mixture containing 35%CO_2/15%N_2/50%CH_4 at 10 bar was used as the feed, the membranes offered an average CO_2 and N_2 permeance of 6432 and 3098 GPU, respectively, and average CO_2/CH_4 and N_2/CH_4 separation factors of 28.5 and 15.5, respectively (Fig. 4e). Taking CO_2 and N_2 together as a single contaminant with a concentration of 50% in the feed gas, we could derive an overall removal permeance of impurities (CO_2+N_2) of 5344 GPU and impurity/CH_4 separation factor, namely $\alpha((CO_2+N_2)/CH_4)$, of 24.6 (Fig. 4e). Again, the pressure-resistant capability of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes provided stable operation at high pressures up to 50 bar (Fig. 4f; Supplementary Fig. 21). The simultaneous removal of CO_2 and N_2 from CH_4 using membranes has scarcely been reported except for rare examples of polymers and mixed-matrix membranes[21], probably owing to poor N_2-removal efficiency under low N_2 concentrations for other membranes. Compared with others, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes exhibit a better separation selectivity and a three orders of magnitude higher permeance.

In addition, pore-aperture-edited MOF membranes exhibited the potential to separate other gases (Supplementary Fig. 22). Through stepwise pore-aperture editing, we could transform originally less effective frameworks into highly selective ones. Furthermore, Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes supported on cheap SSN exhibited similarly excellent separation performance, including high feed pressures up to 50 bar, at low N_2 feed concentrations, and in CH_4 purification including high feed pressures up to 30 bar, at low N_2 feed concentrations, and in CH_4 purification from ternary mixtures (Supplementary Figs. 23-26).

Technoeconomic analysis

To evaluate the energy and cost savings of our membranes for nitrogen rejection, we performed a process simulation using Aspen Plus®. As a base scenario, we first modeled a conventional cryogenic distillation process[22,23] (Supplementary Fig. 27), using 15%N_2/85%CH_4 or 50%N_2/50%CH_4 as feed and targeting a CH_4 purity with 3% N_2[24]. Our model indicates that 3.75 MW of energy duty for a 1000 kmol h^{-1} feed is required.

When membranes are applied, for the 50%N_2/50%CH_4 feed, our membrane alone cannot provide the required purity; therefore, a hybrid system is needed[14], where the membrane acts as a pre-separator to reduce the load on columns (Supplementary Fig. 28). Our model shows 67% of the total energy of distillation columns can be saved using the membrane–distillation hybrid system, translating to 74% utility cost savings (Fig. 4g, Supplementary Fig. 29). For the 15%N_2/85%CH_4 feed, the membrane can virtually replace the cryogenic distillation system (Supplementary Fig. 30). Moreover, because the membrane is N_2-selective and the purified CH_4 retentate is maintained at the high-pressure side, no recompression is needed[8]; therefore, all of the energy associated with the column can be saved (Fig. 4h).

For the total purification costs, massive cost reduction was observed using membranes, regardless of the membrane price or stream composition (Figs. 4j-4k). For the 50%N_2/50%CH_4 feed, ~66 ktonnes of CH_4 was purified, with a ~32% reduction in purification cost (Fig. 4j). Meanwhile, for the 15%N_2/85%CH_4 feed, ~114 ktonnes of CH_4 was purified, with a ~66% reduction in purification cost (Fig. 4k)..

The simultaneous removal of CO_2 and N_2 from natural gas using membranes was also evaluated. Particularly, we simulated amine-based CO_2 capture by simulating methyl diethanolamine (MDEA) absorption[25-28] of a stream composition of 35%CO_2/15%N_2/50%CH_4 (Supplementary Fig. 31), which requires 11.5 MW heating duty and 10.9 MW cooling duty for CO_2-removal, translating to US$ 0.34 $MMBtu^{-1}$ (Metric Million British thermal unit) of purification cost. Combined with the costs of N_2-rejection columns for sequential N_2-removal, the total energy duty and utility cost for the removal of CO_2 and N_2 are 26 MW and US$ 1.58×10^6, respectively (Fig. 4i). Accordingly, the CH_4 purification cost is increased to US$ 0.62 $MMBtu^{-1}$ (Fig. 4l). By contrast, for this particular stream composition (35%CO_2/15%N_2/50%CH_4), our membrane can virtually replace the amine and cryogenic combination to simultaneously remove CO_2 and N_2, saving 100% of the heating and cooling duties (Fig. 4i) and delivering the required purities to reach pipeline specifications (Supplementary table 4). Ultimately, for the 35%CO_2/15%N_2/50%CH_4 feed, ~72 ktonnes of CH_4 was purified, and deployment of our membranes reduced purification costs by ~73%.

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Fig. 1. Schematic illustrations of pore-aperture editing and shape-mismatch-induced separation based on shape difference.

a, Molecular configurations of CH_4 and N_2, and structures of fumaric acid and mesaconic acid, respectively. The tetrahedral CH_4 molecule shows a trefoil-shaped side-view profile, while the linear N_2 molecule shows a circular side-view profile. **b**, Illustrations of the regular trefoil-shaped pore-aperture of Zr-*fum*-**fcu**-MOF and the free diffusions of both CH_4 and N_2 molecules. **c**, Illustrations of the irregular entrance of Zr-*fum-mes*-**fcu**-MOF created by subtle pore-aperture editing. The tetrahedral CH_4 molecule is excluded due to the shape mismatch with the modified irregular entrance, while the linear N_2 molecule can still freely diffuse. (*fum*: fumarate; *mes*: mesaconate)

Fig. 2. Synthetic guide and characterization of pore-aperture-edited Zr-*fum*$_{(100-x)}$-*mes*$_x$-fcu-MOF membranes. **a**, Prediction of the required concentrations of ligands for continuous MOF membranes as functions of ligand pK_a values using an electrochemical approach in an aqueous system. **b**, Required concentrations of fumaric acid and mesaconic acid as functions of targeted *mes* percentages for the preparation of Zr-*fum*$_{(100-x)}$-*mes*$_x$-**fcu**-MOF membranes obtained by using an electrochemical approach. **c**, Comparison of real *mes* percentages in resultant membranes with theoretical targets. Error bars represent the standard deviation obtained from three independent measurements (n = 3) **d**–**i**, Cross-sectional images of (**d**) Zr-*fum*$_{100}$-*mes*$_0$-**fcu**-MOF supported on Anodisc, (**e**) Zr-*fum*$_{79}$-*mes*$_{21}$-**fcu**-MOF supported on Anodisc, (**f**) Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF supported on Anodisc, (**g**) Zr-*fum*$_{60}$-*mes*$_{40}$-**fcu**-MOF supported on Anodisc, (**h**) Zr-*fum*$_{41}$-*mes*$_{59}$-**fcu**-MOF membrane supported on Anodisc, and (**i**) Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membrane supported on stainless-steel nets modified by carbon nanotubes. **j**, 2D ^{13}C–^{13}C MAS solid-state NMR spectra. Polarization of ^{13}C atoms was achieved through direct excitation and a mixing period of 200 ms. Proton-driven spin diffusion using phase-alternated recoupling irradiation schemes was used. The corresponding correlations among atoms from the two ligands are marked. (*fum*: fumarate; *mes*: mesaconate)

Fig. 3. Separation performances of Zr-*fum*$_{(100-x)}$-*mes*$_x$-fcu-MOF membranes and diffusion

energy barriers.

a, Single-gas permeations of Zr-*fum*$_{(100-x)}$-*mes*$_{x}$-**fcu**-MOF membranes as a function of kinetic diameter. **b**, N_2/CH_4 mixed-gas separation performances of Zr-*fum*$_{(100-x)}$-*mes*$_{x}$-**fcu**-MOF membranes. Error bars in panels **a–b** represent the standard deviation obtained from three independent measurements (n = 3). **c**, Schematic illustration of the pseudo-linear profile of ethylene and its permeation through the irregular pore-aperture. **d**, **f**, **h**, Schematic illustrations of the diffusion of N_2 and CH_4 through the pore-apertures of the simulated (**d**) Zr-*fum*$_{100}$-*mes*$_{0}$-**fcu**-MOF, (**f**) Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF, and (**h**) Zr-*fum*$_{33}$-*mes*$_{67}$-**fcu**-MOF membranes. **e**, **g**, **i**, Minimum energy pathways for the diffusion of N_2 and CH_4 through (**e**) Zr-*fum*$_{100}$-*mes*$_{0}$-**fcu**-MOF, (**g**) Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF, and (**i**) Zr-*fum*$_{33}$-*mes*$_{67}$-**fcu**-MOF membranes. **j**, Comparison of the simulated energy barriers for the diffusion barriers of N_2 and CH_4 throughout different MOF frameworks. (*fum*: fumarate; *mes*: mesaconate)

Fig. 4. Comprehensive evaluations of N_2/CH_4 separation performance of Zr-*fum*$_{67}$-*mes*$_{33}$-fcu-MOF membranes under practical conditions and techno-economic comparison of distillation system with membrane or hybrid membrane–distillation system.

a, N_2/CH_4 separation performance comparison between Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes and other previously reported membranes. The solid and dotted lines are eye guides for polymeric and other previously reported membranes. The solid and dotted lines are eye guides for polymeric and zeolite membranes, respectively. **b**, High-pressure separation performance of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes. The inset box highlights the best-performing zeolite SSZ-13 membranes. **c**, N_2 flux comparison and N_2/CH_4 separation factor comparison between Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes and other reported membranes. **d**, Long-term operational stability of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes. After Day 40, the feed pressure was fixed at 10 bar, and the permeate side was kept at atmospheric pressure without sweep gas. **e**, 35%CO_2/15%N_2/50%CH_4 ternary mixed-gas separation performance comparison between Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes and other reported membranes. **f**, High-pressure separation performance of Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membranes when applied to a 35%CO_2/15%N_2/50%CH_4 ternary mixed gas. Error bars in panels **a–c** and **e–f** represent the standard deviation obtained from three independent measurements (n = 3). **g–i**, Energy and utility consumption for both systems for the following feed compositions: (**g**) 50%N_2/50%CH_4, (**h**) 15%N_2/85%CH_4, and (**i**) 35%CO_2/15%N_2/50%CH_4. **j–l**, Evaluation of purification cost per MMBtu of methane for both systems for the following feed compositions: (**j**) 50%N_2/50%CH_4, (**k**) 15%N_2/85%CH_4, and (**l**) 35%CO_2/15%N_2/50%CH_4. (MMBtu: Metric Million British thermal unit, *fum*: fumarate; *mes*: mesaconate)

Methods

Zirconium chloride ($ZrCl_4$, >99.99%, Sigma-Aldrich), formic acid (98% - 100%, Sigma-Aldrich), fumaric acid (>99%, Sigma-Aldrich), mesaconic acid (>99%, Sigma-Aldrich), Anodisc (diameter of 18 mm, pore diameter of 20 nm, partially oxidized, Puyuan Nano Co., Ltd), carbon nanotubes (XFNANO Co., Ltd) and stainless steel net (SungYong Co., Ltd) were utilized in this study.

Preparation of $[Zr_6O_4(OH)_4(O_2C\text{-})_{12}]$ cluster solution

First, 0.24 g $ZrCl_4$ was mixed with 2.7 mL of formic acid and then ultrapure water was added to 20 mL to get a clear aqueous solution. The solution was left undisturbed at room temperature for 12 hours.

clear aqueous solution. The solution was left undisturbed at room temperature for 12 hours.

Preparation of Zr-*fum*$_{(100-x)}$-*mes*$_{x}$-**fcu**-MOF membranes by current-driven assembly

First, fumaric acid and mesaconic acid with pre-calculated mass were added to the above cluster solution and sonicated for 2 min to get a homogeneous solution. The porous support with conductive Pt coatings was immerged into the solution and connected with the working electrode of the potentiostat (as cathode). Two supports with surface pore size < 20 nm were used in this study, Anodisc and carbon nanotubes modified stainless steel nets. Both supports were covered with an aluminum ring in order to be easily handling. A current density of 0.05 mA/cm^2 was applied for 2 h at room temperature, after which the as-synthesized membranes were taken out and rinsed slowly with fresh water and water/methanol solvent for 2 min, respectively. The exact amount of ligands for each Zr-*fum*$_{(100\text{-}x)}$-*mes*$_{x}$-**fcu**-MOF membrane is as follows: Zr-*fum*$_{100}$-*mes*$_{0}$-**fcu**-MOF membrane, fumaric acid 116 mg (1 mmol); Zr-*fum*$_{79}$-*mes*$_{21}$-**fcu**-MOF membrane, fumaric acid 92.7 mg (0.8 mmol), mesaconic acid 56.8 mg (0.44 mmol); Zr-*fum*$_{67}$-*mes*$_{33}$-**fcu**-MOF membrane, fumaric acid 77.6 mg (0.67 mmol), mesaconic acid 93.7 mg (0.72 mmol); Zr-*fum*$_{60}$-*mes*$_{40}$-**fcu**-MOF membrane, fumaric acid 69.5 mg (0.6 mmol), mesaconic acid 113.6 mg (0.87 mmol); Zr-*fum*$_{41}$-*mes*$_{59}$-**fcu**-MOF membrane, fumaric acid 46.3 mg (0.4 mmol), mesaconic acid 170.4 mg (1.31 mmol).

Characterization

XRD patterns were recorded at room temperature under ambient conditions with a Bruker D8 Advance diffractometer with Cu Ka radiation at 40 kV and 40 mA. The morphologies and cross sections of the membranes were observed by SEM using Zeiss Merlin. ^{1}H NMR spectra were collected on a Bruker Advance 400 spectrometer at ambient temperature. Low pressure gas adsorption measurements were performed on Micrometrics ASAP 2420 surface characterization analyzer at relative pressures up to 1 atm. The cryogenic temperatures were controlled using liquid nitrogen baths at 77 K, respectively.

Gas permeation test

Wicke-Kallenbach technique was adopted to study the gas permeation properties of the membranes. Before measurement, each membrane was very carefully activated by on-stream

activation process (0.1 ^{o}C min^{-1} to 120 ^{o}C and kept for 24 h, after which decrease to room temperature at 0.1 ^{o}C min^{-1}. Feed side: N_2 25 mL min^{-1}, sweep side: He 25 mL min^{-1}). For a single-gas permeation measurement, the prepared MOF membrane was fixed in a module sealed with O-rings. A volumetric flow rate of 2000 mL min^{-1} gas was applied to the feed side of the membrane, and the permeate gas was removed from the permeate side by the sweep gas (He). A calibrated gas chromatograph (Varian GC-450) was used to measure the concentration of each gas on the permeate side. The membrane permeance, P_i (mol·m^{-2}·s^{-1}·pa^{-1}), is defined as (1):

$$P_i = N_i/(\Delta P_i \ A) \qquad (1)$$

where N_i (mol·s^{-1}) is the molar flow rate of component i, ΔP_i (Pa) is the transmembrane pressure difference of component i, and A (m^2) is the effective membrane area for testing. The ideal selectivity, $S_{i/j}$, is calculated from the relation between the permeance of component i and component j.

$$S_{i/j} = P_i/P_j \quad (2)$$

For the mixed gas permeation measurement, the prepared MOF membrane was sequentially placed on the top of a 2-mm thick alumina support and another 2-mm thick porous steel plate, and fixed in a module sealed with O-rings in order to make the membranes operable under high pressures. A mixture with targeted ratio was applied to the feed side of the membrane and the feed pressure varied from 1 bar to 50 bar. The feed flow rate was kept constant with a total volumetric flow rate of 2000 mL min^{-1}. For the measurements under high feed pressures, no sweep gas was applied. The total volumetric flow rate of the permeate side was calibrated by ADM flow meter (Agilent). A calibrated gas chromatograph was used to measure the concentration of each gas on the permeate side, which was diluted by He before injected into gas chromatograph. The permeance of individual gas was derived based on the total flow rates measured from the flow meter and the molar fractions measured from gas chromatograph. The separation factor, $\alpha_{i,j}$, of the gas pairs is defined as the quotient of the molar ratios of the components (i, j) in the permeate side, divided by the quotient of the molar ratios of the components (i, j) in the feed side:

$$\alpha_{i/j} = X_{i,\ perm}/X_{j,\ perm}/(X_{i,\ feed}/X_{j,\ feed}) \quad (3)$$

Solid-State Nuclear Magnetic Resonance Spectroscopy

All ^{1}H and ^{13}C related (both 1D and 2D) magic angle spinning (MAS) solid-state nuclear magnetic resonance (ssNMR) spectroscopic experiments were performed on Bruker AVANCE III spectrometers operating at 400 MHz frequency for ^{1}H using a conventional double-resonance 3.2 mm CPMAS HX probe (CP: Cross-polarization). NMR chemical shifts are reported with respect to the external reference adamantine. All NMR measurements were performed at room temperature (298 K) and MAS frequency of 16 kHz (unless specified otherwise in the figure captions). Note that effective sample temperatures can be 5-10 degrees higher due to the frictional heating. For ^{13}C CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with contact time of typically 2 ms, and finally acquisition of the ^{13}C NMR signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^{1}H nuclei, and the number of scans ranged between 10000 and 20000 for ^{13}C and was 32 for ^{1}H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

The 1D ^{13}C direct excitation (DE) spectrum was recorded using a 4 s recycle delay, and 16 ms acquisition time, and an accumulation of 1 or 2k scans.

Two-dimensional double-quantum (DQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double resonance 3.2 mm CP/MAS probe, according to the following general scheme: excitation of DQ coherences, t1 evolution, z-filter, and detection. The spectra were recorded in a rotor synchronized fashion in t1 by setting the t1 increment equal to one rotor period (45.45 µs). One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in w1 was achieved using the States-TPPI method. An MAS frequency of 22 kHz was used. The 90° proton pulse length was 2.5 µs, while a recycle delay of 5 s was used. A total of 128 t1 increments with 128 scans per each increment were recorded. The DQ frequency in the w1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons and correlates in the w2 dimension with the two corresponding proton resonances

2D

^{13}C-^{13}C spectra were recorded using a 2 s recycle delay, 10 ms (F2) and 1.3 ms (F1) acquisition time and an accumulation of 256 scans (both CP and DE). ^{13}C-^{13}C mixing was achieved through proton driven spin-diffusion (PDSD) using Phase-alternated-recoupling-irradiation-schemes (PARIS) for 120 ms (CP) or 200 ms (DE) mixing. 70 kHz SPINAL64 ^{1}H decoupling was applied during both direct and indirect dimensions.

Simulation method

The Zr-*fum-mes*-**fcu**-MOF structural models were built with BIOVIA Materials Studio 2019. Three Zr-*fum-mes*-**fcu**-MOF models made of 4 inorganic hexanuclear Zr_6 clusters and 24 ligands in one unit cell were built with the following fumarate/mesaconate (fum:mes) ratios: 100:0, 67:33 and 33:67, i.e. 24 fumarate, 16 fumarate/8 mesaconate and 8 fumarate/16 mesaconate respectively. Periodic DFT calculations were performed using the projector augmented wave (PAW)[29] formalism with an energy cutoff of 800 eV and the generalized gradient approximation (GGA) method with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. All these calculations were carried out in Vienna Ab Initio Simulation Package (VASP) version 5.4.1.[30-32] We used the D3 method of Grimme[33] to include the dispersion contribution to the interaction energy. The convergence criteria of 10^{-5} and 10^{-2} eV (2×10^{-2} eV for transition state searching) were used for the energy and forces convergence, respectively. The transition states were localized using the climbing image nudged elastic band (CI-NEB) method as implemented in the Transition State Tools for VASP (VTST) module.[34] All calculations were sampled at gamma point.

The three empty structure models were first DFT-fully relaxed (both atomic position and cell parameters) prior to introducing 1 single N_2 and CH_4 guest molecule in each of them. The interaction energy between each guest and the MOFs (E_{int}(guest)) considered to build the potential energy profiles was calculated using equation (4):

$$E_{int}(\text{guest})=E_{tot}(\text{MOF+guest})-E(\text{MOF}) - E(\text{guest}) \quad (4)$$

where E_{tot}(MOF+guest) is the total energy of MOF accommodating the guest molecule, E(MOF) and E(guest) are the total energy of the empty MOF and isolated guest molecules, respectively.

Technoeconomic analysis method

Process distillation simulations were carried out with steady-state simulation models developed in Aspen Plus® V11 software. The selected property method was Redlich-Kwong-Soave. The cryogenic distillation column was simulated using the RadFrac model.

For the cryogenic distillations the number of trays in the column was fixed at 20 with constant pressure. The feed was introduced to the column above the stage 15. Two feed compositions were evaluated, 15% and 50% N_2 in CH_4 with a total feed rate of 1000 kmol h^{-1} and a temperature of 25 ⁰C. Feed pressure was set to 30 bar. The target purity was 3% N_2 in CH_4. The reflux rate was optimized to meet these specifications. Condenser and reboiler temperatures were set at -148 ⁰C and -99 ⁰C respectively. A multistream heat-exchanger was placed prior to the column to precool the feed and reduce the energy load of the condenser and reboiler.

The membrane was modeled as a theoretical component separator. The separation factor was based on the experimental selectivity of the membrane and it was set to 15.7.

The hybrid membrane system was modeled by introducing the membrane before the cryogenic distillation column. The permeate, rich in N_2, comes out of the membrane at 1 bar. The retentate, rich in CH_4, comes out at 30 bar and it is fed to a heat-exchanger and then to the column. The number of trays in the column were kept at 10. The reflux rate was again optimized to meet the above purity specifications. Condenser and reboiler temperatures were set at -119 ⁰C and -99 ⁰C respectively.

For the modeling of the CO_2 separation with amines absorption (methyl diethanolamine, MDEA), the selected method was Electrolyte NRTL with the Redlich–Kwong equation of state. The feed was composed of 35/15/50% $CO_2/N_2/CH_4$ at 25 °C, 30 bar, and 1000 kmol h^{-1}.The absorption was modeled based on the chemical equilibrium between an absorber and a regeneration stripper in a closed cycle. The MDEA feed contained 20% MDEA and 80% H_2O. The absorber exhibited 20 stages and operated at 5 bar and 5 °C, while the striper displayed 10 stages with a reflux ratio of 0.5. The flow of MDEA in the absorber was optimized to achieve a water-free MDEA/CO_2 molar ratio of 2.

Economic analysis was carried out with the Economics Solver extension of Aspen Plus. The distillation columns were mapped with trays of 0.4-meter height per tray. Steam cost was estimated in 9.21e^{-09} \$ per Cal and refrigerant in 3.72e^{-08} \$ per Cal. These values are the standard ones provided by Aspen Plus. The calculation of equipment cost estimation consists of the sum of the installed distillation column and heat exchanger costs. The calculation of utility cost consists of sum of steam and refrigerant costs. The calculation of total energy duty consists of the sum of the condenser and reboiler duties. For the calculation of the purification costs, the annual plant costs were estimated as the sum of the plant operating costs (labor plus maintenance and utilities costs) and the annualized CAPEX, considering a total plant lifetime of 20 years and a straight-line depreciation method (equation (5)). Labor and maintenance costs were estimated with the Economics Solver extension of Aspen Plus using the US system database. In the hybrid system the membrane cost was varied between 50 and 4500 \$ m^{-2} and added to the CAPEX with a 5-year lifetime as base scenario (equation (6)). All replacement, disposal and construction costs related to the membrane were considered to be included in the final membrane cost. The total annual plant cost was then divided by the total natural gas production to estimate the respective purification costs. Our costs do not include the plausible gains of selling the purified N_2 streams that will manifestly reduce the separation costs in a real scenario.

$$AnnualCost$$

20

$$_{singlesystem} = Labor + Maintenance + Utilities + CAPEX/20 \qquad (5)$$

$$AnnualCost_{hybridsystem} = Labor + Maintenance + Utilities + CAPEX/20 + Membrane/5 \qquad (6)$$

High-pressure gas adsorption

High-pressure gas adsorption studies were performed on a magnetic suspension balance marketed by Rubotherm (Germany). Type Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus, composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flow meters, and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere, and is able to perform adsorption measurements across a wide pressure range (i.e., from 0 to 20 MPa). The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount (). Correction for the buoyancy effect is required to determine the excess and absolute adsorbed amount using equations 7 and 8, where $V_{adsorbent}$ and V_{ss} and $V_{adsorbed}$ phase refer to the volume of the adsorbent, the volume of the suspension system, and the volume of the adsorbed phase, respectively.

$$= m_{absolute} - \rho_{gas}(V_{adsorbent} + V_{ss} + V_{adsorbed-phase}) \qquad (7)$$

$$= m_{excess} - \rho_{gas}(V_{adsorbent} + V_{ss}) \qquad (8)$$

The buoyancy effect resulting from the adsorbed phase may be taken into account via correlation with the pore volume or with the theoretical density of the sample.

These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined using the Refprop equation of state (EOS) database and checked experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas-phase density as a function of pressure and temperature is therefore possible.

The pressure is measured using two Drucks high-pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to adsorption experiment, about 150 mg of sample is outgassed at 423 K at a residual pressure of 10^{-6} mbar. The temperature during N_2 and CH_4 adsorption measurements is held constant by using a thermostat-controlled circulating fluid.

Data availability

The datasets analysed and generated during the current study are included in the paper and its Supplementary Information.

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Acknowledgements

We gratefully acknowledge funding from King Abdullah University of Science and Technology and the CCF program 1972. This work was also granted access to the HPC resources of CINES under the allocation A0100907613 made by GENCI.

Author contributions

S.Z. and M.E. conceived the idea and designed the experiments. S.Z. synthesized the materials and carried out most of the characterization. S.Z. and O.S. analysed the results. J.L. performed the gas adsorption experiments. P.B. contributed to the high-pressure adsorption experiments and H_2S-related measurement. E. A-H., J.J., and Z.H. contributed to the NMR characterization. H.J. contributed to the structure simulation. T.J. contributed to the element distribution mapping. P.L. and G.M. performed and analysed the molecular simulations. A.R. and J.G. contributed to the techno-economic analysis. S.Z., O.S., and M.E. wrote the manuscript. All the authors contributed to the revision of the manuscript.

Competing interests

The authors declare no competing financial interests.